Highly Efficient Degradation of Tartrazine with a Benzoic Acid/TiO$_2$ System

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ABSTRACT: The roles of benzoic acid and its derivatives in the photocatalytic degradation of tartrazine (TZ) by titanium dioxide have been studied. A series of comparative experiments were carried out, such as the experimental comparisons of concentrations, pH values, effects on the para-position of benzoic acid, gas atmospheres, and different target pollutants. It should be noted that the degradation rate of TZ solution without benzoic acid and benzoic acid after degradation for 90 min was 28.69 and 99.08%, respectively. The reason for the above results is that benzoic acid acts as an electron donor to react with photogenerated holes, suppressing the recombination of photogenerated holes and electrons, and thus causing a significant increase in the degradation rate. Moreover, the degradation process is mainly induced by O$_2$ and photogenerated holes (h$^+$). It is the first time that the benzoic acid/TiO$_2$ system has been used to degrade the TZ dye. In addition, the benzoic acid/TiO$_2$ system is also suitable for the degradation of other organic dyes such as methyl orange, rhodamine B, methylene blue, and methyl violet.

1. INTRODUCTION

In today’s society, the problem of environmental pollution is getting worse.\textsuperscript{1−3} For example, some azo dye contaminants, which contain aromatic rings and N═N bonds, can be cleaved into aromatic amines, which can lead to cancer.\textsuperscript{4−7} This is the most important cause of global water scarcity and even poses a major threat to human health and living conditions.\textsuperscript{8} Tartrazine (TZ, C$_{16}$H$_9$N$_4$Na$_3$O$_9$S$_2$) is one of many dyes used for coloring foods, medicines, cosmetics, toys, food packaging materials, and the like.\textsuperscript{9−11} Moreover, it is also used in the dyeing of wool and silk and in the manufacture of lake color.\textsuperscript{12} Although it is used as a food coloring, long-term consumption of foods containing excessive amounts of TZ may cause allergies and diarrhea, may also cause hyperactivity, and even affects children’s intellectual development; when the intake exceeds the liver load, it will increase the burden of self-regulation and cause some damage to the kidneys and liver.\textsuperscript{13−15} For these hard-to-degrade organic pollutants, conventional treatment methods include chemical oxidation, physical adsorption, biological treatment, and membrane separation.\textsuperscript{16,17} However, these technologies exist to varying degrees, or the efficiency is low, the pollutants cannot be completely harmless, and secondary pollution is easy to occur, or the scope of use is limited, not broad enough, and can only be applied to specific pollutants, or the energy consumption is relatively high, and it cannot meet the shortcomings of large-scale application promotion.\textsuperscript{18−20} At this time, photocatalytic oxidation has attracted people’s attention because of its advantages such as high processing efficiency, simple process equipment, easy control of operating conditions, no secondary pollution, easy availability of catalytic materials, and the potential to directly use sunlight as a reaction source.\textsuperscript{21−23}

Titanium dioxide is one of the earliest and most widely developed photocatalysts. Although it has been reported in the literature that a certain amount of titanium dioxide may cause some harm to itself in a few days, a small amount of sample is not very influential.\textsuperscript{24−26} In addition, because of its low cost, wide range of materials, and can be carried out without selective catalytic oxidation, titanium dioxide is mainly used in environmentally friendly organic synthesis, the degradation of organic pollutants, and photocatalytic hydrogen production.\textsuperscript{27−30} Although titanium dioxide has many advantages, its disadvantages cannot be ignored. According to the existing theoretical basis, when the metal oxide photocatalyst receives light with a higher energy than its band gap energy, two types of photocarriers are generated: photogenerated electrons and electron holes.\textsuperscript{30} The use of titanium dioxide as a photocatalyst has two most prominent disadvantages: a higher recombination rate of photogenerated electrons and holes and a relatively wide band gap.\textsuperscript{31−33} Therefore, a lot of effective approaches have been developed to improve the photocatalytic properties of titanium dioxide,\textsuperscript{34} for instance, titanium dioxide is doped with a transition metal,\textsuperscript{35} deposited with a noble metal,\textsuperscript{36} and added with an electron donor or acceptor.\textsuperscript{37} Among them, the electron donor or acceptor is provided for the reaction system, the operation is simple and feasible, and the degradation
efficiency can be effectively improved, which has attracted the attention of many researchers. 38–40 The addition of these electron donors, such as glycerol, 41 formaldehyde, 42 formic acid, 39 and oxalic acid, 43 can inhibit the recombination of two types of photocarriers because they can react with holes. Li and his colleague found that oxalic acid can promote the photocatalytic process of some titanium dioxide, 40 and Wang et al. further proposed that the effect of small molecular weight acids on some titanium dioxide photocatalytic systems is particularly good. 44 Wang and Liu et al. reported the excellent effect of oxalic acid and formic acid in the titanium dioxide photocatalytic system, confirming the role of small molecular weight acids in the above system. 45,46 All in all, because small molecular weight acids act as electron donors among photocatalytic systems, the catalytic performance can be greatly improved.

Although there have been many reports on the modification of titanium dioxide, there are not many reports on the effects of aromatic acids in photocatalytic systems. Here, the choice of methyl orange (MO), rhodamine B (RhB), methylene blue (MB), and methyl violet (MV) as the target pollutants, the selection of TZ because of its difficult biodegradability, and the other dyes are common and easy to get, the price is right. The acid represented by benzoic acid and its para-substituted aromatic acids is used to explore the synergistic effect of acid with titanium dioxide in the degradation of TZ system with small molecular weight acids. In this process, the effects of important factors such as pH of solution, structure of benzoic acid with different substituents, free-radical scavenger, and amount of acid on the effect of the system were also studied in more detail.

2. RESULTS AND DISCUSSION

2.1. Effect of pH and the Concentration of Benzoic Acid. The roles of the amount of benzoic acid on the titanium dioxide catalytic degradation of the TZ system are given in Figure 1a. It can be seen from the data in the figure that the degradation efficiency of TZ can be increased with the mass of benzoic acid from 0 to 0.10 g, and its efficiency is increased from 28.65 to 99.08%. This is consistent with the fact that benzoic acid acts as an electron donor to react with photogenerated holes in the TZ degradation system, thereby reducing the recombination rate of photogenerated electrons and holes. Nevertheless, when the mass of benzoic acid in the system increased from 0.05 to 0.10 or even 0.15 g, the degradation rate of TZ increased only from 97.06 to 99.08 and 99.12%, respectively, with almost no significant improvement. This may be because the photogenerated holes generated by a certain amount of titanium dioxide in the degradation system have been completely consumed by the electron donor of benzoic acid, so that the change in the degradation efficiency of TZ is not very obvious when the amount of benzoic acid is increased again. This means that the degradation efficiency of TZ does not necessarily increase with the increase in the amount of benzoic acid, which requires finding a suitable concentration of benzoic acid.

In addition, the specific effect of the pH of the reaction system on the degradation efficiency of TZ was verified by a series of tests, each of which adjusted the pH of the solution. In this experiment, a total of 3, 4, 6, and 8 specific pH values were set. It can be seen from Figure 1b that the final degradation results of the reaction system at pH = 3 and pH = 4 are almost the same, with 99.39 and 99.07% being almost completely degraded. However, the continuous increase in pH reduces the degradation efficiency; especially at pH = 8, the degradation efficiency of the system is as low as 3.91%. This indicates that pH = 3 is the best in the degradation test of TZ at four pH values, and the adsorption and degradation effects of TZ decrease with increasing pH in this interval. The decrease in pH in the solution means that more protons in the system can be used to protonate the reactive groups, resulting in enhanced adsorption of the dye on titanium dioxide, which in turn leads to an enhanced degradation effect. 47 All in all, it can be concluded that the acidic conditions favor the degradation of TZ by the benzoic acid/TiO2 system, whereas the alkaline conditions are not conducive to the degradation of TZ by the benzoic acid/TiO2 system.

2.2. Effect of Ion Traps and Gas Atmosphere on Degradation of TZ. It is known that there are many kinds of active radicals in the photocatalytic degradation system of organic pollutants in general, but the role of each reactive group in the system is generally not the same, and further experimental verification is needed. Furthermore, it is necessary to further combine different degradation experiments for comparison. The results of the degradation experiments under different gas atmospheres were comprehensively considered. It is worth mentioning that the more the degradation efficiency is reduced, the more important the role played by this reactive free radical in the degradation system.
After a series of ion trapping experiments, it was found that the degradation curves after adding ethylenediaminetetraacetic acid (EDTA) disodium and 1,4-phenylenediamine were significantly different from that of the blank group. In other words, photogenerated holes and \( \text{O}_2^+ \) play a major role in the photocatalytic degradation of TZ by TiO₂/benzoic acid. It is noteworthy that the degradation curves of the system after the addition of isopropanol and potassium persulfate were also somewhat different from the blank group. Although the degradation efficiency of the two groups was almost the same as that of the blank group after the irradiation time reached 90 min, the degradation efficiency of TZ could reach about 94% within 40 min after the addition of the above two capture agents.

Moreover, combining the degradation effects of the catalytic system under different gas atmosphere conditions can better prove the active group that plays a major role in the reaction system. From the data curves in Figure 2b, it can be seen that the degradation curves of several systems are different in the experimental comparison of the three insufflation and blank groups and the gap becomes larger and larger with time. It can be found that the degradation efficiency of TZ in the system of argon and carbon dioxide gas blowing is reduced from 99.08 to 61.13 and 87.73%, respectively. This exactly coincides with the following mechanism: \( \text{O}_2^+ \), its major degradation in catalytic degradation systems

\[
\text{O}_2 + \text{e}^- \rightarrow \text{O}_2^{**}
\]

2.3. Effect of Para-Groups of Benzoic Acid. The graph in Figure 3 shows the comparison of various positions of the substituted benzoic acid as aromatic acids in the degradation of TZ. It can be seen from the graphic display that the other four para-substituted structures of benzoic acid and benzoic acid have little difference in the degradation effect of TZ within 10 min, but the contrast between the effects is obvious as the irradiation time increases, especially when the effect of light is about 30 or 40 min. In the photodegradation stage, the effects of the five benzoic acids in the degradation of TZ can be broadly divided into three groups, 4-methoxybenzoic acid and 4-methylbenzoic acid, 4-chlorobenzoic acid and 4-nitrobenzoic acid, and benzoic acid. Although the degradation efficiency of several systems can reach 98, 99%, or even higher after 90 min of photodegradation, however, after 60 min of degradation, the reaction system of 4-methoxybenzoic acid and 4-methylbenzoic acid can reach about 98.51% and even about 95.06% can be reached in about 40 min. At the same time, the degradation system of 4-chlorobenzoic acid and 4-nitrobenzoic acid was only about 93.05 and 77.21% at 60 and 40 min, respectively. The efficiency of adding benzoic acid is lower, only about 82.57 and 55.81%.

In summary, in the experiment of aromatic acid/titanium dioxide as a catalyst for photocatalytic degradation of TZ, several acids can be used as electron donors to react with photogenerated holes. The reaction reduces the recombination rate of photogenerated holes and electrons, thereby greatly improving the degradation efficiency of the system. That is, the methoxy group and methyl group as an electron-donating group have a better synergistic effect with titanium dioxide when substituted at the para-position of benzoic acid than a chlorine atom and a nitro group as an electron-withdrawing group.

2.4. Effect of Benzoic Acid on Photocatalytic Performance. Figure 4 shows the photodegradation of the TZ solution, photocatalysis, and a comparison of the degradation effects after each addition of benzoic acid. As can be seen from the graphs in the figure, for the photodegradation system of TZ and the benzoic acid system added by photodegradation, there is almost no change in absorbance throughout the photodegradation stage. That is to say, the TZ in these two systems is almost not degraded.
However, for the process of photocatalytic degradation of TZ, the absorbance of the target contaminants has been decreasing in the system after adding only 0.1 g of titanium dioxide. Although the magnitude is not large, the final degradation rate reaches 28.69%. However, after the addition of benzoic acid on the basis of the above system, the degradation rate of the whole system was greatly improved from the beginning of the light to the end of the reaction and increased from the original 28.69 to 99.08% after 90 min of illumination. It shows that the change of the degradation rate of the system after adding benzoic acid is very obvious. The kinetic process of photocatalytic degradation of organic compounds generally follows the following pseudo first-order kinetic model

\[ \ln \left( \frac{C_0}{C_t} \right) = k_1 t \]

wherein, the meanings of \( C_0 \) and \( C_t \) have the same meaning as the related symbols in the above, and \( k_1 \) represents the pseudo first-order kinetic rate constant. As shown in Table 1, the kinetic rate constant of the benzoic acid/titanium dioxide system is 0.050949 min\(^{-1}\), which is more than 13 times that of the simple photocatalytic process (\( k_1 = 0.003742 \) min\(^{-1}\)). In addition, it is 1306 times more than the direct photodegradation process (\( k_1 = 0.000039 \) min\(^{-1}\)).

### 2.5. Degradation of Different Target Pollutants in River Water

Figure 5 shows the visible light degradation of target contaminants in the titanium dioxide/benzoic acid system, including several common organic dyes such as TZ, RhB, MO, MB, and MV. The comparison of the degradation curves of the target pollutants in the figure is still quite obvious. In the visible light degradation stage, the absorbance of most pollutants will decrease with the increase of irradiation time but the degradation of these substances is quite different. Among them, the degradation efficiency of MO in the deionized water environment is the lowest, only 13.32%, whereas the degradation efficiencies of RhB, MB, MV, and TZ under the same conditions were 64.36, 74.89, 87.88, and 99.08%, respectively. It is worth mentioning that the degradation efficiency of TZ can reach 82.57% when the photodegradation time reaches 60 min, and it can reach 55.81% even when the illumination time is 40 min. This phenomenon is much stronger than the effect of MO and RhB after 90 min degradation. Moreover, we can see that it is better when using the river water to do the degradation experiments of the above target pollutants, this may be because the water contains many microorganisms that promote photocatalytic degradation. In addition to the dye MO, the degradation of several other dyes is superior to the degradation of dyes in deionized water.

### 2.6. Effect of Several Water Matrices

The degradation of TZ in four different water matrices is shown in Figure 6. Several water bodies are taken for filtration before they can be

### Table 1. Pseudo-First-Order Kinetic Parameters of TZ Degradation

| reaction system                  | \( k_1 \) (min\(^{-1}\)) |
|---------------------------------|-------------------------|
| photodegradation                | 0.000039                |
| photodegradation + benzoic acid | 0.000107                |
| photocatalysis                  | 0.003742                |
| photocatalysis + benzoic acid   | 0.050949                |

Figure 4. Degradation performance of direct photodegradation and photocatalytic degradation of TZ in the absence and presence of benzoic acid derivatives (\( C_{TZ} = 20 \) mg/L, \( m_{benzoic acid} = 0.1 \) g, pH = 3).

Figure 5. Visible light degradation performance of several common organic dyes as target pollutants in deionized water and river water with the benzoic acid/titanium dioxide system (\( C_{organic dyes} = 20 \) mg/L, \( m_{benzoic acid} = 0.1 \) g, pH = 3).

Figure 6. Comparison of the effects of water matrix on the degradation of TZ (\( C_{organic dyes} = 20 \) mg/L, \( m_{benzoic acid} = 0.1 \) g, pH = 3).
used for catalytic experiments. We can find that the degradation effect of TZ in rainwater and pond water is better than that in river water, which is better than degradation under deionized water. We suspect that pond water and rainwater contain a certain amount of microorganisms that can promote photocatalytic degradation. After analysis, it can be known that the degradation rate of TZ solution prepared with rainwater and pond water can reach 96.38% after 50 min of illumination, whereas the solution prepared with river water can only reach 97.41% degradation rate after 70 min of illumination. As for the deionized water, it takes 80 min of light. This indicates that the benzoic acid/TiO₂ system can also be used to degrade organic dyes in actual water bodies, and it still has certain practical application value.

2.7. Stability of the Benzoic Acid/TiO₂ System. In order to ensure the stability of the system before and after the reaction, we performed scanning electron microscopy (SEM) and X-ray diffraction (XRD) tests of titanium dioxide before and after the reaction. Whether it is from the comparison of Figure 7a,b or the comparison of Figure 7c,d, it is not difficult to find that the surface morphology of titanium dioxide has not changed substantially before and after the reaction. However, it is worth mentioning that although there is a certain agglomeration phenomenon on the SEM images of the same magnification, it can be clearly found that the morphology on the outermost surface of titanium dioxide is not much different before and after the reaction. This suggests that the stability of the system before and after the reaction is still good.

The XRD patterns of titanium dioxide before and after the reaction are shown in Figure 7e. By analyzing and comparing the XRD pattern of titanium dioxide before and after the reaction with the standard card diagram, it can be known that the crystal form of titanium dioxide before and after the reaction did not change. This result is consistent with the obtained SEM results, indicating that the stability of the catalyst system is quite good.

At the same time, we also tested the stability of the photocatalyst. The experimental results are shown in Figure 7f. Because benzoic acid is used as an electron donor in the catalytic process, that is, a sacrificial agent, it is necessary to additionally add benzoic acid into the system in advance for the next experiment. There is no significant decrease in the catalytic activity of the benzoic acid/TiO₂ system after four cycles of the cycle test, indicating that the stability of the system is relatively good and suitable for practical applications.

2.8. Photocatalytic Mechanism. Figure 8a is the ultraviolet diffuse reflection spectrum, and Figure 8b is the forbidden band width information of the material obtained by the Kubelka–Munk conversion. The absorption band edge of the TiO₂ sample is around 400 nm, and the absorption intensity of ultraviolet light below 400 nm is very high, and a small amount of visible light having a wavelength of less than

![Figure 7](image-url)
600 nm is absorbed. In addition, from Figure 8b, the forbidden band width of titanium dioxide is 3.05 eV. Figure 8c shows the Mott–Schottky (M–S) plot with $1/C^2$ versus potential. The linear parts of the curves are extrapolated to $1/C^2 \rightarrow 0$, and the values of Fermi level ($U_{FL}$) are estimated to be 0.21 eV, which is $CB = 0.12$ eV for the sample. According to the formula $E_g = VB - CB$, the VB of the sample can be obtained to be about 3.26 eV.

Figure 8d shows the photocatalytic degradation mechanism of TZ in the benzoic acid/titanium dioxide system and the role of benzoic acid in the catalytic system. After experimental comparison of different gas atmospheres, after drawing, it was found that the degradation process of TZ was inhibited in the system of argon and carbon dioxide blowing, but the degradation process of TZ in the air-inflated system has been promoted. It was estimated that oxygen in the air played a certain role.

Combined with additional ion capture experiments, a degradation curve was drawn and it was found that the degradation of TZ in the system of EDTA disodium and 1,4-p-benzoquinone was greatly inhibited; even with the addition of p-benzoquinone, there is a rising trend in the degradation curve. The degradation curve of the system shows a rising trend, and these two are the trapping agents of photogenerated holes and $O_2^{-•}$, which can be presumed to play a major role in the degradation of the system. More importantly, this combination is not only applicable to the degradation of TZ solution but also applies to organic dyes such as MO, RhB, MB, and MV.

3. CONCLUSIONS
In this experiment, aromatic acids such as benzoic acid and its derivatives played a very important role in titanium dioxide photocatalytic degradation of the TZ system, which can greatly improve its degradation efficiency, and the original 28.69% degradation efficiency was improved to 99.08%. When 20 mg/L TZ solution was degraded, the optimum amount of benzoic acid added was 0.10 g based on the mass of 0.10 g of TiO$_2$ added. The optimum pH of the degradation system was 3, and $O_2^{-•}$ and optical holes ($h^+$) play a major role in the degradation of the system. More importantly, this combination is not only applicable to the degradation of TZ solution but also applies to organic dyes such as MO, RhB, MB, and MV.

4. EXPERIMENTAL SECTION
4.1. Materials. TiO$_2$ (99.8%, anatase, average size 40 nm) was purchased from Aladdin Reagents (Shanghai) Co. Ltd. Other chemical reagents were purchased from Shanghai Jingjing Reagent Co. Ltd and Aladdin Reagents (Shanghai) Co. Ltd and were used as received, unless stated otherwise. All solutions were diluted with deionized water. The pH of the system was adjusted with a 1 mol/L hydrochloric acid solution and a sodium hydroxide solution.

4.2. Experimental Procedures. In order to control the variables and reduce the influence of various nonessential factors on the experiment, it is a prerequisite to keep the temperature constant during the series of experiments.
Therefore, in the dark reaction adsorption and photocatalytic degradation process, the reaction system is always in the oil bath and the set temperature is about room temperature (about 25 °C). It is worth noting that a fresh TZ solution with a concentration of 20 mg/L was prepared prior to the start of the experiment, which was obtained by diluting the mother liquor at a concentration of 1.000 g/L.

At the same time as the dark reaction adsorption phase begins, the high-pressure xenon lamp (300 W, PLS-SXE300C) is turned on for preheating for about half an hour. After the reaction system reaches the equilibrium of adsorption (i.e., the concentration of the system does not change much, and the specific manifestation is that the absorbance of the solution system does not change significantly), the photolysis can be performed. Subsequently, a light source equipped with a 420 nm cutoff filter and a reaction device were placed opposite to each other.

From previous experiments, it was known that TZ can reach adsorption equilibrium in the presence of titanium dioxide and benzoic acid when dark reaction adsorption reaches approximately half an hour. It is worth mentioning that in all of the experimental processes, 100 mL of reaction system was degraded. Therefore, in this basic experiment, 0.1 g of titanium dioxide and 0.1 g of benzoic acid were added to 100 mL of 20 mg/L TZ solution. Then, use hydrochloric acid solution (0.5 mol/L) and sodium hydroxide solution (0.5 mol/L) to adjust the solution pH around 3. Before the photodegradation process was carried out, a mixed solution containing TZ, titanium dioxide, benzoic acid, and derivatives thereof was stirred under a dark condition with a magnetic stirrer for approximately half an hour in order to achieve equilibrium of adsorption and desorption. A series of comparative experiments, such as different concentrations of benzoic acid, experimental comparison of different pH values, the effects of different para-positions of benzoic acid, different gas atmospheres, and different target contaminants, were performed. Furthermore, in order to confirm the role of aromatic small acid such as benzoic acid in the catalytic degradation of TZ by titanium dioxide, a series of experimental comparisons are also needed, including photodegradation of TZ itself, photocatalytic degradation of TZ in the presence of titanium dioxide, and the remaining two groups of laboratories added benzoic acid to this condition based on photodegradation and photocatalysis. Moreover, after the photocatalytic degradation process begins, samples are taken every 10 min or so and about 3 mL of each sample is taken. The removed liquid sample is filtered through a 0.45 μm filter into a 5 mL centrifuge tube. The absorbance test is used to determine the concentration change of the target pollutant, and removal efficiency (RE) can be calculated by the following formula

\[
RE_{TZ} (%) = \frac{C_0 - C_t}{C_0} \times 100
\]

C₀ and Cₜ represent the concentration of TZ at the initial time and at each sampling.

### 4.3 Ion Capture Experiments

In order to determine the role of each active free radical in the catalytic system, a series of ion trapping experiments are needed and in order to make the experimental effect more obvious, one ion trapping agent should be added at each time for each group of experiments. In this system experiment, EDTA disodium, potassium persulfate (K₂S₂O₈), isopropyl alcohol (i-PrOH), and 1,4-p-benzoquinone were selected as the trapping agents for photoactive holes (h⁺), photoelectrons (e⁻), hydroxyl radicals (HO⁰), and superoxide radicals (O₂⁻), respectively. The amount of various capture agents can be known from the previous literature. Specifically, the amount of each capture agent is taken as 1 mmol/L, and then, the ion capture experiment can be carried out by calculating the specific amount of the respective relative molecular mass.

### 4.4 Mechanism Analysis Method

It is well known that the absorbance measured by an UV–visible spectrophotometer can be used to accurately determine the degradation concentration of a target pollutant in a photocatalytic system over time. At the same time, combined with some of the previous experience and a series of ion capture experiments, we can know which active groups are playing a major role in the system of benzoic acid and titanium dioxide catalytic degradation of TZ. Moreover, the results of UV–visible spectroscopy show that the presence of benzoic acids in the TZ solution system has little effect on the absorption wavelength (Figure 9a). For the target contaminant TZ solution, prepare its standard concentration solution and test its absorbance to obtain a standard curve and its equation is in Figure 9b.

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