

Research Article

A Study of Photocatalysis of Methylene Blue of TiO_2 Fabricated by Electric Spark Discharge Method

Kuo-Hsiung Tseng,¹ Meng-Yun Chung,¹ Chaur-Yang Chang,¹ and Ting-Shou Cheng²

¹Department of Electrical Engineering, National Taipei University of Technology, Taipei, Taiwan

²Department of Power Supply, Taiwan Power Company, Taipei, Taiwan

Correspondence should be addressed to Kuo-Hsiung Tseng; khtseng@ee.ntut.edu.tw

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This study used the Electric Spark Discharge Method (ESDM) to prepare nano-Ti colloid. The results showed that the process efficiency increased according to the current and selecting different discharge periods ($T_{\text{ON}}-T_{\text{OFF}}$). The preparation process is pollution-free and very contributive to using TiO_2 for photocatalytic reaction to degrade organic compounds. This study used 99.9% pure Ti metal to examine the effects of different discharge parameter settings on the photocatalysis of methylene blue. The experimental results showed that the discharge period ($T_{\text{ON}}-T_{\text{OFF}}$) has an effect on the characteristics of the prepared nano-Ti colloid but affects its concentration. The nano-Ti colloid, as prepared under different parameters, has poor photocatalytic reaction with methylene blue at the concentration of 50 mg/L. The nano-Ti colloid does not have favorable effect on degrading methylene blue above 50 mg/L. For degrading methylene blue at a low concentration of 10 mg/L, the 100-100 nano-Ti parameter is preferable. For degrading methylene blue at a high concentration of 30 mg/L, nano-Ti colloid with T_{ON} exceeding 100 and T_{OFF} fixed at 100 is better. As the nano-Ti colloid prepared by ESDM was free of chemical agents, when TiO_2 was used in photocatalytic reaction to degrade organic compounds, there was no secondary pollution to the environment.

1. Introduction

The development of science and technology has brought convenience to people's life but also led to environmental pollution [1]. As 70% of the earth surface is covered with water, water pollution has become a serious issue. The available fresh water resource is less than 1%, and it is often polluted by human activities, and recovering a polluted body of water is a challenging task [2]. Moreover, the man-made pollutants are difficult to be decomposed by biotechnology. Waste water is usually treated by physical and chemical coagulation, adsorption, biological treatments, treatments temperature, or advanced oxidation processes [3, 4]. For example, dye wastewater has complex molecular structure, a biotoxic benzene ring, and NH_2 functional groups [5], which cannot be decomposed by biotechnology, and the chemical cleaning of pools will cause secondary pollution. In recent years, scientists have found that the TiO_2 photocatalytic reaction and nanocarbon have potential for treating waste water [6–8].

Ti is a silvery transition metal, characterized by light weight, high strength, metallic luster, and good resistance to corrosion and is known as “space metal” [9]. However, as Ti metal is a rare metal, its price is relatively high [10]. At present, about 95% of Ti ore is refined into TiO_2 , which is mostly used in coatings, cosmetics, papers, and toothpaste [11]. Powdered TiO_2 has chemical inertness and is fadeless and light resistant in the sun. These properties render the gray or brown chemicals for making household plastics bright white. Using TiO_2 as a catalyst to form a photocatalyst can purify water [12]. The light wavelength is about 400 nm, and because TiO_2 is made into the nanoscale in the preparation process, its catalytic effect is better [13, 14].

The pollutants in our environment affect human health and are difficult to degrade only by the force of nature, while biotechnological degradation can cause secondary pollution. Therefore, due to its stable chemical properties, nontoxicity, and photocatalysis, TiO_2 is used to degrade the various toxic organic pollutants generated by industrial processes [15].

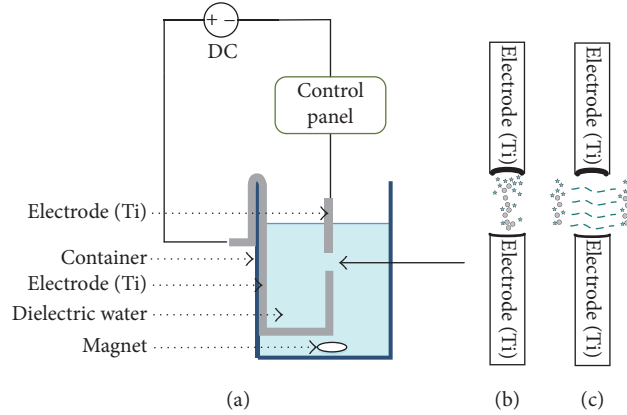


FIGURE 1: Principle of the ESDM. (a) The illustration of the ESDM, (b) metal nanoparticles generated, and (c) the DI water is stirred.

TABLE 1: Nano-Ti colloid parameter setting.

Metal wire diameter	1 mm	Ip	1
Metal purity	99.99%	Voltage	140 V
Test glass capacity	40 ml	Pressure	1 atm
Discharge period	5 min	Temperature	25°C
Dielectric fluid	Deionized water	$T_{ON}-T_{OFF}$	10-100
			50-100
			100-100
			150-100
			200-100
			300-100

In recent years, nano-TiO₂ has been extensively used as a photocatalyst, as its photocatalytic reaction can effectively damage pollutants in air and water. Photocatalytic oxidation can remove and decompose indoor air pollutants, as the reaction interface catches organic compounds for chemical oxidation, transforming them into CO₂ and water. The reaction interface can be operated at room temperature, and it is free of the issue of pressure. Hence, using photocatalysis to solve the problem of pollution is a topic worth exploring [16]. These days, the most popular way of fabricating the nano-TiO₂ is chemical method. But this kind of fabricating method contains chemical agents which is secondary pollution to the environment. In this study, the Electric Spark Discharge Method (ESDM) was used to prepare nano-Ti colloid and using TiO₂ for photocatalytic reaction to degrade organic compounds.

2. Material and Methods

2.1. Electric Spark Discharge Method (ESDM). The ESDM is the easiest and fastest method to prepare nanometal. As it only requires DI water and the metal to be prepared, it can be implemented at 1 atm and normal temperature [17, 18]. Its principle is that when the distance between the upper and lower electrodes (metallic Ti in this paper) of an electrical discharge machine is 30 μ m, the outshoot on the Ti surface generates arc, which is known as electrical spark [19], as shown in Figure 1(a). As its temperature is as high

as 8000 k [20], it melts the electrode surface and generates metal nanoparticles, as shown in Figure 1(b). The DI water is stirred by a magnet and dispersed in liquid, which is called nanometal colloid, as shown in Figure 1(c). Advantages of ESDM are the following: the production process is conducted in dielectric fluid; thus, there will be no dust. It has rapid and mass preparation and is energy efficient, producing uniform particles [21].

The parameter settings for the nano-Ti colloid prepared by an electrical discharge machine in this paper are shown in Table 1. The surface particles are analyzed by FEG-SEM [22]. As a result of the instrument magnification, SEM cannot photograph fine particles, as shown in Figure 2(a). The nano-Ti of different $T_{ON}-T_{OFF}$ parameters, which is prepared using an electrical discharge machine, has the appearance of round particles. The nano-Ti fluid must be centrifuged before SEM imaging; thus, there is an agglomeration of coarse particles. The mean particle size of the nano-Ti particles prepared in this study is about 100 nm. The energy dispersive spectrometer (EDS) of SEM is used for analysis. The components are Ti, C, and O elements, where C is the carbon paste for SEM, and EDX analysis shows Ti and O; thus, the nano-Ti made by an electrical discharge machine is TiO₂, as shown in Figure 2(b).

2.2. Photocatalytic Analysis of Nano-TiO₂ Corresponding to the Same Parameter Value at Different Concentrations. ESDM was used for preparation. $T_{ON}-T_{OFF}$ was set as 10-100, 50-100, 100-100, 150-100, 200-100, and 300-100. The total process time

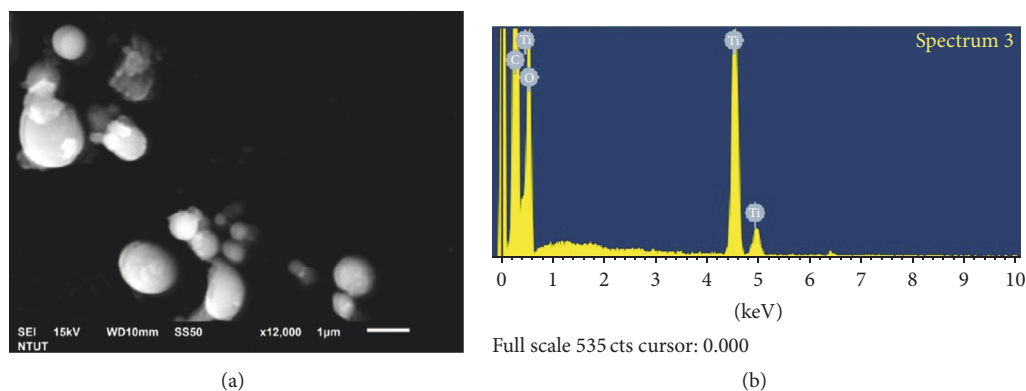


FIGURE 2: (a) SEM and (b) EDX of nano-Ti colloid prepared by ESDM.

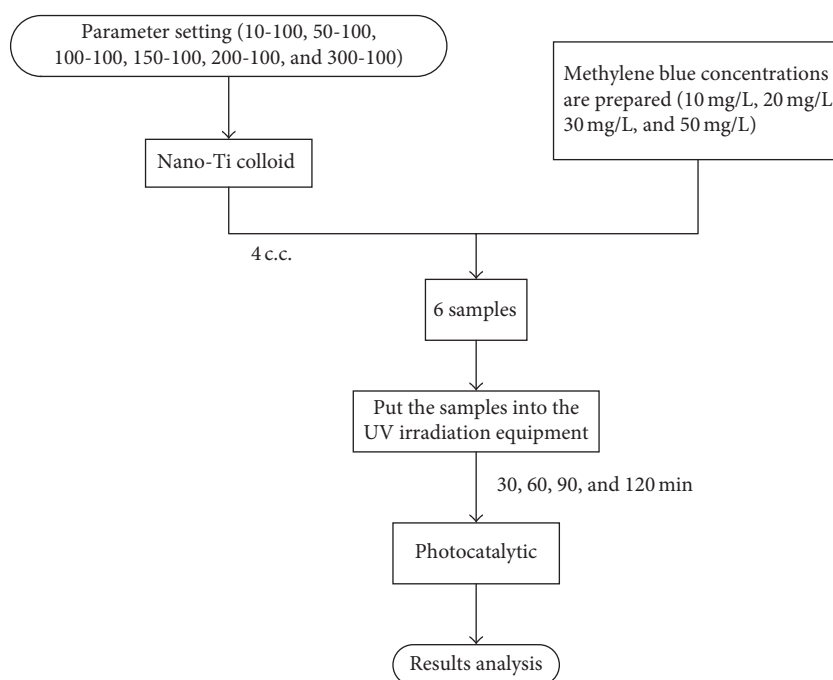


FIGURE 3: Photocatalytic process of nano-Ti corresponding to the same parameter value at different concentrations.

was 5 min. Finally, the nano-Ti was diluted with deionized water for quantification. Four methylene blue concentrations were prepared, which are 10 mg/L, 20 mg/L, 30 mg/L, and 50 mg/L. Then, 4 cc nano-Ti colloid was added in the methylene blue at four concentrations, irradiated by self-made UV irradiation equipment for 30, 60, 90, and 120 min, respectively. The samples were taken in timed intervals in order to analyze absorbance using the UV-visible spectrometer (UV-Vis) [23, 24]. The UV irradiation equipment was a self-made dual luminous tube UV irradiation box. There was an additional piece of aluminum-foil behind the luminous tubes to enhance the light source. The power of the luminous tubes was 8 W, and the UV wavelength was 256 nm. The sample was put in a 20 cc bottle, placed on a shelf in a box, and the switch was turned on for direct radiation. The photocatalytic process of nano-Ti corresponding to the same parameter value at different concentrations is shown in Figure 3.

2.3. Degradation Rate. This study used UV-Vis to measure the methylene blue concentration change. The absorbance of nano-Ti was determined through UV-Vis [25, 26]. As the concentration was directly proportional to absorbance, the concentration change was obtained according to the change in the absorbance in a specific wavelength [27]. The theoretical structure was the Beer-Lambert Law, which is the fundamental law of light absorption. It is applicable to all light-absorbing materials, including gases, solids, liquids, molecules, atoms, and ions [28]. A beam of monochromatic light irradiates a solution through a medium in a certain thickness. As the medium absorbs a part of the light energy, the intensity of the transmitted light is reduced. The higher the concentration of the absorbing medium, the thicker the medium and the more significant the attenuation of light intensity [29]. Provided the light penetration length is fixed and the solute and solution are identical, the

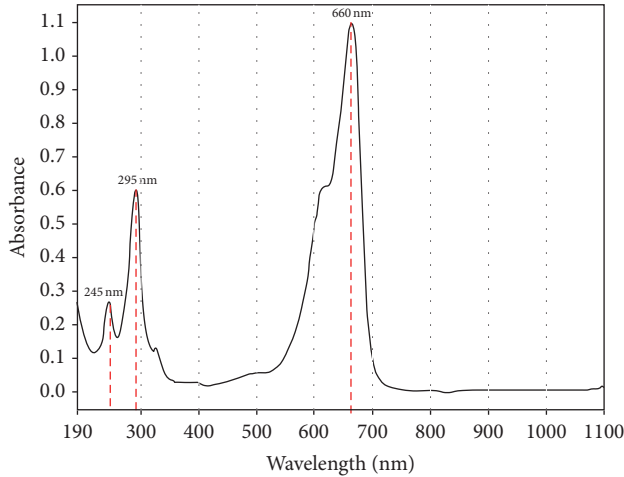


FIGURE 4: Methylene blue absorption spectrum.

concentration of solution is directly proportional to the absorbance.

According to the Beer-Lambert Law, the methylene blue concentration is linearly related to absorbance [30].

The degradation rate is expressed as (1) and as the concentration is proportional to absorbance, expressed as (2), the methylene blue concentration ratio reduced by the photocatalyst can be obtained by (2). The concentration is calculated without complex chemical formulae.

$$X = \frac{(c_0 - c)}{t}, \quad (1)$$

$$X = \frac{(A_0 - c)}{t}, \quad (2)$$

where X is degradation rate, c_0 is concentration before photocatalysis, c is concentration when the photocatalysis time is t , A_0 is absorbance before photocatalysis, and t is the photocatalysis time.

3. Results and Discussion

This study degraded organic pollutants and observed the degradation effect. As methylene blue has considerable adsorption on the surface of many materials and is unlikely to be decomposed by irradiation, it is suitable for experimental research on photocatalytic decomposition. Figure 4 shows the methylene blue absorption spectrogram made by UV-Vis equipment. There are obvious absorption peaks at three wavelengths, respectively: 660 nm, 295 nm, and 245 nm, where 660 nm is the maximum absorption peak in the visible light wave band. This study used this peak to analyze the photocatalytic degradation effect of methylene blue.

The nano-Ti of $T_{ON}-T_{OFF}$ 10-100 is mixed with 50 mg/L methylene blue for photocatalysis experimentation, where the absorbance decay rate is the lowest, meaning the 10-100 nano-Ti has poor ability to decompose high concentrations of methylene blue, as shown in Figure 5(a). After the degradation rate is converted, the 10 mg/L methylene

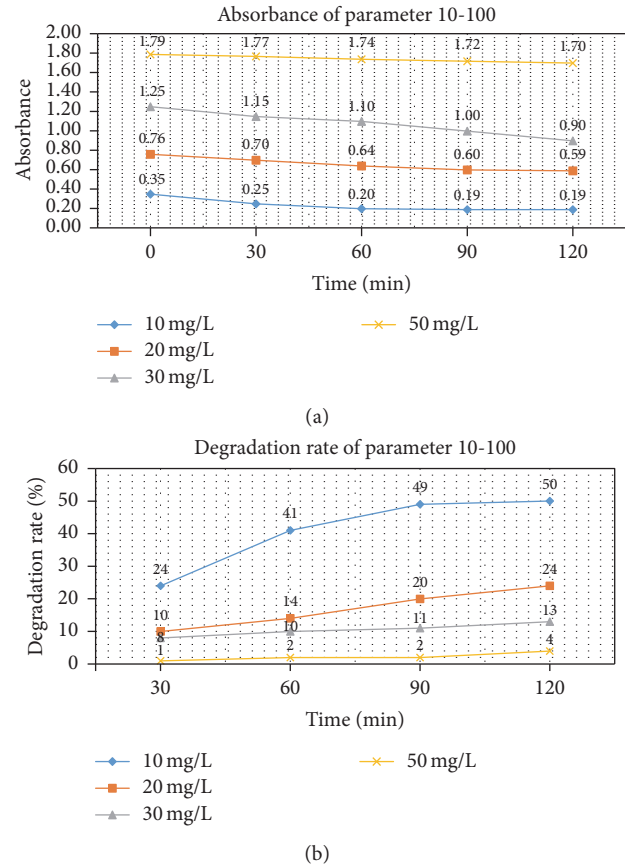


FIGURE 5: Nano-Ti of parameter 10-100: (a) absorbance and (b) degradation rate.

blue has the maximum decomposed concentration ratio after illumination. In other words, the 10-100 nano-Ti has higher concentration decomposition effect on low concentration methylene blue, followed by 50 mg/L, 20 mg/L, and 30 mg/L, respectively, as shown in Figure 5(b).

The nano-Ti of $T_{ON}-T_{OFF}$ 50-100 is added in methylene blue at different concentrations for photocatalysis experiments, and 50 mg/L has the lowest absorbance decay rate, meaning the 50-500 nano-Ti has the lowest ability to decompose high concentration methylene blue. The decomposition rates for methylene blue at concentrations of 10 mg/L, 20 mg/L, and 30 mg/L are better than 50 mg/L, as shown in Figure 6(a). After the degradation rate is converted, the 10 mg/L methylene blue has the maximum decomposed concentration ratio after illumination. Therefore, the 50-100 nano-Ti has a higher concentration decomposition effect on low concentration methylene blue. The concentrations in descending order of decomposition effect are 10 mg/L, 20 mg/L, 30 mg/L, and 50 mg/L, as shown in Figure 6(b).

When the parameter is 100-100, 50 mg/L has the lowest absorbance decay rate, meaning the lowest ability to decompose high concentration methylene blue. The absorbance decay rate of 30 mg/L is higher than that of 20 mg/L, and 10 mg/L methylene blue is the best, as shown in Figure 7(a). While the 10 mg/L methylene blue has the maximum decomposed concentration ratio after illumination, 30 mg/L

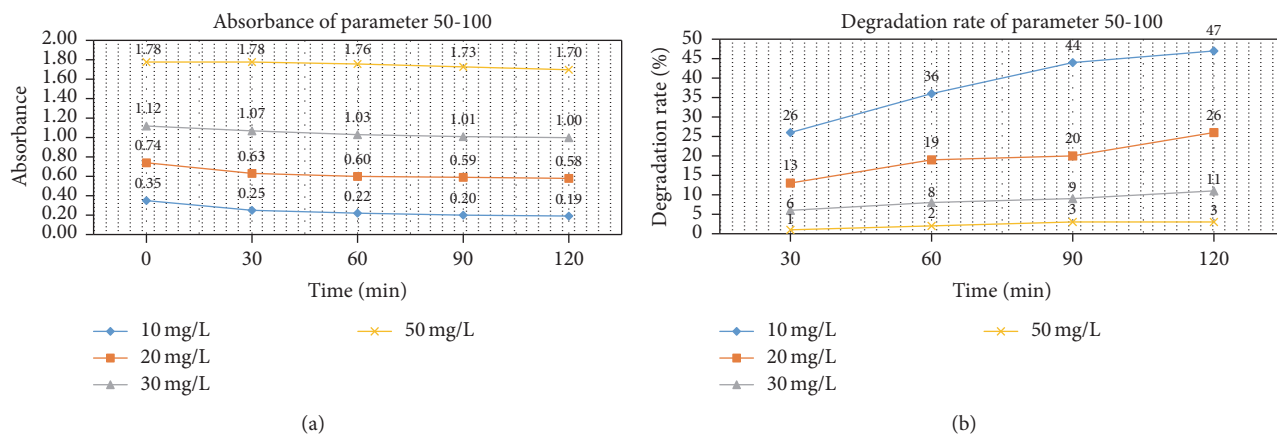


FIGURE 6: Nano-Ti of parameter 50-100: (a) absorbance and (b) degradation rate.

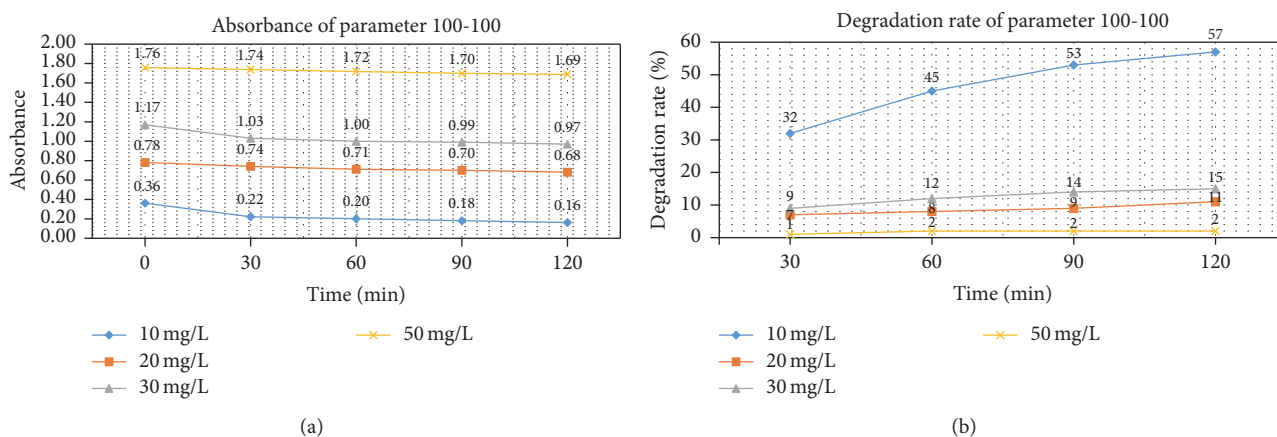


FIGURE 7: Nano-Ti of parameter 100-100: (a) absorbance and (b) degradation rate.

has a higher concentration decay rate than 20 mg/L, and the 50 mg/L still has the lowest concentration decay rate. The concentrations in descending order of decomposition effect are 10 mg/L, 2 mg/L, 30 mg/L, 20 mg/L, and 50 mg/L, as shown in Figure 7(a).

When the parameter is 150-100, 50 mg/L has the lowest absorbance decay rate, meaning the lowest ability to decompose high concentration methylene blue; 30 mg/L has the best absorbance decay rate, and 10 mg/L has the second highest absorbance decay rate, as shown in Figure 8(a). The 30 mg/L of methylene blue has the maximum decomposed concentration ratio after illumination, 10 mg/L has the second highest concentration decay rate, and 50 mg/L still has the lowest concentration decay rate; however, it is higher than the degradation rate of T_{ON} and smaller than T_{OFF} . The concentrations in descending order of decomposition effect are 30 mg/L, 10 mg/L, 20 mg/L, and 50 mg/L, as shown in Figure 8(a).

When the parameter is 200-100, 50 mg/L has the lowest absorbance decay rate, meaning the lowest ability to decompose high concentration methylene blue, while 30 mg/L has the best absorbance decay rate, and 10 mg/L has the second highest absorbance decay rate, as shown in Figure 9(a). The 30 mg/L methylene blue still has a higher decomposed

concentration ratio after illumination than 10 mg/L, meaning 10 mg/L still has the second highest concentration decay rate, while 50 mg/L still has the lowest concentration decay rate. The concentrations in descending order of decomposition effect are 30 mg/L, 10 mg/L, 20 mg/L, and 50 mg/L, as shown in Figure 9(b).

When the parameter is 300-100, 30 mg/L has the best absorbance decay rate, while 10 mg/L still has the second highest absorbance decay rate, as shown in Figure 10(a). In terms of degradation rate, 30 mg/L methylene blue has higher decomposed concentration ratio after illumination than 10 mg/L, while 10 mg/L still has the second highest concentration decay rate. Compared with the other three concentrations, while 50 mg/L is the lowest, the nano-Ti of T_{ON} smaller than T_{OFF} has better concentration decay rate. The concentrations in descending order of decomposition effect are 30 mg/L, 10 mg/L, 20 mg/L, and 50 mg/L, as shown in Figure 10(b).

4. Conclusions

This study used ESDM to prepare nano-Ti colloid under different T_{ON} - T_{OFF} parameters (10-100, 50-100, 100-100, 150-100, 200-100, and 300-100). The concentration was

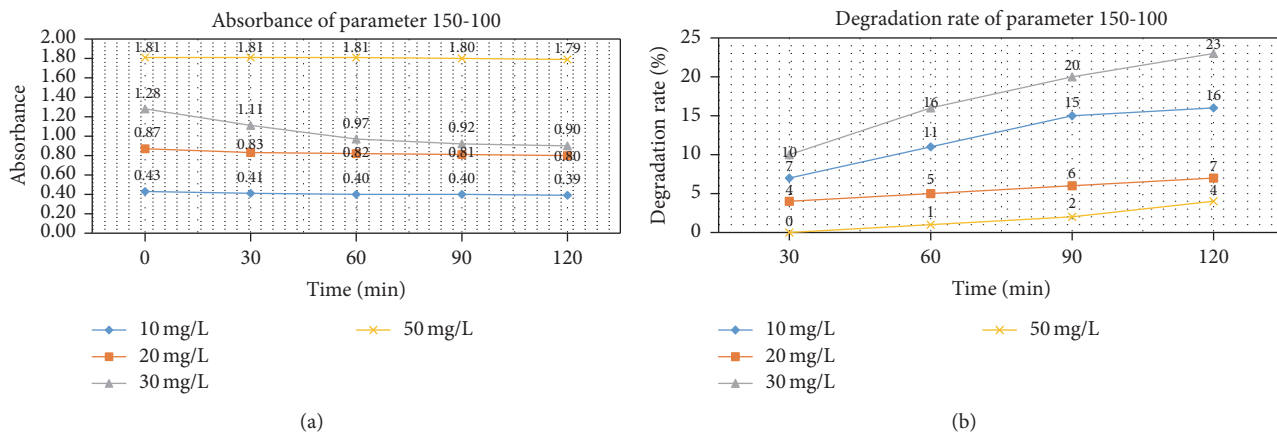


FIGURE 8: Nano-Ti of parameter 150-100: (a) absorbance and (b) degradation rate.

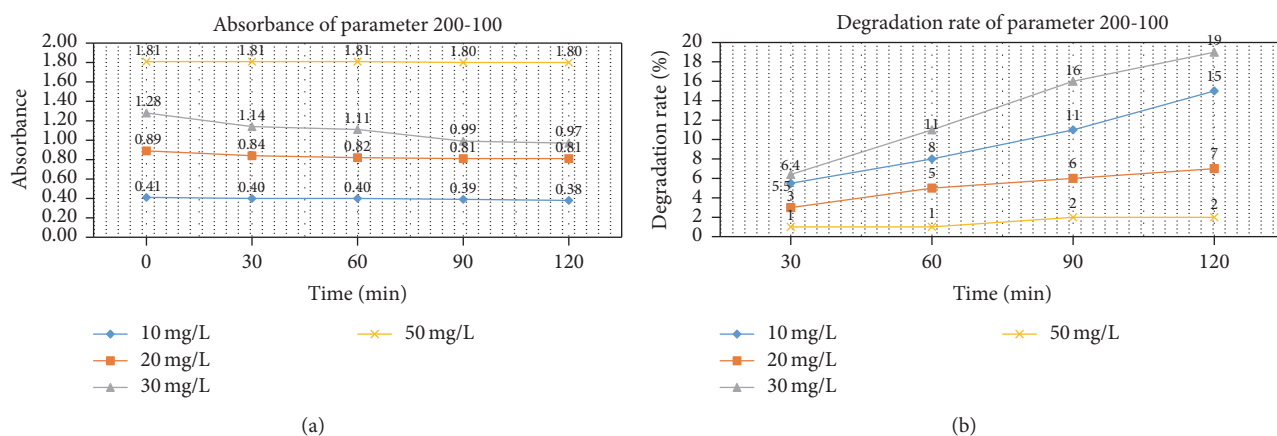


FIGURE 9: Nano-Ti of parameter 200-100: (a) absorbance and (b) degradation rate.

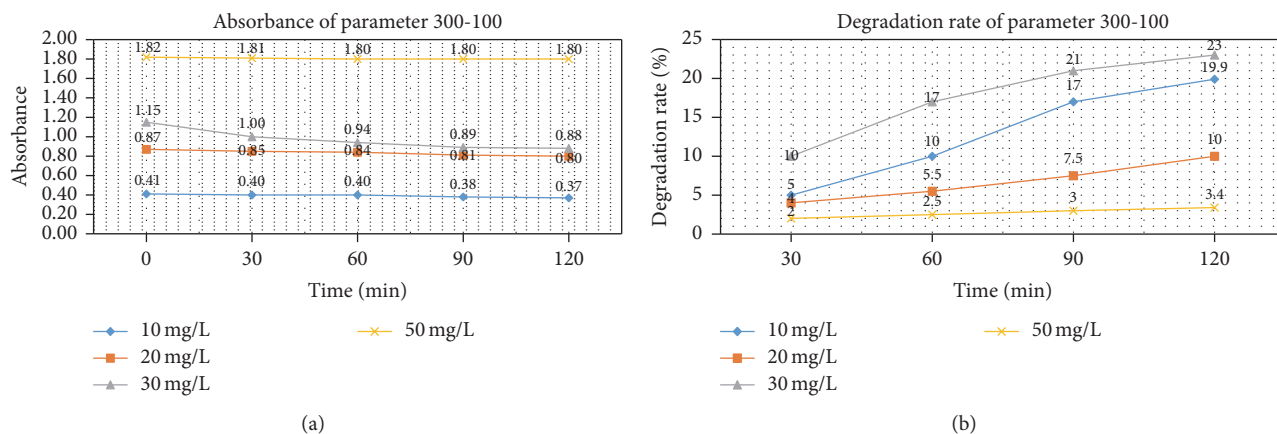


FIGURE 10: Nano-Ti of parameter 300-100: (a) absorbance and (b) degradation rate.

changed, and it was round in appearance. The particles had similar shapes. As the nano-Ti colloid prepared by ESDM was free of chemical agents, when TiO_2 was used in photocatalytic reaction to degrade organic compounds, there was no secondary pollution to the environment. The conclusions were drawn as follows:

- (1) Nano-Ti parameters of 10-100, 50-100, and 100-100 perform better at degrading 10 mg/L, and the maximum degradation rate at 120 min of degradation is 50.5%, 46.3%, and 56.9%, respectively. The nano-Ti parameter of 100-100 performs better in degrading concentration (10 mg/L).

- (2) The nano-Ti parameters of 150-100, 200-100, and 300-100 can degrade high concentration methylene blue (30 mg/L), where the maximum degradation rate at 120 min of degradation is 22.5%, 19.6%, and 22.9%, respectively. The parameter of 300-100 performs best in degradation rate.
- (3) When the concentration of methylene blue is 50 mg/L, the nano-Ti colloid of six parameters has poor degradation rate. Therefore, when the concentration is higher than 50 mg/L, only the nano-Ti made by an electrical discharge machine has no preferable degradation effect.
- (4) For degrading low concentration (10 mg/L), the 100-100 nano-Ti parameter is selected. For degrading high concentration (30 mg/L), the nano-Ti colloid of T_{ON} exceeding 100 and T_{OFF} fixed at 100 is preferred.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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