

## Decolorization of methylene blue in aqueous suspensions of titanium peroxide

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### Abstract

The pretreatment of TiO<sub>2</sub>-photocatalysts in solutions of H<sub>2</sub>O<sub>2</sub> was studied by examining the decolorization of methylene blue in the dark. Incubation of TiO<sub>2</sub> particles in H<sub>2</sub>O<sub>2</sub> solutions increased the oxidizing capacity of TiO<sub>2</sub>. Methylene blue (0.3 mM) was degraded in the presence of pretreated TiO<sub>2</sub>, and a decolorizing ratio of 47% was obtained after a 48-h incubation period in the presence of 5.0 g/L pretreated TiO<sub>2</sub>. Titanium peroxide as a stable oxidant, which can be synthesized with the reaction of titanium sulfate and H<sub>2</sub>O<sub>2</sub>, was studied in the decolorizing process of methylene blue. Concentrations of methylene blue were significantly reduced in the presence of titanium peroxide, and a greater extent of decolorization was obtained with larger amounts of titanium peroxide. A 63% decrease in methylene blue concentration was achieved in 5 h incubation in the presence of 4.0 g/L titanium peroxide. H<sub>2</sub>O<sub>2</sub> accelerated the decolorizing process in the presence of titanium peroxide. The addition of 100 mM H<sub>2</sub>O<sub>2</sub> to a methylene blue solution containing 2.0 g/L titanium peroxide increased the decolorizing ratio to 85% after 5 h incubation. The addition of a hydroxyl radical scavenger, dimethyl sulfoxide, significantly decreased the decolorizing ratio, indicating the role of hydroxyl radicals in the oxidation process.

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### 1. Introduction

Photocatalysts have been studied extensively as excellent materials for the elimination of hazardous organic compounds in contaminated air or water [1–4]. Titanium dioxide (TiO<sub>2</sub>) is undoubtedly the best-studied inorganic photocatalyst, and the degradation of a number of different chemicals by TiO<sub>2</sub> under UV irradiation has been reported in the literature [5–7]. The application of TiO<sub>2</sub> photocatalysts in ultrasonic systems has also been reported to enhance chemical reactions [8–11]. It is known that as a synergistic effect, the addition of TiO<sub>2</sub> particles, together with the oxidative power of the positive holes produced under UV irradiation, can enhance sonochemical reactions [12]. TiO<sub>2</sub> was found to improve the yield of sonochemical reactions under appropriate conditions, not only in the presence but also

in the absence of UV irradiation. However, the mode of action that TiO<sub>2</sub> exerts in this system has not been clarified.

Different mechanisms have been studied and proposed to explain the enhancing effect of photocatalysts in ultrasonic systems. It has been hypothesized that this enhancement may be caused by the induction of cavitation nuclei in irradiating solutions, similar to the enhancements obtained in the presence of inert particles such as Al<sub>2</sub>O<sub>3</sub> [13,14]. However, the oxidizing power obtained in the presence of TiO<sub>2</sub> was higher than that of materials like Al<sub>2</sub>O<sub>3</sub> [11,15]. While it has been reported that the sonoluminescence caused by cavitation may induce the excitation of TiO<sub>2</sub> in an ultrasonic system [16], Tuziuti et al. [17] have introduced another mechanism in this regard, namely, the appearance of titanium peroxide on the surface of TiO<sub>2</sub> during ultrasonic irradiation. It has been recognized that the exposure of air-saturated water to ultrasonic irradiation leads to the formation of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) [18,19]. Further, the formation of a yellowish substance on the surface of TiO<sub>2</sub> particles occurs in H<sub>2</sub>O<sub>2</sub> solutions, and the yellow coloration of TiO<sub>2</sub> after

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treatment with  $\text{H}_2\text{O}_2$  is believed to arise from the presence of a surface titanium peroxide complex [20–22]. Accordingly, the interaction of  $\text{H}_2\text{O}_2$  in the vicinity of the  $\text{TiO}_2$  surface might result in the formation of a stable oxidizing agent, i.e., a titanium peroxide complex, suggesting a mechanism based on the formation of long-lived active species on the surface of  $\text{TiO}_2$  by ultrasonic irradiation.

In the present study, pretreatment of a  $\text{TiO}_2$  photocatalyst in a solution of  $\text{H}_2\text{O}_2$  was investigated by examining the decolorization of methylene blue solution. Also, the decolorization of methylene blue in the presence of titanium peroxide was studied kinetically to confirm the high activity of this chemical substance in the color-removal process.

## 2. Experimental

### 2.1. Materials

$\text{TiO}_2$  (MT-150A, rutile) was obtained from Tayca Co. (Osaka, Japan) and was employed as the catalyst. The content of the rutile phase, the particle size and the specific surface area of the  $\text{TiO}_2$  powder were 99.9%, 2.27  $\mu\text{m}$  and 110  $\text{m}^2/\text{g}$ , respectively. Methylene blue [3,7-bis(dimethylamino) phenothiazin-5-ium chloride], dimethyl sulfoxide [DMSO;  $(\text{CH}_3)_2\text{SO}$ ] and  $\text{H}_2\text{O}_2$  were obtained from Wako Pure Chemical Industries (Osaka, Japan). Oxo[5,10, 15, 20-tetra(4-pyridyl)-porphinato] titanium (IV) was obtained from Tokyo Kasei Kogyo Co., Ltd. (Tokyo, Japan) for the analysis of  $\text{H}_2\text{O}_2$ . All other chemicals used in this study were of guaranteed reagent grade and were used without further purification. Laboratory-grade water was prepared with a Milli-Q water purification system.

Titanium peroxide was prepared according to the procedures described in the literature [20,22]. Fifty milliliter of  $\text{H}_2\text{O}_2$  (30%) was added to a solution of 10% titanium sulfate (150 mL) and stirred thoroughly. With the formation of titanium peroxide, a yellow solution was obtained, which was then neutralized (pH 7–8) with a solution of 10%  $\text{NH}_3$  to precipitate the titanium peroxide particles. Precipitates were separated and dried in a desiccator containing concentrated sulfuric acid. The particle size, the specific surface area and the pore diameter of the titanium peroxide particles were 6.5  $\mu\text{m}$ , 73.7  $\text{m}^2/\text{g}$  and 40.4 Å, respectively.

### 2.2. Methods

A solution of 0.3 mM methylene blue was prepared and used in this study. The decolorization of methylene blue was first examined in the presence of pretreated  $\text{TiO}_2$ .  $\text{TiO}_2$  powder (50 mg) was incubated in a 110-mM  $\text{H}_2\text{O}_2$  solution (10 mL) in the dark for 24 h. The concentration of  $\text{H}_2\text{O}_2$  was analyzed during the incubation period by a spectrophotometric method [23]. The suspension was then centrifuged at 8000 rpm for 10 min and the incubated  $\text{TiO}_2$  was separated and washed three times with distilled water (10 mL each). After washing and drying, incubated  $\text{TiO}_2$  (50 mg) was suspended in 0.3 mM methylene blue solution (10 mL). All solutions were incubated in the dark without agitation to avoid possible complicating effects of illu-

mination or mixing. Samples were taken at designated times and analyzed according to the change in the concentration of methylene blue, which was measured with a spectrophotometer (U-3010, Hitachi, Tokyo, Japan) at 661 nm. The measured absorption was converted to a concentration using a standard calibration curve for methylene blue.

The decolorizing ratio was defined by the following formula:

$$\text{Decolorizing ratio (\%)} = \frac{(\text{ABS} [\text{Init}] - \text{ABS} [\text{Test}])}{\text{ABS} [\text{Init}]} \times 100$$

where ABS [Init] and ABS [Test] represent the absorbances of the methylene blue solution for the initial (without treatment) and test samples, respectively; thus, (ABS [Init] – ABS [Test]) indicates the net decrease of the absorbance.

## 3. Results and discussion

### 3.1. Pretreatment of $\text{TiO}_2$ by incubation in $\text{H}_2\text{O}_2$ solution

Pretreatment of the  $\text{TiO}_2$  photocatalyst was carried out by incubation in a solution of  $\text{H}_2\text{O}_2$ . Fig. 1 shows the change in  $\text{H}_2\text{O}_2$  concentration in the presence of  $\text{TiO}_2$  during a 24-h incubation period. The  $\text{H}_2\text{O}_2$  concentration gradually decreased with increasing incubation time and reached a steady value of about 60 mM after 6 h of incubation. A pale yellowish powder was obtained after 6 h of incubation in the presence of  $\text{H}_2\text{O}_2$ , and this color did not change after washing with distilled water. These results suggested the possibility that  $\text{H}_2\text{O}_2$  was consumed in a chemical reaction with  $\text{TiO}_2$  and that titanium peroxide could have formed on the surfaces of the  $\text{TiO}_2$  particles. The formation of titanium peroxide reached its peak at 6 h incubation time under these experimental conditions. This suggestion was supported by the study of Ohno et al. [21] using X-ray photoelectron spectroscopy analysis, indicating the generation of titanium peroxide on the rutile  $\text{TiO}_2$  surface after treatment with  $\text{H}_2\text{O}_2$ . After the treatment with  $\text{H}_2\text{O}_2$ , a new band appeared at 533 eV on the X-ray photoelectron spectrum, and this band was considered to

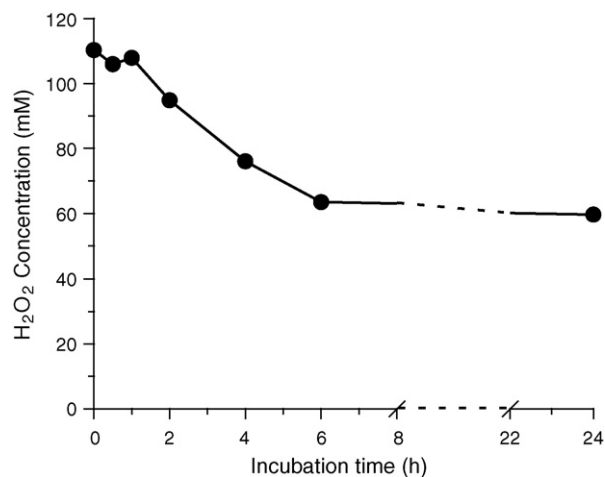


Fig. 1. Reduction of  $\text{H}_2\text{O}_2$  in the presence of  $\text{TiO}_2$  during incubation in the dark.  $\text{TiO}_2$  powder (50 mg) was suspended in a 10-mL volume of  $\text{H}_2\text{O}_2$  solution (concentration, 110 mM). Data are means of three replicate experiments.

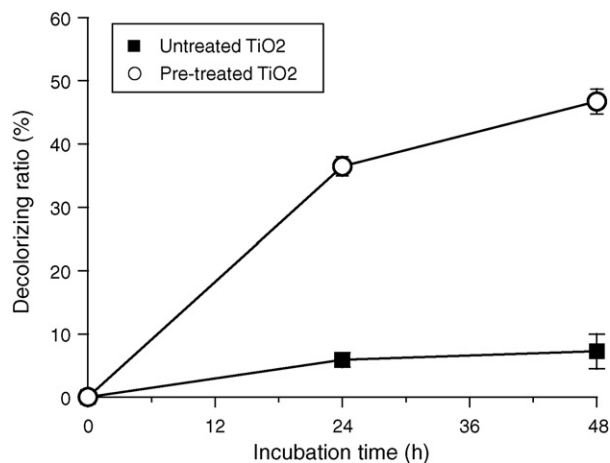


Fig. 2. Decolorization of methylene blue with H<sub>2</sub>O<sub>2</sub>-pretreated TiO<sub>2</sub> in distilled water. Initial concentration of methylene blue was 0.3 mM. For pretreatment, 50 mg TiO<sub>2</sub> was incubated in 10 mL of H<sub>2</sub>O<sub>2</sub> solution (concentration, 110 mM) for 24 h, then washed with distilled water. Data are expressed as means  $\pm$  standard error ( $n=3$ ).

be due to the peroxide generated on the surface. This assumption was confirmed by comparing the peak to that of a titanium peroxide powder, which showed a strong peak at 532.8 eV.

To evaluate the oxidizing power of pretreated TiO<sub>2</sub>, the decolorization of methylene blue in the presence of pretreated TiO<sub>2</sub> was examined. Fig. 2 shows the decolorizing ratios of methylene blue in the presence of TiO<sub>2</sub> particles pretreated in H<sub>2</sub>O<sub>2</sub> solution and distilled water (control), respectively. Pretreatment of TiO<sub>2</sub> in 100 mM H<sub>2</sub>O<sub>2</sub> solution for 24 h was found to improve the decolorizing ratio of methylene blue from 7% to 47% within a 48-h incubation period. A decolorizing ratio of 36% was obtained in the presence of 5.0 g/L pretreated TiO<sub>2</sub> after a 24-h incubation period. However, incubation of TiO<sub>2</sub> in distilled water had no significant effect on the decolorizing ratio (6%) and afforded only a slight decrease in the concentrations of methylene blue, which may have been due to its adsorption on the surfaces of the TiO<sub>2</sub> particles. Therefore, the interaction of TiO<sub>2</sub> particles with H<sub>2</sub>O<sub>2</sub> enhanced the decolorization of methylene blue, even in the absence of UV or ultrasonic irradiation. This interaction likely increased the adsorption capacity of the TiO<sub>2</sub> surfaces and/or induced the oxidizing power of TiO<sub>2</sub>, which resulted in an acceleration of the decolorizing process.

### 3.2. Decolorization of methylene blue in the presence of titanium peroxide

The decolorization of the methylene blue solution was investigated in the presence of titanium peroxide, a probable active agent that can be formed on the surface of TiO<sub>2</sub> upon its interaction with H<sub>2</sub>O<sub>2</sub>. Various amounts of titanium peroxide were added to the solutions of methylene blue, which were then incubated at room temperature in the dark without agitation. Fig. 3 shows the decolorizing ratio of methylene blue in the presence of titanium peroxide. During incubation, approximately 50% of the methylene blue was degraded in the presence of 2.0 g/L titanium peroxide within 5 h, and more than 95% decolorization was

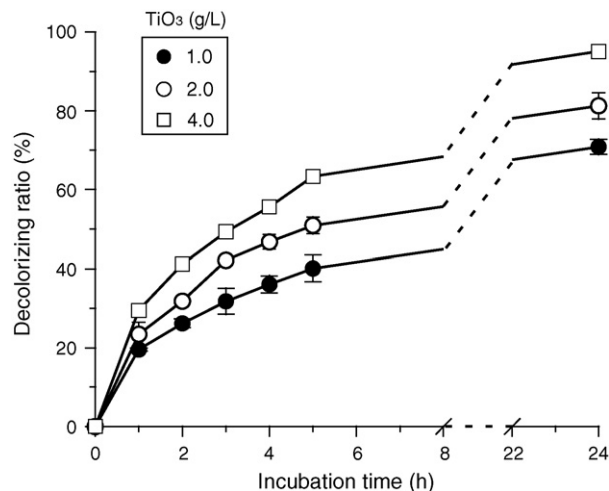


Fig. 3. Decolorization of methylene blue in the presence of titanium peroxide during incubation in the dark. The initial concentration of methylene blue was 0.3 mM.

obtained in the presence of 4.0 g/L titanium peroxide after 24 h. These results also indicate the dependency of the decolorizing ratio on the titanium peroxide concentration.

Reactions occurring on the surface usually include several steps, such as diffusion of reacting molecules to the surface, adsorption on the surface, reaction on the surface, desorption of products, and diffusion of the desorbed products. One of these steps is expected to limit the rate of methylene blue decolorization. Adsorption of methylene blue on the surface of titanium peroxide was confirmed by the color change on the surface of titanium peroxide during the incubation period. Accordingly, the titanium peroxide changed from yellow to black in the methylene blue solutions, indicating the progress of the adsorption. Adsorption of methylene blue on the surface of titanium peroxide was so rapid that it accelerated the decolorization of the methylene blue solution. These particles of titanium peroxide remained black for an extended period of time, with their yellow color being recovered gradually after several days of incubation. These findings indicated the slow decolorization of methylene blue on the surface of titanium peroxide. Color removal from the methylene blue solution was likely caused by its adsorption on the surface of titanium peroxide and/or its decolorization into oxide forms. Considering the time required to decolorize the methylene blue solution and comparing it with the time required to recover the original color of the titanium peroxide particles, it was concluded that the rate of adsorption on the surface of titanium peroxide was higher than the rate of oxidation. Therefore, the decolorization of methylene blue could be considered to be a consecutive process including two steps, i.e., adsorption and oxidation, with the oxidation step being the limiting one.

### 3.3. Effects of H<sub>2</sub>O<sub>2</sub> concentration

On the other hand, it has been reported that the decolorization of methylene blue can be accelerated with an alkaline pH in photocatalytic systems [5]. Therefore, variations of pH in the presence of titanium peroxide were considered in this study. It

was observed that the addition of 2.0 g/L titanium peroxide to distilled water increased the pH from  $5.7 \pm 0.1$  to  $7.6 \pm 0.1$ . This shift in pH could be caused by the hydration of titanium peroxide and formation of an anionic hydroxyl layer on the surfaces of the particles. Due to the positive charge of the methylene blue molecule, it can be concluded that the formation of this negative layer on the surface of titanium peroxide may facilitate and accelerate the adsorption step.

The rate of decolorization of methylene blue in an aqueous  $\text{TiO}_2$  suspension can be accelerated photocatalytically [5] and sonocatalytically [111] by addition of  $\text{H}_2\text{O}_2$ .  $\text{H}_2\text{O}_2$  has been known to be an enhancing agent in the color removal process, because it acts as a source of hydroxyl (OH) radicals. Addition of  $\text{H}_2\text{O}_2$  to a solution of methylene blue (0.3 mM) containing titanium peroxide also accelerated the decolorizing rate in this study. Fig. 4 shows the effects of different concentrations of  $\text{H}_2\text{O}_2$  on the decolorizing rate in the presence of 2.0 g/L titanium peroxide. Titanium peroxide (200 mg) was suspended in a 10-mL volume of methylene blue solution (0.3 mM), and 100 or 50  $\mu\text{L}$  of the  $\text{H}_2\text{O}_2$  solution (10 M) was then added to prepare the 100 or 50 mM  $\text{H}_2\text{O}_2$ -containing solutions, respectively. It was found that the decolorizing ratio of methylene blue improved from 51% to 85% in a solution of 100 mM  $\text{H}_2\text{O}_2$  and 2.0 g/L titanium peroxide with a 5-h incubation period.

Fig. 5 shows the effect of titanium peroxide concentration on the decolorization of methylene blue in a solution of 100 mM  $\text{H}_2\text{O}_2$ . The decolorizing ratio in a solution containing only  $\text{H}_2\text{O}_2$  with no titanium peroxide was very low; only 12% of the methylene blue was degraded within a 24-h incubation period. In contrast, the synergistic effect of titanium peroxide on the decolorization of methylene blue was able to be seen in the presence of  $\text{H}_2\text{O}_2$ . This figure also shows the dependency of the decolorizing ratio on the concentrations of titanium peroxide in the presence of  $\text{H}_2\text{O}_2$ . It is noteworthy that the appearance of black particles of titanium peroxide in the solution containing  $\text{H}_2\text{O}_2$  confirmed the adsorption of methylene blue on the particle surfaces. However, contrary to the previous observations, described

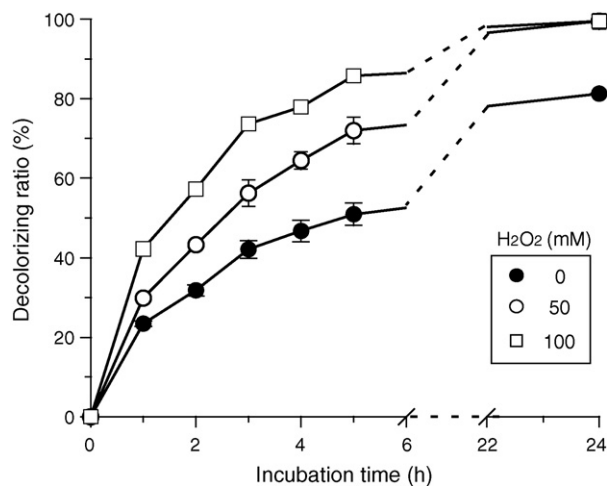


Fig. 4. Decolorization of methylene blue in the presence of titanium peroxide and various concentrations of  $\text{H}_2\text{O}_2$ . The initial concentrations of methylene blue and titanium peroxide were 0.3 mM and 2.0 g/L, respectively.

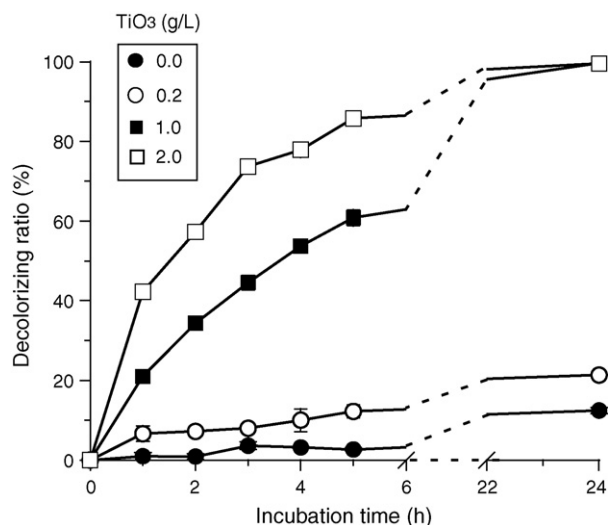


Fig. 5. Decolorization of methylene blue in the presence of  $\text{H}_2\text{O}_2$  and various concentrations of titanium peroxide. The initial concentrations of methylene blue and  $\text{H}_2\text{O}_2$  were 0.3 mM and 100 mM, respectively.

in Section 3.2, the yellow color of the titanium peroxide particles was recovered very quickly (within several hours instead of several days of incubation in the absence of  $\text{H}_2\text{O}_2$ ), indicating simultaneous adsorption and oxidation processes under these conditions. These results show that using  $\text{H}_2\text{O}_2$  as a source of OH radicals increases the rate of oxidation and accelerates the decolorization of methylene blue on the surface of titanium peroxide.

#### 3.4. Effects of dimethyl sulfoxide (DMSO)

It has been reported that the photocatalytic and sonocatalytic decolorization of methylene blue in the presence of  $\text{H}_2\text{O}_2$  and  $\text{TiO}_2$  follows a radical oxidation pathway [5,11]. This pathway may be taken due to hydrogen peroxide being a source of OH radicals when decomposed homolytically. To study the role of OH radicals in the oxidation system of titanium peroxide, we examined the effects of DMSO as an OH-radical scavenging agent in this process. It has been reported that OH radicals react with DMSO to give high yields of  $\text{CH}_3$  radicals, which leads to methane and ethane as final products [24]. Fig. 6 shows the suppressive effects of DMSO on the decolorization of methylene blue in a solution containing titanium peroxide and  $\text{H}_2\text{O}_2$ . We mixed the reagents as follows: we first prepared methylene blue solution at the concentration of 0.37 mM. Because the density of DMSO is 1.10 g/mL, 1.82 mL of DMSO and 8.18 mL of methylene blue solution was mixed to produce the 10 mL mixture of 0.3 mM methylene blue solution and 200 g/L DMSO. Then 50  $\mu\text{L}$  of 10 M  $\text{H}_2\text{O}_2$  and 20 mg titanium peroxide were added to the mixture. As can be seen in Fig. 6 the decolorizing ratio decreased from 99.4% to 64.1% in the presence of 200 g/L DMSO over a 24-h incubation time. This suppressive effect was dependent on the concentration of DMSO under these conditions. These results may indicate the role of OH radicals in the decolorizing process, which is enhanced by  $\text{H}_2\text{O}_2$  and suppressed by DMSO. It is worth noting here that the effects

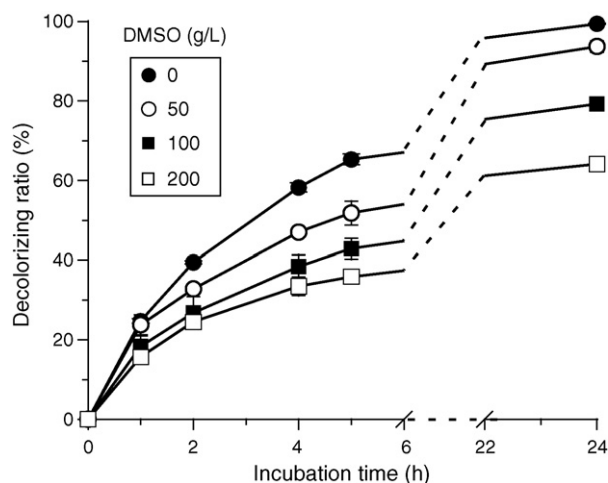


Fig. 6. Effects of various concentrations of DMSO on the decolorization of methylene blue in the presence of titanium peroxide and  $\text{H}_2\text{O}_2$ . The initial concentrations of methylene blue,  $\text{H}_2\text{O}_2$ , and titanium peroxide were 0.3, 50 mM, and 2.0 g/L, respectively.

of the scavenger were not clearly detected at 1 h of incubation time. This result suggested that the adsorption of methylene blue on the surface of the titanium peroxide might be dominant during this period and that DMSO did not significantly interfere with the adsorption process. However, scavenging effects were significant after longer periods of incubation time (24 h), when the decolorizing rate was limited by the oxidation of methylene blue. It seems likely that the processes of adsorption and oxidation occur simultaneously in the presence of  $\text{H}_2\text{O}_2$ .

In this study, the pretreatment of the  $\text{TiO}_2$  photocatalyst and the interaction of its surface with  $\text{H}_2\text{O}_2$  were found to enhance the decolorization of methylene blue, even in the absence of UV or ultrasonic irradiation. This interaction increased the adsorption capacity and induced the oxidizing power of  $\text{TiO}_2$ . It was shown recently that the decomposition of  $\text{H}_2\text{O}_2$  on the surface of  $\text{TiO}_2$  could result in the formation of OH radicals [25]. Consequently, these interactions could intensify the oxidizing power of  $\text{TiO}_2$  by improving the formation of both OH radicals and more stable oxidants on the surface of  $\text{TiO}_2$ . The present results clearly indicate that the oxidizing power of  $\text{TiO}_2$  is enhanced by pretreatment in the presence of  $\text{H}_2\text{O}_2$ . The appearance of yellow titanium peroxide on the surface of pretreated  $\text{TiO}_2$  also confirmed the formation of this oxidant on the surface of  $\text{TiO}_2$ . These results are in good agreement with previous studies on the formation of titanium peroxide in ultrasonic and electrochemical systems. Accordingly, the interaction of  $\text{H}_2\text{O}_2$  formed in the ultrasonic system and in the vicinity of the  $\text{TiO}_2$  surface may result in the formation of stable oxidants [17]. Also, electrochemical studies of anodic oxide films formed on titanium during potential sweeps indicated a cathodic peak below 0.5 V that might be due to the formation of an oxidizing agent on the surface of titanium [26]. Considering these results under different conditions, it may be concluded that this oxidizing surface can be formed as a separate layer of titanium peroxide, or it might form in the near-surface region of the film, for which the main structure is still  $\text{TiO}_2$ .

To evaluate the oxidizing power of titanium peroxide as a probable oxidant formed during this interaction, the decolorization of methylene blue solution was studied in the presence of titanium peroxide. The results obtained in this regard indicated a high oxidizing power for titanium peroxide, particularly in the presence of  $\text{H}_2\text{O}_2$ . Also, the suppressive effects of DMSO on the decolorizing rate indicated the primary role of OH radicals in the oxidation process. Furthermore, it was shown that the addition of titanium peroxide to a solution increased the pH, likely by hydration and formation of an anionic layer on its surface. This negative layer may facilitate the adsorption of methylene blue cations on the surface of titanium peroxide, which would then result in a higher decolorizing ratio. Consequently, the adsorption of methylene blue on the surface of titanium peroxide, as well as the decomposition of  $\text{H}_2\text{O}_2$  into OH radicals at the surface, would provide the high oxidizing power required for the decolorization of methylene blue.

#### 4. Conclusions

A  $\text{TiO}_2$  photocatalyst was activated in a solution of  $\text{H}_2\text{O}_2$ , and the decolorization of methylene blue was improved in the presence of these pretreated particles. The activation of  $\text{TiO}_2$  was achieved by the interaction of its surface with  $\text{H}_2\text{O}_2$ . Titanium peroxide, which was proposed as an active oxidant and which can be formed on the  $\text{TiO}_2$  surface as a result of this interaction, was examined in the methylene blue decolorizing process. The decolorization of methylene blue was achieved in the presence of titanium peroxide and was enhanced by the addition of  $\text{H}_2\text{O}_2$ . The mechanism of the decolorization was further investigated by the addition of DMSO. DMSO suppressed the decolorizing process in the presence of titanium peroxide and  $\text{H}_2\text{O}_2$ , indicating the primary role of OH radicals in the oxidation pathway.

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