

Influence of TiO₂ Surface Properties on Water Pollution Treatment and Photocatalytic Activity

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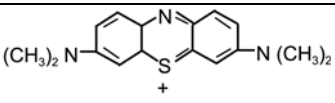
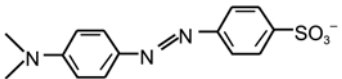
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Nowadays, waste water with color is plentifully generated from many industries including textile, leather, paper, printing, dye stuff, plastic and so on.¹⁻³ Degradation and removal of dye materials from contaminated water is very important, because the water quality is severely reduced by even quite slight color. Methyl orange (MO, C₁₄H₁₄N₃NaO₃S) is one of the well-known anionic dyes, and has been widely used in textile, printing, paper, food and pharmaceutical industries and research laboratories.² Methylene blue (MB, C₁₆H₁₈NSCl) is one of the most common dyeing materials for wood, silk and cotton.^{2,3} The structures of MO and MB are shown in Table 1. The degradation and removal of MO and MB from waste water is very important due to their toxicity and even carcinogenicity.

The high photocatalytic activity of titanium oxide (TiO₂) has been well-documented in many literatures and widely used in purification of waste water.¹⁻⁵ The TiO₂ (110) surface structures are shown in Figure 1 and it is believed that the surface structure is the most primitive and essential property that functions in photocatalytic activity.^{5,6} The studies on TiO₂ photocatalytic reactions have shown that the overall kinetics depend on both amount of adsorbed substrate on the surface be reduced or oxidized by photoexcited electron (e⁻) or positive hole (h⁺), respectively, and rate of geminate recombination of e⁻ and h⁺.^{4,6} Therefore, the different electric charge's influence of dye in aqueous heterogeneous suspensions may be complicated by possible competing reactions of direct photocatalyzed oxidation, dye photosensitized catalysis, and photolysis of the adsorbed dye.^{2,4,7-10} In this research, the dyes of MO and MB for reasons stated above were selected, respectively representing anionic dye and cationic dye, to study the TiO₂ photocatalytic reactions properties.

Table 1. Dye names and structures

Dye name	Structure
Methylene blue C ₁₆ H ₁₈ NSCl	
Methyl orange C ₁₄ H ₁₄ N ₃ NaO ₃ S	

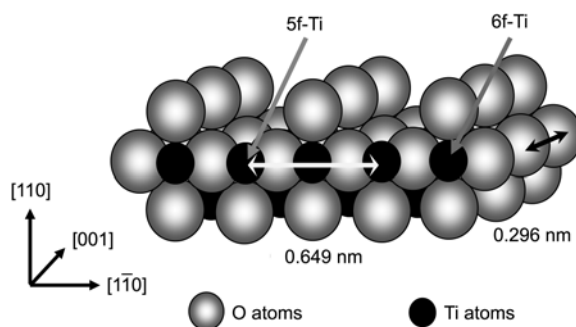


Figure 1. A ball stick model of the TiO₂ (110) surface.

Experimental

Materials. The dyes of MB and MO, the anatase TiO₂ ($S_{\text{bet}} = 43 \text{ m}^2/\text{g}$), and the other chemicals were of AR (Analytical reagent) grade and procured from Sinopharm Chemical Reagent Co., Ltd. (China). Distilled water was used to prepare the solutions. A Degussa P25 catalyst provided by the Degussa Company (Germany) was used without further modification throughout this work. Its main physical parameters are as follows: $S_{\text{bet}} = 65 \text{ m}^2/\text{g}$; average primary particle size, around 20 nm; purity, > 99%; anatase/rutile content (w/w), 80:20. The XRD patterns of the anatase TiO₂ (a) and P25 powders (b) were shown in Figure 2.

Adsorbed of OH⁻ or H⁺ ions. To research the surface characteristics of the TiO₂ particles, we had determined the pH change of aqueous solution due to the desorption of the different electric charges OH⁻ ions or H⁺ ions on the TiO₂ surface, in the range of pH₀ from *ca.* 1 to 13. The initial pH₀ at 25 °C represented by the pH value of an 20 mL aqueous solution of HNO₃ or NaOH; the final pH₁ is the pH value after aging at 25 °C for 2 h, to be mixed with 1 g of (a) anatase TiO₂ or (b) P25 powders.⁷⁻⁹ From the intersection between the pH₀-pH₁ curve and the diagonal straight line, such as shown in Figure 3, the point of zero charge (PZC) of TiO₂ could be obtained.⁷

Adsorption of the Dyes. The adsorption isotherms of dye molecules on the P25 and the anatase TiO₂ surface were measured as follows: The 20 mL of MB or MO dyes aqueous solutions with different concentrations were prepared, and 1 g of the TiO₂ powder was added to the solution, which

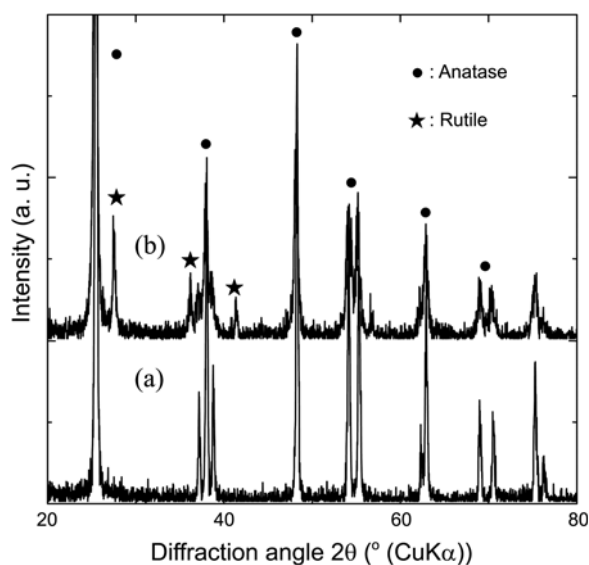


Figure 2. The XRD patterns of the (a) anatase TiO₂ powders and (b) P25 powders.

was to be kept at 25 °C for 2 h. The UV-vis absorption of the dye solution was measured before and after the adsorption. The adsorbed amount was estimated from the difference between the optical absorption by using the working curve. The MB and MO dyes are neutral solution, and we measured the adsorbed amount from 1×10^{-5} mol/L to 6×10^{-5} mol/L.

The Photocatalytic Activity. The photocatalytic activity was measured as follows: 100 mL of 1.5×10^{-5} mol/l MB or MO aqueous solutions were prepared, and 0.1 g of the anatase TiO₂ powder or the P25 powder were added to the solution. The solution was stirred at 500 r.p.m. without UV irradiation for 30 min. Irradiation of the UV light (20 W, 300 nm-400 nm) was then started using black lights. Three millilitres of the solution was separated once per 10 min. The concentrations of MB and MO were calculated from the optical absorbance by using the working curve.

Results and Discussion

Catalyst Characterization. Figure 3 shows the pH changes of aqueous solution with the final pH₁ as a function of the initial pH₀ at 25 °C for 2 h, due to the desorption of the different electric charges OH⁻ ions or H⁺ ions on the TiO₂ surface. The PZC of anatase TiO₂ such as shown in Figure 3(a) is 6.1, as given from the intersection between the pH₀-pH₁(a) curve and the diagonal straight line. This PZC value of anatase TiO₂ is in good agreement with the reported values in the literature.⁷⁻⁹

On the other hand, the PZC of P25 TiO₂ such as shown in Figure 3(b) is 5.2, shows that the P25 surface has a strong adsorption of ionic. From Figure 3(b), the plateau of final pH₁ in the range of pH₀ from *ca.* 5.2 to 13 is due to the adsorption of negative OH ions in the TiO₂ precipitate in a limited pH range, from *ca.* 1 to 5.2 is due to the direct adsorption of negative H⁺ ions through hydrogen. From this result, the hydroxyl of the titanium oxide surface is negative

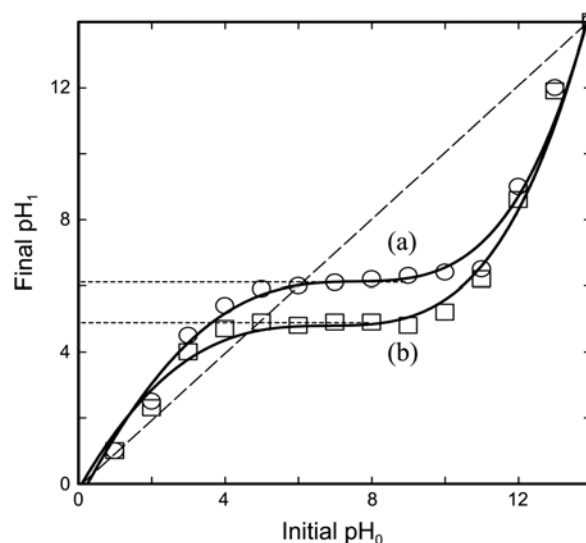
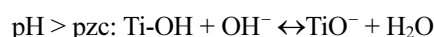
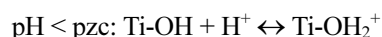


Figure 3. The point zero charge (PZC) of the (a) anatase TiO₂ and (b) P25 powders show with final pH₁ as a function of initial pH₀.

in pH more than 5.2, and it is positive in less than 5.2, according to the following equilibria:



This figure strongly supports the above argument concerning the behavior of the negative OH ion, similar to previously reported results.⁷⁻⁹

Adsorption of the Dyes. The adsorption isotherms of the dye molecules were measured in order to investigate the interaction between the dye molecules and the titania surface. Figure 4(I) and Figure 5(I) shows the adsorption isotherms of (a) MO and (b) MB on the P25 and anatase TiO₂ particles surface. For MO, the adsorption quantity suddenly increased from the low concentration, and the negative ion-related dyes been strongly adsorbed with titanium oxide. For MB that is a positive ion-related dye has little quantity of adsorption, and the increase of adsorption quantity for solution

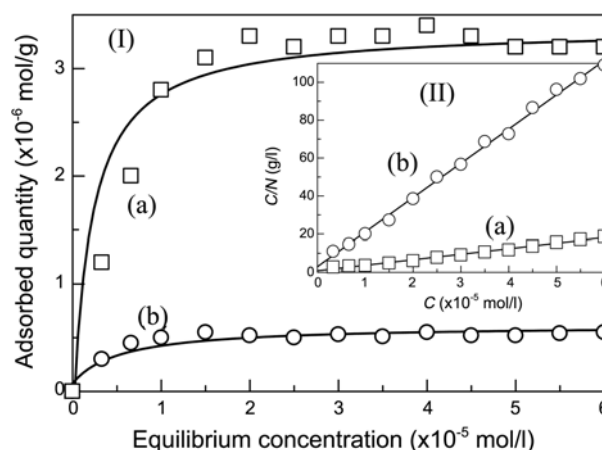


Figure 4. The adsorption isotherms of the dye molecules on the P25 surface in the aqueous solutions of the dyes: (a) methyl orange and (b) methylene blue.

concentration increase is slow. The curve is reminiscent of a Langmuir type isotherm, for which the rate value of adsorption first increases sharply and then reaches a saturation value at high concentrations dye. The black line showed the results of the curve fitting to the Langmuir equation by using the least square method.

According to the Langmuir adsorption models:

$$N = N_0KC/(1+KC) \quad (1)$$

where N is the adsorption quantity on the surface, N_0 is the maximum amount of adsorption corresponding to complete monolayer coverage on the surface, C is the concentration of solution, and K is a Langmuir constant. The Langmuir constant K is the Langmuir adsorption constant, which increases with the increase in the strength of adsorption. Taking reciprocals and rearranging, the equation can be used when data demonstrate linearity plotted as follows:

$$C/N = 1/(N_0K) + C/N_0 \quad (2)$$

Figure 4(II) and Figure 5(II) shows the dependence of C/N values on the respective equilibrium concentrations, the linear transform of C/N vs C is gained. According to the equation, as shown in Figure 4, the Langmuir adsorption constant $K_{MO} = 3.47 \times 10^5$ L/mol of MO is bigger than that of MB: $K_{MB} = 6.05 \times 10^4$ L/mol, and the maximum amount N_0 of MO was 3.46×10^{-6} mol/g and MB was 5.5×10^{-7} mol/g, the difference in K values clearly indicates that the negative ion dye MO is more strongly adsorbed on P25 TiO_2 surface than the positive ion dyes MB.^{2,3} For the anatase TiO_2 as shown in Figure 5, the Langmuir adsorption constant $K_{MO} = 1.21 \times 10^5$ L/mol of MO is bigger than that of MB: $K_{MB} = 4.81 \times 10^4$ L/mol, and the maximum amount N_0 of MO was 1.4×10^{-6} mol/g and MB was 5.4×10^{-7} mol/g. The difference in K values and N_0 clearly indicates that the P25 surface has a strong adsorption than anatase TiO_2 , similar to Figure 3 results.

Here the MB and MO dyes are around the neutral solution. It is thought that the negative ion-related MO has been adsorbed in TiO_2 precipitate surface, the same as the negative

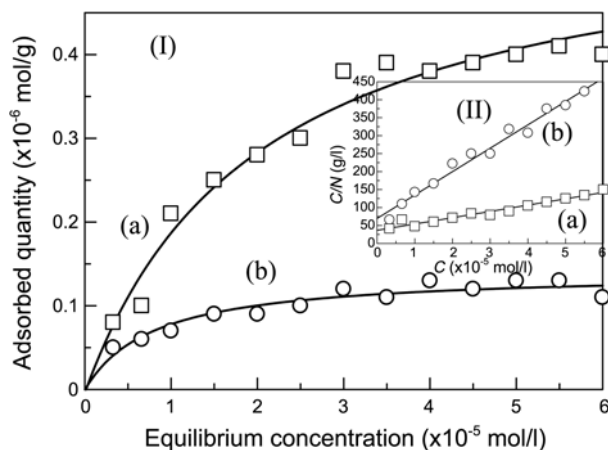


Figure 5. The adsorption isotherms of the dye molecules on the anatase TiO_2 surface in the aqueous solutions of the dyes: (a) methyl orange and (b) methylene blue.

OH ion. And the positive ion-related MB had been adsorbed in negative hydroxyl group. According to the above results, the MO, which is an anionic dye molecule, is strongly adsorbed than that of the cationic dye; we can therefore conclude that the MO molecules were adsorbed on the positively charged sites, which are mainly 5f-Ti ions on the titania surface,^{2,3} as shown in Figure 1. On the other hand, there were fewer negatively charged sites on which the MB molecules could be adsorbed than positively charged sites on which the MO molecules could be adsorbed.

The Photocatalytic Activity. Figure 6 shows the relation between the decomposition ratio of MB and MO with the UV irradiation time. As shown in Figure 6(a), the dyes completely decomposed after the UV light was irradiated for more than 4 h. Furthermore, decomposition process of MB and MO followed the different kinetics. The decomposition curve of MO, which is an anionic dye, followed a sigmoid (S -type) curve. But the decomposition kinetics of MB molecules by the photocatalytic activity usually follows the first-order rate law, as shown in Figure 6(b). This result indicates that the decomposition mechanism of MO is different from that of MB. Furthermore, the interaction between dye molecules and the titania surface greatly depended on the charge of the dye molecules.

In general, the Avrami equation describes the relation between the volume and molar fraction of the phase obtained by nucleation and growth process and the reaction time. The kinetics of the photocatalytic reaction can also be described by using the Avrami equation,⁴ since the assumptions to obtain the Avrami equation are not restricted to the particle formation process. If the decomposed molar fraction of dye molecules F follows the Avrami equation, F can be described as follows:

$$F(t) = 1 - \exp(-k^*t^n) \quad (3)$$

where $F(t)$ is the crystalline volume fraction developed at time t and constant temperature, and K and n are suitable parameters. According to the original theory, n should be an integer from 1 to 4, the value of which should only depend

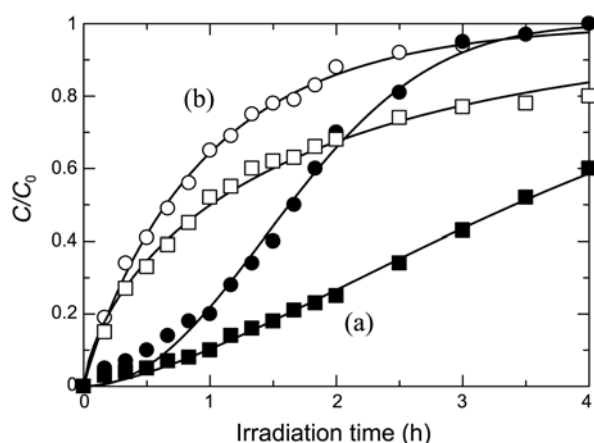


Figure 6. The photocatalytic activity of the titania particles: \circ \bullet P25 and \square \blacksquare anatase TiO_2 , in the aqueous solutions of the dyes: (a) methyl orange and (b) methylene blue.

on the type of the statistical model; however, it has become customary to regard it as an adjustable parameter that may be non-integral. The equation has been derived for spheres, discs and line segments, representing three-, two- and one-dimensional form of isotropic constant rate growth.

In this study, the MO molecules, which are anionic dye, were decomposed by the photocatalytic activity with the UV irradiation, the n values remained between 2 and 3, actually 2.1 and 2.4, as shown in Figure 6(a). This result indicates that the photocatalytic decomposition of the MO dye molecules occurred on the surface of the titania particles and that the dominant decomposition process was a 2D process. On the other hand, when the MB molecules, which are cationic dye, were decomposed by the photocatalytic activity with the UV irradiation, the n values were close to 1, were 0.93 to 1.1, as shown in Figure 6(b). This result indicates that the photocatalytic decomposition of the MB molecules occurred independently in the aqueous solution, by OH⁻ generated and migrated from TiO₂ surface to liquid. Therefore, the kinetic results are in agreement with the adsorption of the dye molecules on the titania particle surface.

Conclusion

The titania surface showed different characteristics depending on the charge of the dye molecules. Compared with the MB molecules, the negatively charged MO molecules strongly adsorbed on the titania surface. Furthermore, the decomposition kinetics of the dye molecules by the photocatalytic activity also deepened with the charge of the dye molecules. The relation between the UV irradiation time and the molar

ratio of the decomposed dye molecules followed the Avrami equation. According to the results of the analysis by using the Avrami equation, the MO molecules were decomposed on the titania particle surface. In contrast, the MB molecules were decomposed in the aqueous solution. The difference in kinetics was related to the interaction of the dye molecules and the titania surface. These preferential adsorption and decomposition characteristics will improve its applications in water pollution treatment.

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