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Photocatalytic Degradation of Methyl Orange in Aqueous TiO_2 Suspensions

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The degradation of methyl orange was studied using advanced oxidation process by exposed to UV irradiation in the presence of TiO_2. TiO_2 or UV light has a negligible effect when used alone. The effect of TiO_2 dosage, initial pH of dye solution and the solution area exposed to UV light were studied. It is found that in the investigated range, degradation rate of methyl orange increases with the increase in TiO_2 concentration and exposure area of solution. Acidic media is fvaourable to methyl orange degradation. The photodestruction of methyl orange is significantly inhibited by addition of KI as active holes scavenger at pH 2. However, the roles of ·OH and H_2O_2 are increased gradually as the increase of initial pH value of dye solution.

Key Words: TiO_2, Photocatalytic degradation, Methyl orange, Active species.

INTRODUCTION

Since Fujishima and Honda[1] firstly reported water splitting on TiO_2 electrode under UV illumination, photocatalytic degradation of toxic dyes in water by TiO_2 semiconductor has received increasing concerns[2,3]. In the past decades, it has been widely applied to environmental treatments on account of its low cost, innoxiousness, chemical inertness and high photocatalytic performance[2].

Large quantities of highly coloured and toxic dye effluents are produced from printing and dyeing industry. The release of these effluents causes serious pollution to environment[4,5]. Extensive studies have been conducted on dyes degradation and mineralization in aqueous system. Among the method developed, the photocatalytic technology assisted by titanium oxide (TiO_2) is a promising method for dye removal and water purification and has been intensively studies in recent years[6]. Through this method, dye contaminants can be completely degraded and mineralized[7].

In photocatalytic oxidation process of dyes, a large number of oxidizing species including active holes (h^+), hydroxyl radicals (·OH) and hydrogen dioxide (H_2O_2), are produced[8-12]. These active oxidizing species are formed through the direct irradiation by UV or visible light and transformed from the reaction of active holes and electrons. They play a crucial role for dye degradation. However, to date, the proportion of different oxidizing species under different pH condition is unclear. Hence, in order to understand the photocatalytic mechanism of TiO_2 at different pH, the roles of active oxygen species, ·OH, h^+ and H_2O_2 were investigated in the photodegradation of methyl orange. In addition, to achieve the optimal degradation, the effects of amount of TiO_2, pH value of dye solution and the solution area exposed to UV irradiation on photodegradation of methyl orange were also investigated.

EXPERIMENTAL

Degussa P25 was obtained from Degussa AG company in Germany, which is a mixture of anatase (80 %) and rutile (20 %) with an average size of 20 nm. All other regents were of analytical reagent quality and used directly.

Degradation procedures of methyl orange: Photocatalytic degradation of methyl orange (20 mg/L) was performed on XPA-system photoreactor, which was purchased from Xujiang electromechnical plant, Nanjing of China. The distance between the lamp and the surface of dye solution was 16 cm. A certain amount of P25 was added into 100 mL breaker with a dye solution volume of 100 mL. The pH of methyl orange solution was adjusted by perchloric acid or aqueous sodium hydroxide solution and not controlled in reaction process. The mixture was stirred for 0.5 h in the dark and then was exposed to 300 W medium-pressure mercury lamp (output mainly at 365 nm). During the degradation process, the suspension was kept stirring vigorously. At a set time intervals, the samples were analyzed after removal of catalyst by centrifugation at 14000 rpm for 8 min. The UV-VIS spectrum of methyl orange was recorded from 200 to 700 nm using Shimadzu 2450 UV-VIS spectrophotometer. The methyl orange degradation rate can be calculated by the following equation:

$$\text{Degradation (\%)} = \frac{A_0 - A}{A_0} \times 100\%$$

where, A_0 is original absorbance of methyl orange solution at its maximum absorption wavelength (λ_{max}), A is absorbance of methyl orange solution after irradiation for t min.

RESULTS AND DISCUSSION

In this paper, methyl orange is used as a contaminant model because it is widely used in textiles, foodstuffs, papers and leathers industries. Its release causes serious danger to human and animal health due to its toxicity, carcinogenicity, mutagenicity and slow biodegradability. Methyl orange is also an acid-base indicator ($pK_a = 3.5$) in the laboratory. It can be changed from azo structure (yellow colour) to quinoid structure (red colour) as pH value is changed from 4.5 to 3.1. Meanwhile, its maximum absorption peak is shifted from 463 nm under nearly neutral condition to 507 nm at pH 2.0, which is due to the delocalization of lone pair electrons on the azo group. The structure change of methyl orange at different pH also leads to the increase in the peak intensity at their maximum absorption wavelength[13].

Effect of catalyst dose: The influence of catalyst dose on the photocatalytic degradation of methyl orange was studied by varying catalyst concentration from 0.2 g/L to 4 g/L. The results obtained are shown in Fig. 1. In the dark, degradation of methyl orange is hardly observed in the presence of P25. When the dye solution is exposed to UV radiation for 40 min in the absence of catalyst, only 1.40 % methyl orange is removed (Fig. 1). However, the percentage of degradation increases dramatically from 71.41 to 97.91 % as the catalyst concentration is increased from 0.2 to 2.0 g/L. When we further increase catalyst concentration to 4 g/L, no increase in percentage of degradation is observed. Therefore, the optimal dose of TiO_2 for methyl orange degradation is 2 g/L. This phenomenon was also observed in the photocatalytic treatment of other dyes by other system containing TiO_2[14-17]. It is commonly believed that at a low catalyst concentration, the increase in catalyst concentration can provide more reactive sites and increase the number of photons absorbed by TiO_2 particles[15-17]. Hence the degradation rate is enhanced. When excess catalysts are added, additional catalysts makes the solution cloudy and opaque, which reduces the light transmittance of the dye solution to some extent. Hence, fewer incident photons can reach the catalysts surface, resulting in decrease of percentage of degradation. In addition, high catalyst concentration may be result in loss in surface area of catalyst due to the agglomeration of the catalyst particles, subsequently decreases the degradation rate[15,17].

Effect of initial pH value of methyl orange solution: The pH value of dye wastewater has a significant influence on the percentage of degradation of dye. Many studies have been carried out in this field and different conclusions have been found in the photodegradation process of methyl orange[18-21]. In this paper, the effect of initial pH value of solution was also examined by varying pH of methyl orange solution from 2 to 10 and the results are illustrated in Fig. 2. Methyl orange remains quinone structure and azo structure as pH is below 3.1 and above 4.5, respectively. The degradation of methyl orange was determined by measuring the absorbance at 506, 463 and 463 nm, which corresponds to the maximum absorption wavelength of methyl orange in visible region at pH = 2, 5.8 and 10, respectively. The percentage of degradation of methyl orange is 98.31 % at pH 2, 97.91 % at pH 5.8, 63.22 % at pH 10, respectively. It is obviously seen that the photocatalytic degradation rate of dye solution decreases with increasing of initial pH. The highest degradation rate is obtained at lower pH.

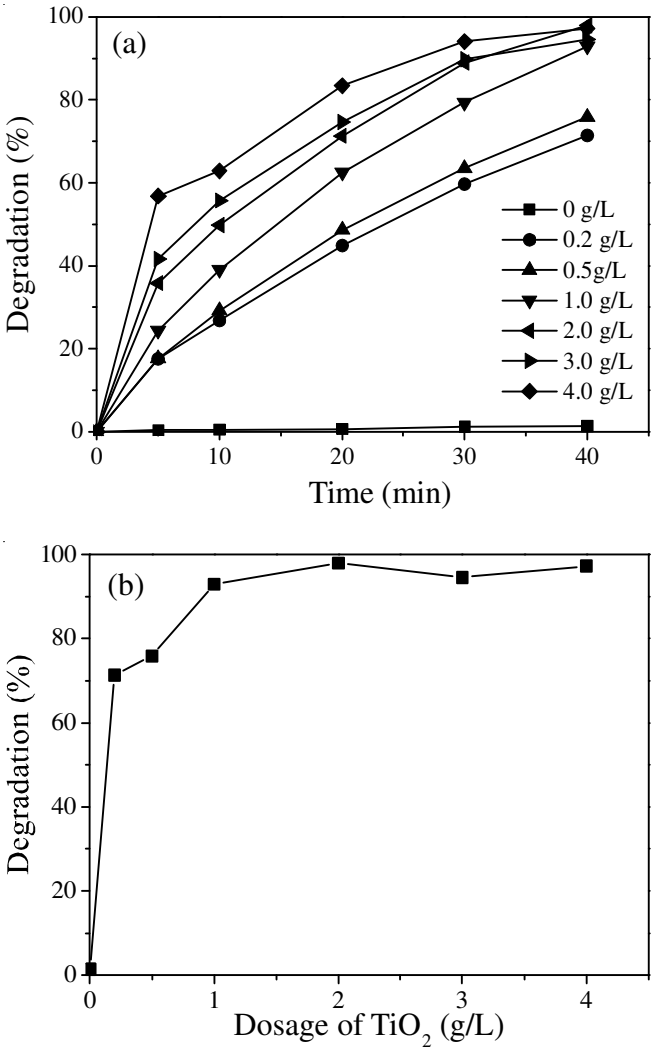

Fig. 1. Effect of P25 dosage on the photocatalytic degradation of methyl orange

The increase in degradation rate with a decrease in pH value of dye solution can be explained by zeta potential of catalysts. The zero point charge pH_{zpc} for TiO_2 varies in the range of 6-7[20,21] and the surface of TiO_2 is an abundance of hydroxyl[18]. Therefore, TiO_2 surface becomes positively charged (due to combined with H^+) or negatively charged (when reacted with OH^-) as pH is lower than pH_{zpc} and larger than pH_{zpc}, respectively[19-21]. The positively charged surface can accelerate electron transfer at acidic condition, facilitating the separation of electron-hole pair. The electrons can react with O_2 adsorbed on catalyst surface to generate H_2O_2. Both H_2O_2 and h^+ (redox potential is 1.8 V and 3.0 V *vs*. NHE, respectively) are strong oxidant, which can result in the complete

degradation of methyl orange. Although hydroxyl radicals are readily formed in alkaline media with abundance of hydroxyls, the oxidant power of ·OH is inferior to holes. Hence, low degradation rate is obtained under alkaline condition. Another reason for fast degradation of methyl orange at acidic condition is the structure change of methyl orange when the pH is below 3.1. The quinoid structure has relatively lower bond energy, which is more easily photodecomposed than azo structure[20,22]. The precise roles of oxidizing species formed in different pH value are discussed in detail in the following section.

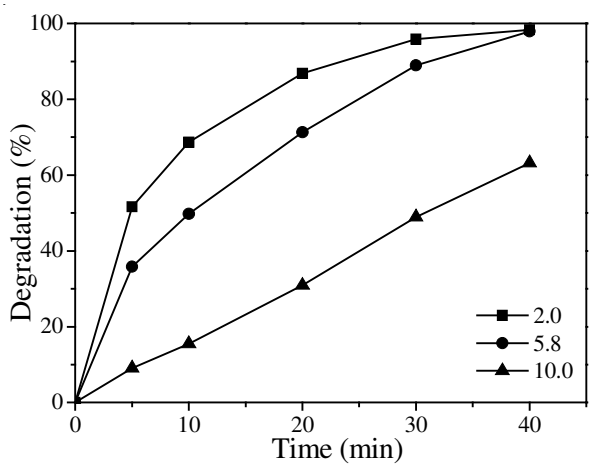

Fig. 2. Effect of pH on the photocatalytic degradation of methyl orange

Effect of surface area of dye solution: The effect of surface area of the dye solution exposed to the UV light on the percentage of dye degradation was also estimated. In our experiments, the breaker with different diameter (4.8, 5.8, 7.0, 8.3 and 12.3 cm) was selected to change the area exposed. The volume of dye solution and the initial concentration of catalyst were 100 mL and 2 g/L, respectively. It can be found in Fig. 3 that increasing the exposure area can increase the percentage of dye degradation and reduce the time of dye complete removal. When the reactor cell with diameter of 12.3 cm (area is 118.8 cm^2) is used, more than 98 % of methyl orange is degraded in just 15 min. Two reasons can be used to explain above results[23]. One is that the irradiation power received by the dye solution can be increased with the increase of surface area exposed to light, consequently increases the percentage of dye abatement. On the side, when the other conditions are the same, increase area will reduce the depth of the solution, which makes UV light travel a much shorter path through the suspension, then increases the effective (or average) UV irradiation intensity received by P25 particles. Hence, the higher degradation rate is obtained at larger surface area.

Effect of oxidizing species at different pH: A large number of oxidizing species, such as h^+, ·OH and H_2O_2, are involved in the photodegradation process of dyes. The role of active species in the degradation process has been studied extensively by addition of appropriate species quenchers, yet lots of controversies still exist[8-12]. In order to evaluate the roles of these primary oxidizing species under different pH value, KI, isopropanol and catalase were used as quenchers of active holes and ROSs. The dosage of KI, isopropanol and catalase was determined according to previous research work[10]. The degradation of methyl orange in the presence of different scavengers is shown in Figs. 4-6. As shown in Fig. 4, addition of quenchers of ·OH and H_2O_2, isopropanol and catalase, has little effect on percentage of methyl orange degradation. These results show that ·OH and H_2O_2 are not involved in dye degradation at pH 2. When potassium iodide, an excellent quencher of valence band holes and ·OH radicals, is used, the degradation of methyl orange is greatly suppressed. Only 20.40 % of methyl orange was abated when the concentration of KI is up to 1 mM. This result suggests that valance band holes play an overwhelming role for methyl orange degradation at pH 2.

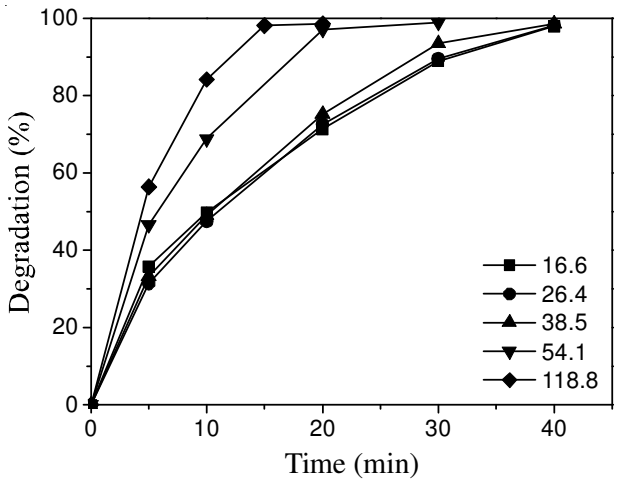

Fig. 3. Variation of the dye degradation rate with exposed area of methyl orange solution

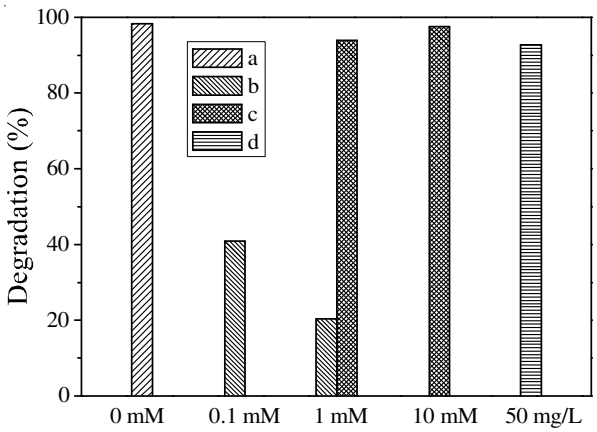

Fig. 4. Effect of KI, *i*-PrOH and catalase on degradation of orange solution at pH 2: (a) without additives, (b) with [KI] = 0.1 or 1.0 mM, (c) with [*i*-PrOH] = 1 or 10 mM and (d) with [catalase] = 50 mg/L

As observed in Fig. 5, when isopropanol is added at pH 5.8, the degradation rate of methyl orange was decreased to 77.99 % and 74.59 % in the presence of 1 mM and 10 mM of isopropanol, respectively. The addition of catalase, a quencher of H_2O_2, makes the degradation rate fall by 13 %. In the case where KI is added, only 52.53 % and 24.59 % of methyl orange is degraded when the concentration of KI is 0.1 mM and 1 mM. It could be estimated from the results shown in Fig. 5 that the role of holes is decreased and the role of ·OH and H_2O_2 are enhanced as the increase of initial pH value of dye solution.

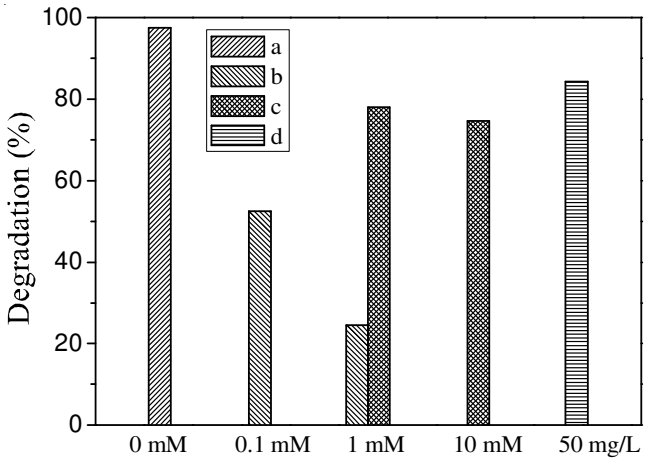

Fig. 5. Effect of KI, i-PrOH and catalase on degradation of methyl orange at pH 5.8: (a) without additives, (b) with [KI] = 0.1 or 1.0 mM, (c) with [i-PrOH] = 1 or 10 mM and (d) with [catalase] = 50 mg/L

The oxidizing species that is most probably responsible for the photodegradation of methyl orange at pH 10 is ·OH radicals. This can be proved by the results shown in Fig. 6. Degradation of methyl orange is hindered to a significant extent when alcohol is added. When added 1 mM KI to methyl orange solution, only 6.37 % of dye disappears, showing that holes also play a certain role. When catalase with concentration of 50 mg/L is added, the percentage of dye abatement after 40 min irradiation is 41.06 %. These data state that ·OH radicals play a major role under alkaline condition. From the results shown in Figs. 4-6, it is found that the role of holes is reduced gradually, however, ·OH and H_2O_2 account for increasing proportion in degradation process of methyl orange as the increase of initial pH value of dye solution. The predominant species is changed from holes in acidic medium into ·OH in alkaline condition.

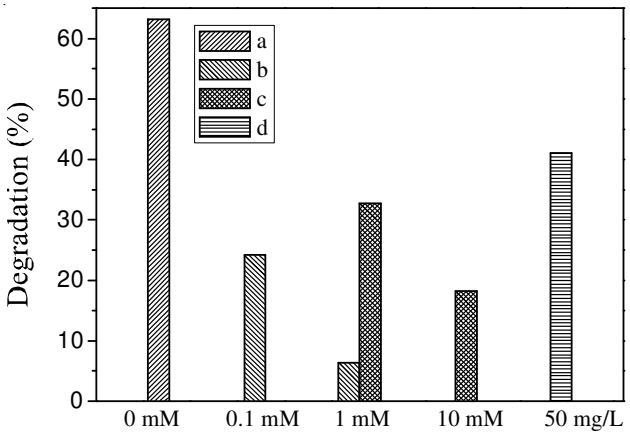

Fig. 6. Effect of KI, i-PrOH and catalase on degradation of methyl orange at pH 10.0: (a) without additives, (b) with [KI] = 0.1 or 1.0 mM, (c) with [i-PrOH] = 1 or 10 mM and (d) with [catalase] = 50 mg/L

Conclusion

The photocatalytic degradation of methyl orange dye is relatively fast at pH 2 and pH 5.8. In addition, it is increased with the increase of amount of catalyst P25 and surface area exposed to light source. The roles of active species at different pH have been studied by addition of appropriate species quenchers. It is found that the photodestruction of methyl orange is significantly inhibited by addition of KI as active holes scavenger at pH 2. However, with the increase of initial pH value of dye solution, reactive oxygen species, ·OH and H_2O_2, account for increasing proportion in degradation process of methyl orange. This study will provide valuable information in the photocatalytic mechanism of TiO_2-contaning photocatalyst at different conditions.

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