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Promoting effect of adding carbon black to TiO_2 for aqueous photocatalytic degradation of methyl orange

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ABSTRACT

The photocatalytic activity and the promoting effect of titania (TiO_2) incorporated with carbon black (CB) for removing the pollutant in wastewater were investigated. The TiO_2/CB composite photocatalysts with various ratios of TiO_2 to CB were prepared by the sol–gel method. The degradation of methyl orange (MO), as the model reaction, was carried out in the aqueous slurry solution using these photocatalysts at 20 °C. Experimental results reveal that the ratio of TiO_2 to CB largely affected the performance of composite catalyst. An optimal weight ratio of 1 for the highest photocatalytic capability was found. The photocatalytic performances of TiO_2/CB catalysts were also found better than those of TiO_2 incorporated with activated carbon. The better promoting effect might be attributed to the larger pores of CB which allow a faster diffusion of the adsorbed MO from CB toward TiO_2 and the high electrical conductivity of CB which can reduce the recombination of electrons and holes generated in TiO_2.

1. Introduction

Titanium dioxide (TiO_2) is widely used as the photocatalyst for removing pollutants in water because of its high chemical stability, non-toxicity, less manufacturing cost and higher redox potential of generated electron–hole pairs. To improve the performance of purification process, an adsorbent with high pollutant adsorption capability, such as the activated carbon (AC), has been added to the reactor with TiO_2 as the suspended mixture [1–7] mounted with TiO_2 or as a support for TiO_2 [8–15]. The enhancement is attributed to the so-called synergistic effect because the adsorbent may adsorb a large amount of pollutant and then the pollutant will further transfer to TiO_2 surface where the photodegradation of pollutant takes place.

When the AC was employed as a support, TiO_2 was deposited onto carbon surface by the hydrothermal method [15] and the sol–gel method [8–11] to prepare the TiO_2/AC composite catalysts. Another kind of composite catalyst was prepared by coating a carbon-containing organic compound, as the precursor of carbon, onto TiO_2 particles followed by carbonization [12–14].

When TiO_2 was deposited on carbon materials through sol–gel method or hydrothermal method to prepare a composite catalyst, carbon can not only adsorb organic pollutants but also promote the catalytic property of TiO_2. Wang et al. [10] investigated the effect of annealing temperature on the performance of composite catalyst prepared by depositing TiO_2 on the AC. As shown by Tryba et al. [9], when small-sized TiO_2 particles were deposited on AC, the particles could aggregate and hence caused clogging in the micropores of AC. As a result, the available surface area for adsorbing pollutants could decrease. However, the chemical mixing mode, by which TiO_2 is deposited on the activated carbon, may reduce the particle size of TiO_2 and promote the photocatalytic activity of TiO_2 due to the strong interaction between the AC and TiO_2.

Recently, in a series of study [12–14], Tryba's research group coated polyvinylbenzene, as the carbon source, onto TiO_2 surface and then calcined to prepare the carbon/TiO_2 composite catalyst. They found that this approach could improve the ability to adsorb pollutants and gave a slight promotion in the photocatalytic activity without the occurrence of clogging problems in the micropores. However, they pointed out the following advantages of coating carbon onto TiO_2 surface: (1) suppression of the transformation of anatase phase of TiO_2 to the rutile phase; (2) increase in the surface area and the adsorption capability; (3) easy separation of the catalyst.

Although AC has a large surface area to adsorb a large quantity of pollutant and hence can increase the removal rate of pollutant, the pores (micropores) in the AC are very small and the diffusion rate of the pollutant adsorbed in the micropores toward the surface of TiO_2 is slow, the synergistic effect is not as high as expected. Furthermore, TiO_2 deposited on AC will reduce the surface area and pore volume of AC because a large amount of TiO_2 will deposit in micropores of AC as to be confirmed later in this study.

Due to the fact that TiO_2 is easily aggregated in the micropores of AC and that the adsorbed pollutant cannot diffuse out easily, other

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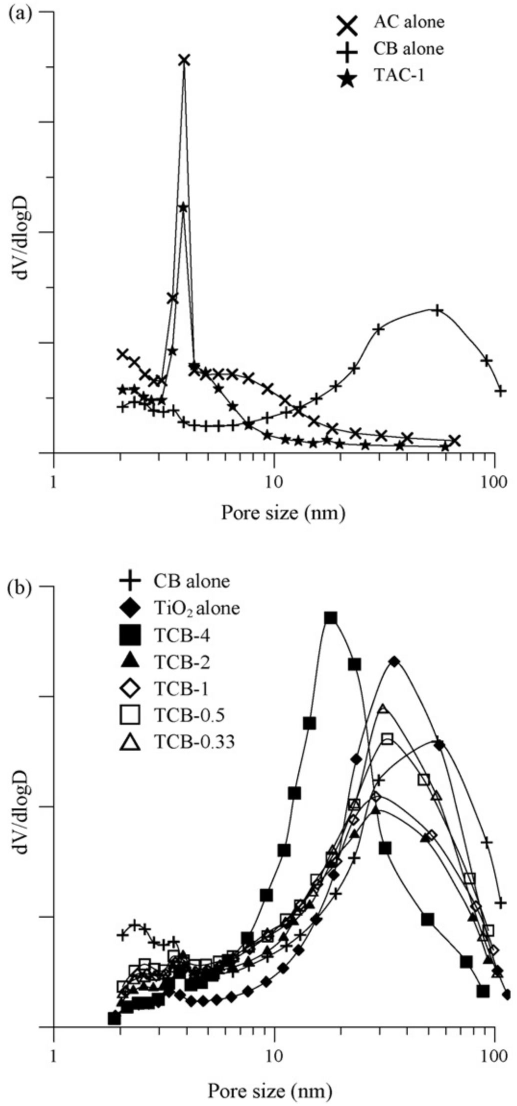

Fig. 1. Comparison of the pore size distributions of (a) activated carbon (AC), and carbon black (CB) and TiO_2/AC-1; (b) TCB composite catalysts with various ratios of TiO_2 to CB.

carbon substrates, such as fullerenes [16] and multi-wall carbon nanotubes [17], were used as supports to replace the AC. Carbon black (CB) might be another choice of carbon material as an adsorbent or support accompanying with TiO_2 [18]. Rincon et al. [19,20] attempted to deposit TiO_2 as a thin film onto CB by the sol–gel method and investigated the influence of preparation method and mixing mode (including physical and chemical mixing) on the photocatalytic activity. They found that the composite catalyst of TiO_2 and CB prepared by the sol–gel method had the highest photocatalytic activity.

The advantages of using carbon black as the adsorbent may be attributed to the following facts: (1) it has larger pores compared with activated carbon (Fig. 1a), and hence the pollutant adsorbed can diffuse in and out more easily; (2) it has less micropores and hence less TiO_2 will be deposited into the micropores; (3) it has a higher electrical conductivity which can reduce the recombination of electron–hole pair generated in TiO_2. With the above-mentioned characteristics, the incorporation of CB to TiO_2 is anticipated to give a better synergistic effect on removing pollutants. However, only a few studies have investigated this topic.

Therefore, in this work, the TiO_2/CB composite photocatalysts were prepared by depositing TiO_2 to carbon black with the sol–gel method and the photocatalytic activities and the promoting effects of mounting CB were investigated and compared with TiO_2/AC composite catalysts which were prepared with the same method. The photocatalytic degradation of methyl orange (MO) was employed as a model reaction.

2. Materials and methods

2.1. Preparation of TiO_2/CB

Sol–gel method was employed to deposit TiO_2 onto the surface of CB. CB used in this work is Vulcon XC-72 (Cabot) which has a BET surface area of 222 m^2/g. Its pore size distribution is shown in Fig. 1a. The precursor of TiO_2, titanium ethoxide ($Ti(OC_2H_5)_4$, Alfa-Aeser, 99%), was first dissolved in an ethanol solution and dispersed with the addition of a proper amount of citric acid (Riedel-deHaen, 99.5%, monohydrate). After having all the reagents well mixed for 1 h, a homogeneous solution was obtained. Subsequently, various amounts of CB, having been washed with 6N HNO_3 in advance, were dumped into the solution according to the preset ratios of TiO_2 to CB and mixed for 10 h. Then the mixed solutions were dried at 80 °C overnight and calcined at 400 °C for 1 h to obtain TiO_2/CB (abbreviated as TCB) composite catalysts with various ratios of TiO_2 and CB. The composite catalyst was labeled as TCB-x where x is the weight ratio of TiO_2 to CB. For comparison, the activated carbon (Sigma–Aldrich, untreated granular, 20–60 mesh), having been washed with 6N HNO_3 in advance, was also used as the support to prepare TiO_2/AC (labeled as TAC) photocatalysts. The TAC photocatalyst was prepared with the same method and procedure.

The crystalline structure of TiO_2 powder was determined by XRD (RINT2000, Rigaku), using Cu K_α radiation ($\lambda = 0.15418$ nm) operating at 40 kV and 40 mA in the range $2\theta = 20$–$60°$. The crystalline size of TiO_2 powder was calculated from the full width at maximum half height (FWMH) by the Scherrer's equation. The morphology and structure were obtained from TEM (H-7500 TEM, Hitachi). N_2 adsorption–desorption isotherm experiment was carried out at 77 K with Micromeritics ASAP 2010 device. The specific surface area data were evaluated in the equilibrium points P/P_0 ranging from 0.05 to 0.20 by the BET method and the pore size distribution was obtained from BJH desorption data. The carbon contents were determined by thermogravimetric analysis (TGA) performed at room temperature to 800 °C with a heating rate of 10 °C/min.

2.2. Photocatalytic degradation experiments

The photocatalytic degradation experiments were carried out using a Pyrex reactor (700 mL capacity) equipped with a circulating cooling tube made of quartz at the center of the reactor. The light source, a 100 W high-pressure mercury light with a main wavelength of 365 nm (HL100CH-5, SEN Light Corp.), was placed in the inner tube of the cooling tube through which the cooling water (20 °C) was flowing. The TCB composite catalyst containing 0.05 g of TiO_2 (content of CB was varied) was dumped into 500 mL solution containing 1.23×10^{-4} mol/L (40 ppm) of methyl orange and sonicated for 5 min. Subsequently, the adsorption of MO by TCB composite catalyst was carried out in dark for 2 h to ensure the adsorption reaching an equilibrium state. Then the UV light was turned on for initiating the photocatalytic degradation reaction. Two kinds of commercial photocatalysts, Degussa P-25 and Merck anatase TiO_2, were also tested for comparing with the home-made TiO_2 and TCB composite catalysts.

To monitor the concentration of MO in the solution, a sample was taken out and filtered at an interval of 15 min and was analyzed

Table 1
Physical and chemical properties of TiO_2/CB and TiO_2/AC composite catalysts.

Composite catalyst	Crystallite size of TiO_2 anatase phase (nm)[a]	Carbon content (wt%)[b]	BET surface area (m^2/g)	Apparent removal rate constant, k_{app} (min^{-1})	Intrinsic photocatalytic reaction rate constant, k_{int} (min^{-1})	TOC removal at 1 h (ppm)[c]
Photolysis	–	–	–	0.0029	0.0029	0.9
Bare TiO_2	9.4	0	83	0.0078	0.0078	3.6
TCB-4	8.0	18.6	116	0.0096	0.0096	
TCB-2	9.0	27.5	108	0.0342	0.0279	8.6
TCB-1	7.7	42.4	124	0.0364	0.0292	9.1
TCB-0.5	7.0	60.2	151	0.0254	0.0203	7.5
TCB-0.33	6.5	71.4	155	0.0124	0.0103	
Bare CB	–	100	222	0.0016	–	
Degussa P-25	–	–	55	0.0720	0.0720	13.9
Merck TiO_2	–	–	1	0.0084	0.0084	
TAC-2	–	23.9	191	0.0060	0.0052	
TAC-1	–	31.0	292	0.0076	0.0065	
TAC-0.5	–	50.1	439	0.0098	0.0082	
Bare AC	–	96.6	710	0.0057	–	

[a] The crystallite size of TiO_2 (1 0 0) is calculated by Scherrer's equation.
[b] Determined by TGA, and TiO_2 is the residual material.
[c] The TOC value of the MO solution with an initial concentration of 1.23×10^{-4} M is 20.7 ppm.

by HPLC which consisted of an isocratic pump (Waters 600E), an auto-sample apparatus (Shimadzu SIL-9A), a UV detector (Jasco UV-2075Plus) and an analytic column (Hibar 250-4.6 Purospher Star RP-18). Millipore disk (0.22 μm) was used to remove the catalyst particles before HPLC analysis. Total organic carbon (TOC) in some of the solutions was measured by using a portable TOC analyzer (Sievers 900).

3. Results and discussion

3.1. Crystal phase and dispersion of TiO_2

The XRD patterns reveal that the anatase crystal phase of TiO_2 could be obtained when the composite catalysts were calcinated at 400 °C for 1 h. However, a small fraction of rutile phase was formed in both TCB-1 and TCB-2 catalysts. When TiO_2 deposited on the surface of CB, the size of TiO_2 crystallite would be smaller than that of TiO_2 alone, and would decrease with decreasing the ratio of TiO_2 to CB. It can be inferred that the dispersion of TiO_2 on the surface of CB inhibits the aggregation of TiO_2 hence the particle size of TiO_2 reduces. Note that none of peaks of CB appears in the XRD patterns.

Carbon contents in TCB composite catalysts were determined by TGA carried out from the room temperature to 800 °C. TiO_2 was the only residual material at the end of analysis. Table 1 reveals that both carbon content and BET surface area increase with decreasing the ratio of TiO_2 to CB. The increase in surface area is due to the increase in carbon content.

As shown in Fig. 1b, although the pore size distribution of TiO_2 and CB are somewhat similar, the latter has bigger pores and a far larger surface area. In addition, the mean particle size of CB (~30 nm) is larger than that of TiO_2 (~10 nm). In the preparation of TCB composite catalysts, CB particles were dumped into the precursor solution of TiO_2, therefore TiO_2 could reside on both exterior and interior surface (pores) of CB while CB could not reside in the pores of TiO_2. Based on the above-mentioned facts, when a small amount of TiO_2 was incorporated with CB (e.g., TCB-0.33), the size and the number of pores, in turn, the surface area of CB would be reduced. In addition, the pore volume and the surface area of TCB decreased with increasing the TiO_2-to-CB ratio. However, when a large amount of TiO_2 was incorporated with CB (e.g., TCB-4), the segregated phase of TiO_2 would appear except those deposited on the exterior and interior surface of CB. In such a case, the pore size distribution of TCB would be dominated by the segregated phase of TiO_2. Because TiO_2 particles were separated by CB, their sizes would be smaller than those of TiO_2 alone, in turn, the pore sizes would be smaller as well.

Moreover, the TEM images (Fig. 2) show that the incorporation with CB can effectively promote the dispersion of TiO_2 and, therefore, TiO_2 can be more uniformly dispersed on the surface of CB. As shown in Fig. 2a, the crystallite size of TiO_2 is about 10 nm, which agrees with the value calculated from the XRD pattern, and evidently smaller than those of CB (about 20–30 nm as shown in Fig. 2d). When the ratio of TiO_2 to CB is large (carbon content is low), the particles of CB will be mostly covered by TiO_2 crystallites as indicated in Fig. 2b. For the case of high carbon content, the crystallites of TiO_2 will be well dispersed on the surface and they will be small as revealed in Fig. 2c. The TEM images confirm the above inference based on the BET results.

3.2. Photodegradation of methyl orange

Three blank experiments were carried out in advance. First, the experiment of photoreaction without catalyst (i.e. photolysis), as shown in Fig. 3a, gave about 15% of MO removal in 60 min. Second, the adsorption experiment of MO by CB (0.05 g) in dark showed about 10% removal within 30 min. Finally, the photodegradation experiment of MO by CB under UV irradiation showed that about 20% of MO was removed. The removal of MO in this experiment might be via adsorption and photodegradation. However, if the amount of MO adsorbed by CB was deducted, only 10% of MO was removed by photodegradation which was less than the amount of MO degraded by photolysis reaction. Therefore it can be confirmed that CB has no photocatalytic activity under irradiation but can adsorb MO and even shelter the irradiation. Besides, the experiment shows that TiO_2 almost cannot adsorb MO in dark.

Subsequently, the removal of MO was carried out with the present of TiO_2 alone and TCB composite catalysts under UV illumination. The results shown in Fig. 3a reveal that about 30% of MO can be removed by bare TiO_2 for 60 min. However, when TiO_2 incorporated with CB, the removal rate is enhanced and increases with increasing the fraction of CB in the composite catalyst up to the ratio of TiO_2 to CB is one, but decreases when the ratio exceeding one. The enhancement might be attributed to the following factors: (1) the crystallite sizes of TiO_2 were reduced and well dispersed on surface of CB as revealed by TEM images and XRD patterns; (2) CB can adsorb a larger amount of MO (see Fig. 3a) and the MO adsorbed on the surface of CB can quickly transfer to the surface of TiO_2 by a large concentration gradient.

Although adding more CB to TCB composite catalyst adsorbs more MO, it also absorbs and shelters more irradiation and reduces illumination on the TiO_2 surface reducing the effective photocatalytic activity of TiO_2. Hence, there exists an optimal ratio of TiO_2 to

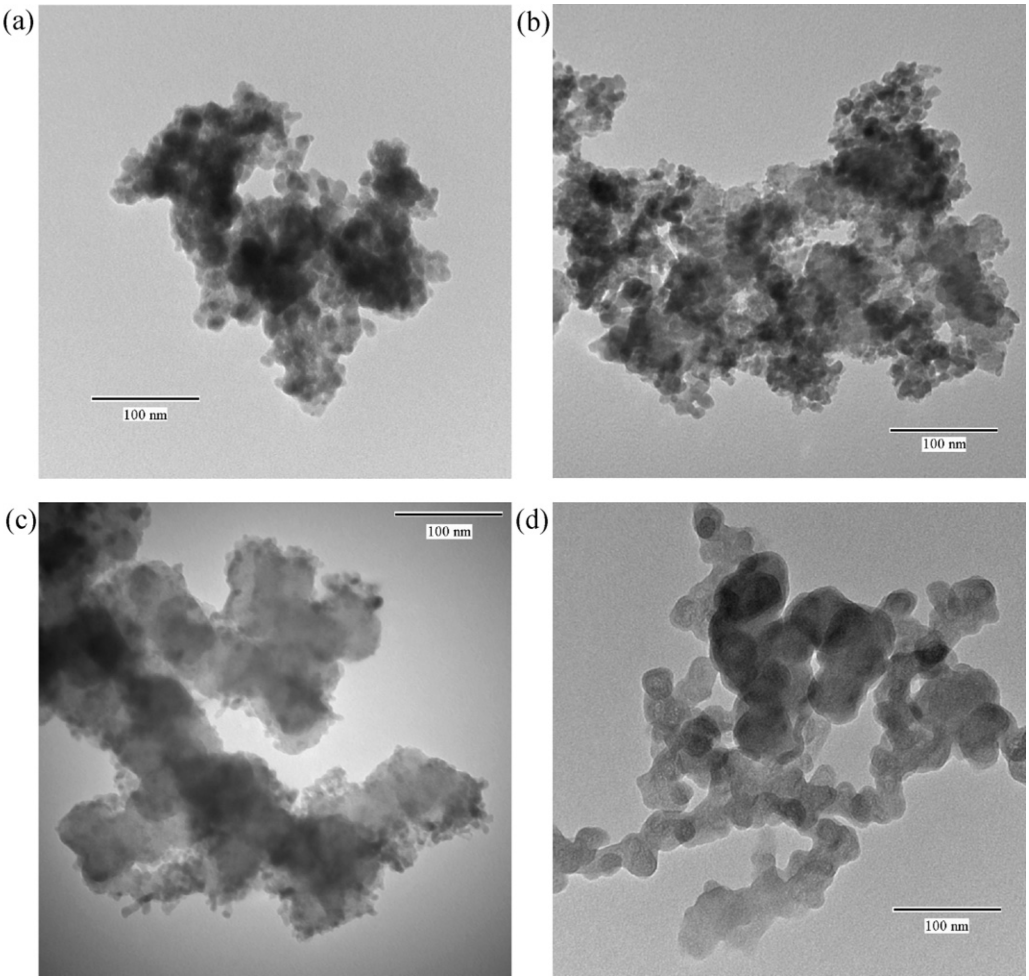

Fig. 2. TEM images of TiO_2/CB composite catalysts. (a) TiO_2 alone, (b) TiO_2/CB-2, (c) TiO_2/CB-0.33 and (d) CB alone.

CB for the photocatalytic degradation reaction of MO. Experimental data reveal that the promoting effect of CB in the TCB-1 composite catalyst is the highest among those composite catalysts prepared and bare TiO_2. Some data of total organic carbon are also listed in Table 1 for reference.

Nevertheless, the TCB-1, the best photocatalyst in our experiment, gave a lower removal rate than Degussa P-25 did but higher than Merck TiO_2 under UV irradiation as shown in Fig. 4. It was probably owing to that the activity of TiO_2 prepared in this study was lower than P-25. Even though the presence of CB could greatly enhance the apparent activity of TiO_2 under optimal ratio of TiO_2 to CB, but its activity was still low. Hence, the activities of bare TiO_2 and TiO_2 in TCB composite catalysts should be further improved by changing the preparation procedure and conditions or even using other preparation method in the future.

The photodegradation rate is often expressed by $r = k\mathrm{K}C/(1 + \mathrm{K}C)$ [21]. However, when the value of KC is far smaller than 1, the reaction can be considered as of the pseudo-first-order. In our case, the adsorption equilibrium constant (K) of TiO_2 alone is about $30\,\mathrm{M}^{-1}$ and the initial concentration of MO (C_0) is 1.23×10^{-4} M, because the value of KC is less than 0.004, far less than 1, therefore the photodegradation reaction is considered as pseudo-first-order [$r = -\mathrm{d}C/\mathrm{d}t = k_{\mathrm{app}}C$]. Upon integration, $\ln(C_0/C) = k_{\mathrm{app}}\ t$ is obtained and the plot of $\ln(C_0/C)$ vs. t will give a straight line. The apparent removal rate constant, k_{app}, obtained from the slope of straight line can be considered as an index for the promoting effect by adding CB to TiO_2. As shown in Table 1, the apparent removal rate constant increases with decreasing the ratio of TiO_2 to CB, when the ratio is larger than one. This result accords with the above explanation for the adsorption of MO by CB. However, when the ratio of TiO_2 to CB is less than one, the shelter effect of CB is larger than its adsorption effect and hence the apparent removal rate constant decreases with decreasing the ratio. Therefore, the optimal TiO_2-to-CB ratio is one based on the apparent rate constants obtained from the current experiments.

The intrinsic photocatalytic reaction rate constant of composite catalyst can be evaluated provided with the amount of MO adsorbed by CB having been deducted. Our preliminary experiment revealed that the amount of MO adsorbed by CB was constant when the equilibrium concentration of MO in solution exceeded 2×10^{-5} M as shown in the inset of Fig. 3b. Because the adsorption of MO by TCB composite catalyst was carried out in dark for 2 h to ensure the adsorption reaching an equilibrium state before illumination, it is reasonable to assume that the adsorption of MO is nearly at equilibrium state in the course of photoreaction and the amount of MO adsorbed is constant provided with the concentration of MO higher than 2×10^{-5} M. By subtracting the amount of MO adsorbed by CB initially before illumination from the total amount removed from the solution, the amount of MO photodegraded by TiO_2 can be determined, and hence the intrinsic photocatalytic reaction rate. This intrinsic photocatalytic reaction rate can be also simulated by a pseudo-first-order equation and hence the intrinsic photocatalytic reaction rate constants (k_{int}) can be obtained. These rate constants for a variety of composite catalysts are larger than that using bare TiO_2 as listed in Table 1. This result reveals that the intrinsic photocatalytic activity of TiO_2 can be improved at the

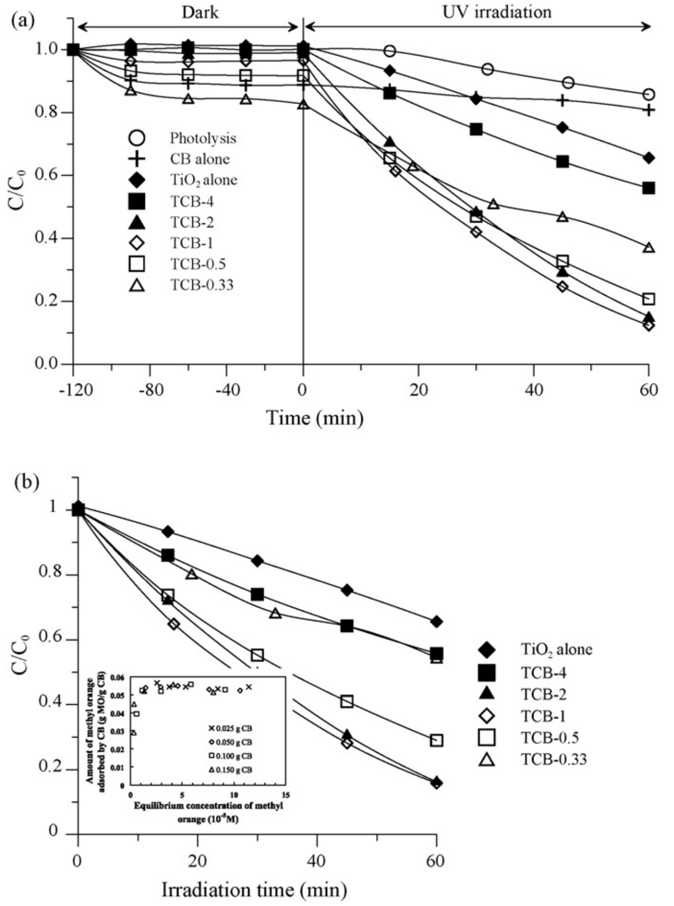

Fig. 3. (a) Apparent MO removal and (b) intrinsic MO removal by the TiO_2/CB composite catalysts with various ratios of TiO_2 to CB. The initial concentration of MO is 1.23×10^{-4} M (500 mL solution) and the weight of catalyst is the sum of TiO_2 (0.05 g) and CB (varied). *Inset*: the relations between the adsorbed amount of MO and equilibrium concentration for various weights of CB.

presence of CB because CB has a high electron-conductivity except it can adsorb MO. This feature expedites the transport of the electrons (or holes) generated from TiO_2, and hence reduces the chance of electron–hole recombination. Among these composite catalysts, TCB-1 has the highest activity because it gives the largest intrinsic photocatalytic reaction rate constant.

For comparison, TiO_2 was also deposited onto the AC with the same procedure to prepare the TiO_2/AC (abbreviated as TAC) composite catalysts and were used for the photocatalytic degradation of MO. The performance and the synergistic effect of the prepared TAC were compared with those of TCB-1, which is the best among TCB catalysts.

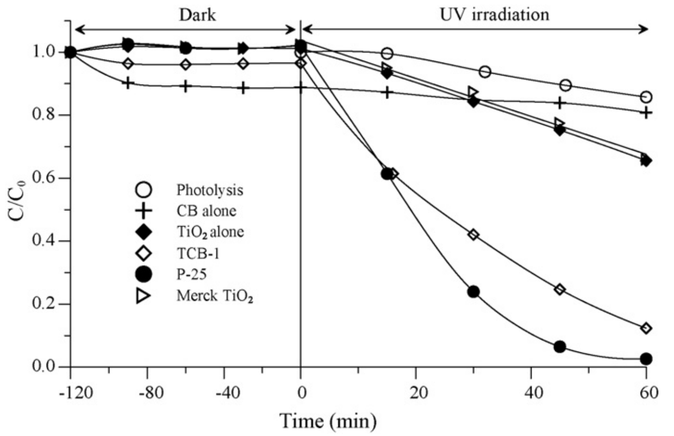

Fig. 4. Comparison of the photocatalytic activities of TCB-1 composite catalysts and commercial Degussa P-25 and Merck TiO_2 catalysts.

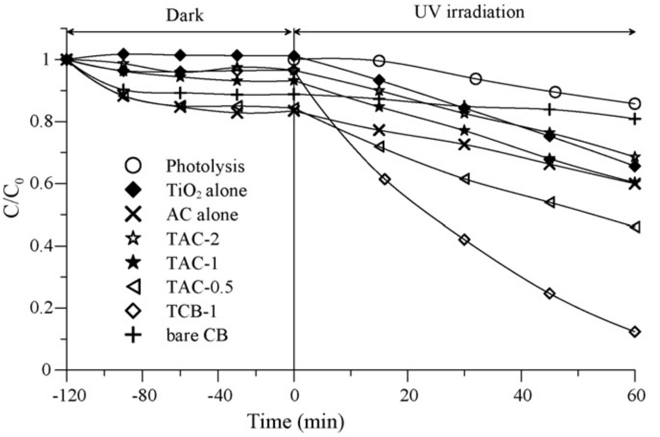

Fig. 5. Comparison of the photocatalytic activities of TAC and TCB-1 composite catalysts.

As shown in Fig. 5, the removal rates of all TAC composite catalysts are higher than that of bare TiO_2. This result is attributed to a large amount of MO being adsorbed by AC before illumination. Although the incorporation of AC improves the capability of TAC to remove MO, however, when the amount of MO adsorbed by AC is deducted from the total amount of MO removed, the intrinsic photocatalytic reaction rate constants of TAC composite catalysts are lower than that of bare TiO_2. This fact indicates that the larger adsorption capacity of AC is a major factor for removing MO by TAC composite catalysts. Nevertheless, the intrinsic photocatalytic reaction rates of TiO_2 for all TAC composite catalysts are slower than that of bare TiO_2. In other words, no enhancement could be obtained when TiO_2 was incorporated with AC in this study. This is owing to (1) part of the TiO_2 precursor deposited in the micropores of AC leading to a less amount of TiO_2 on the exterior surface of AC, (2) AC sheltered the illumination and (3) the MO adsorbed in micropores of AC cannot easily transfer to the surface of TiO_2. The deposition of TiO_2 in the micropores of AC can be confirmed by checking the pore size distribution and BET surface areas shown in Fig. 1a and Table 1. For example, the surface area of TAC-1 (the ratio of TiO_2 to AC = 1) reduced to 292 m^2/g from 710 m^2/g of bare AC.

Fig. 5 also reveals that the performances of all TAC composite catalysts and bare TiO_2 are lower than that of TCB-1 catalyst. This is attributed to the fact that AC has far more micropores than CB, as depicted in Fig. 1, hence (1) larger amount of the TiO_2 precursor will deposit in the micropores of AC leading to a less amount of TiO_2 on the exterior surface of AC and (2) the MO adsorbed in the micropores of AC will be more difficulty to diffuse out for being photodegraded. In addition, the electrical conductivity of AC is lower than CB. Therefore, the overall removal rate of TAC composite catalyst is lower than that of TCB composite catalyst.

4. Conclusions

This work investigates the effect of titania (TiO_2) incorporated with carbon black on its performance for photocatalytically removing methyl orange in water. The causes of enhancement on the photodegradation capability of TiO_2 by CB might be attributed to (1) a higher concentration of MO on TiO_2 surface because MO adsorbed by CB can quickly transfer to TiO_2 surface; (2) smaller crystallite sizes and better dispersion of TiO_2 on the surface of CB; and (3) less chance of recombination of electrons and holes because of the high electrical conductivity of CB.

Although adding more CB to TiO_2/CB adsorbs more MO, it also absorbs and shelters more irradiation from the light source and reduces illumination on the TiO_2 surface reducing the effective photocatalytic activity of TiO_2. Therefore, there exists an optimal TiO_2-to-CB ratio for the highest photocatalytic capability. An optimal ratio of 1 was found in this study.

On the other hand, no enhancement was observed when TiO_2 incorporating with activated carbon because part of TiO_2 deposited in the micropores of AC and MO adsorbed in these micropores is difficult to transfer to the surface of TiO_2 on the exterior surface of AC and some of AC resided on the exterior surface of TiO_2 will shelter the irradiation of UV light on TiO_2.

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