

A TiO₂/AC composite photocatalyst with high activity and easy separation prepared by a hydrothermal method

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Abstract

In the present work, a TiO₂/activated carbon (AC) photocatalyst with high activity and easy separation was prepared using a hydrothermal method. Phenol, methyl orange (MO) and Cr(VI) were used as target pollutants to test the activity and decantability. SEM, XRD, FTIR, diffuse reflectance spectra (UV/DRS) and N₂ adsorption isotherms were used to characterize the crystalline and electronic structure. Results show that the AC composite has a significant effect on the TiO₂ activity. With suitable AC content, the TiO₂/xAC catalysts prepared were much more active. The TiO₂/5AC catalyst exhibited easy separation and less deactivation after several runs, and was less sensitive to pH changes. UV/DRS revealed that no electronic bandgap changes in TiO₂ occurred on addition of the AC. SEM and XRD results suggest that better TiO₂ distribution can be achieved when an optimal AC content is used. A Ti–O–C bond was formed and a slight conjugation effect appeared between the AC bulk and TiO₂. The advantages of the obtained TiO₂/5AC catalyst revealed its great practical potential in wastewater treatment.

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1. Introduction

The application of TiO₂-based heterogeneous photocatalysis in environmental purification has been widely studied in recent decades [1–3]. Owing to the use of dioxygen, light and completely mineralized organic and inorganic substrates, especially bio-recalcitrant, this method is considered to be environmentally friendly for pollution treatment. Recent reports indicate that simultaneous removal of inorganic pollutants such as Cr(VI) and organic pollutants, such as 4-CP can be realized in TiO₂-based photocatalytic reaction systems [4]. Thus, it is highly desirable that this method can be applied on a large scale for water and wastewater treatment.

However, several shortcomings, i.e., the deactivation and separation of fine TiO₂ powder from the aqueous phase after use, prevents the large-scale application of this promising method [1–3]. Several attempts have been adopted to enhance the separation performance of TiO₂, such as immobilization of TiO₂ pow-

der onto supports like glass [5], porous nickel [6] and activated carbon [7–12]. However, simple mobilization has been found to decrease the reaction efficiency by reducing TiO₂ dispersion and its contact with light, as well as introducing a potential mass transfer limit [5–12]. Escape of TiO₂ particle from the supports has also been observed after a period of usage. In addition, some authors have fabricated a type of TiO₂ microsphere that is different from the powder to both maintain dispersion and accelerate separation [6], because microspheres can be suspended by air bubbling and can rapidly settle on the reactor bottom with the aid of gravity after such air bubbling. TiO₂ microspheres can degrade some organic compounds that are strongly adsorbed onto TiO₂, such as sulfosalicylic acid (SSA) and salicylic acid (SA), with an equivalent efficiency to the powder counterpart. The relatively high activity appears to be attributed to strong adsorption [6]. On the other hand, the activity for the degradation of other softly adsorbed organic molecules still remains unreported. These results indicate that for separation of used TiO₂, the following two points should be considered: (i) the good dispersion of suspended TiO₂ should be retained for efficient light use and to prevent potential mass transfer limits, and (ii) organic adsorption onto the TiO₂ surface should be improved as far as possible.

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Activated carbon (AC) is highly adsorptive owing to its developed pore structure and high specific area. Moreover the particle size of commercial AC is usually in the micro-scale range, so the particles can be suspended by air bubbling and then settle on the reactor bottom by gravity as TiO₂ microspheres [6]. Other authors have reported a synergistic effect for AC-supported TiO₂ systems [7–14]. Fast decantability of a mixture of TiO₂ and AC was also observed [8]. However, the TiO₂ powder escapes from the AC when TiO₂ is mechanically mixed with the AC [7,9,11] or immobilized on the AC using a co-binder [12], prompting the development of an alternative method to obtain a new form of TiO₂/AC photocatalyst with high activity and better separation performance.

The hydrothermal method, using an aqueous solvent as the reaction medium, has frequently been applied for the synthesis of nanosized materials, including TiO₂ photocatalysts, because the morphology, crystalline phase and thermal stability of hydrothermally obtained samples can be controlled [15,16]. The hydrothermal method is also environmentally friendly, since, the reactions are carried out in a closed vessel and the contents can be recovered and reused after cooling down to room temperature. Therefore, for the development of a TiO₂/AC composite photocatalyst in this study, a hydrothermal method was used.

In this study, a hydrothermal method was used, aiming to develop a new form of TiO₂/AC photocatalyst with the following advantages. (i) The catalyst can be suspended by air bubbling and can be separated from the aqueous phase after use by gravity settling. (ii) No or negligible amounts of TiO₂ particles escape from the AC support during use and reuse processes. (iii) It exhibits high photocatalytic activity and low deactivation. Two organic compounds, phenol and methyl orange (MO), and one inorganic compound of Cr(VI) were selected as substrates to evaluate the activity of the prepared TiO₂/AC samples. Such substrates are representative of aromatic pollutants, dyes and heavy metals commonly present in water and wastewater. Their environmental toxicity and resistance to bio-degradation have attracted great concern and photocatalysis is often used to remove them from water.

2. Experimental

2.1. Synthesis of TiO₂/xAC samples

In a typical procedure, 200 mg of commercial AC powder ($S_{\text{BET}} = 1150 \text{ m}^2/\text{g}$, Tianda Chemical Factory, China) was suspended in aqueous solution by continuous stirring. Then, 25 mL of TiCl₄ (AR, Dongda Chemical Factory, China) was added drop-wise at a temperature of $2 \pm 2 \text{ }^\circ\text{C}$, which was maintained for 1 h. A solution of (NH₄)₂SO₄, HCl and water (1:2:10 by mol) was then added and stirred for 30 min. The mixture was heated to 98 °C at a rate of 5 °C/min and kept at this temperature for 1 h. Thereafter, NH₃·H₂O was used to adjust the pH to 8 and the mixture was kept at 98 °C for 1 h. The TiO₂/AC precursor thus obtained was aged at room temperature for 10 h, washed with double-deionized water and dried in vacuum at 70 °C for 24 h. Finally, the prepared sample was heated in an N₂ atmosphere to

500 °C at 20 °C/min and was maintained at 500 °C for 2 h. The prepared catalyst was grinded and stored in a desiccator before use. The synthesized samples were denoted as TiO₂/xAC, where x is 0, 2, 5, and 20, representing the wt.% of AC.

2.2. Characterization of TiO₂/xAC samples

The surface structure and particle size of the synthesized TiO₂/xAC samples were first observed using scanning electron microscopy (SEM, QUANTA 200). The specific surface area of samples was measured using a Micrometrics ST-2000 automated apparatus based on the Brunauer–Emmett–Teller (BET) method at 77 K with N₂ as adsorbent and H₂ as the carrier gas. FTIR analysis was conducted on a Nicolet Magna 560 spectrophotometer, using KBr pellets for sample preparation. In addition, XRD and UV/DRS were used to identify the crystalline phase and determine the size of the synthesized TiO₂ crystals. XRD measurements were carried out on a D/max-rB X-ray diffractometer (XRD) using Cu K α radiation and the TiO₂ crystallite size was calculated from the Scherrer equation. Diffuse reflection spectra (UV/DRS) of the photocatalyst powder in the range 200–600 nm were recorded on a TU-1900 UV–vis spectrometer equipped with an integral sphere using BaSO₄ as a reference.

2.3. Experimental procedure

A cylindrical quartz photoreactor surrounded by a water jacket was used to evaluate the photocatalytic activity of the synthesized TiO₂/xAC samples [17] using phenol, MO and chromium as model substrates. An 8 W UV lamp with emission at 365 nm was positioned inside the quartz vessel. In each batch experiment, 0.25 g of TiO₂/xAC sample was added into 250 mL of reaction solution to form a suspension. Prior to UV irradiation, the suspension was magnetically stirred in the dark for 30 min to establish a substrate adsorption/desorption equilibrium. During pre-set reaction intervals, 5 mL suspension samples for chemical analysis were withdrawn from the reactor and immediately centrifuged at 4000 rpm for 10 min.

2.4. Separation performance

To evaluate the separation performance, 100 mL of an aqueous solution of the catalyst at a concentration of 1 g/L was placed in a 100 mL graduated cylinder and was shaken vigorously for 30 min. Then the solid catalyst was allowed to settle. The height of the solid–liquid interface was then measured using the graduations on the cylinder at various time intervals [18].

2.5. Deactivation test

To assess catalyst deactivation, 0.25 g photocatalyst powder was added into 250 mL of 50 mg/L aqueous phenol solution, magnetically stirred in the dark for 30 min, and then reacted under UV irradiation for 100 min. After gravity settling, the supernatant solution was discarded by decantation, and the remaining catalyst was reused for photocatalytic reaction.

2.6. Chemical analysis

The concentration of phenol and MO after illumination was determined spectrophotometrically on a TU-1900 UV–vis instrument at 270 and 465 nm, respectively. The concentration of Cr(VI) was determined by atomic adsorption spectroscopy at 365 nm using a TAS-900 instrument. The pH of the aqueous solutions were adjusted with 1 M HNO₃ and NaOH using a PHS-3C pH meter.

3. Results and discussion

3.1. Characterization of the TiO₂/xAC samples

The TiO₂/xAC products calcined at 500 °C were analyzed by XRD and the results are shown in Fig. 1. It can be observed that the TiO₂/xAC composite photocatalysts were dominated by anatase. Based on the XRD results, the crystal size of the microspheres was determined using the Scherrer formula:

$$L = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

where L is the crystalline size in nm, λ (0.15418 nm) the wavelength of the X-ray radiation, K the usually taken as 0.89, and β is the line width at half-maximum height after subtraction of equipment broadening for the peak at $2\theta = 25.15^\circ$. As listed in

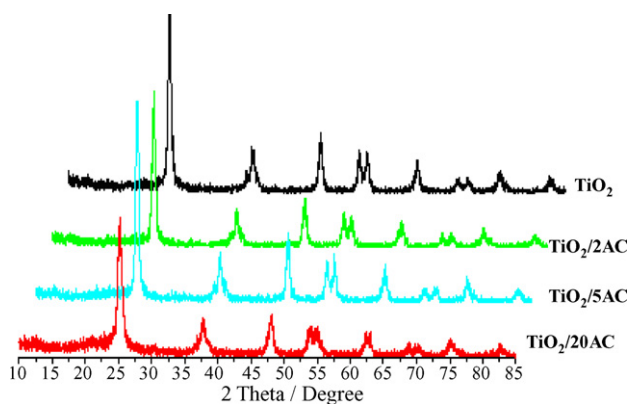


Fig. 1. XRD pattern for TiO₂ and TiO₂/xAC catalysts.

Table 1, with increasing AC content, the diffraction peak broadened and the size of the TiO₂ particles decreased slightly.

The SEM images of TiO₂/xAC in Fig. 2 show that both the AC pores and the TiO₂ particles can be differentiated. The AC pore size was as large as approximately 3 μm, which was able to accommodate TiO₂. It is interesting that TiO₂ particles were mainly distributed within the AC macro-pores. More careful observation showed that the aggregate size of TiO₂ particles strongly depended on the AC content. For naked TiO₂, the aggregation of TiO₂ crystallites was significant, with a largest size of approximately 500 nm. However, with increasing AC content,

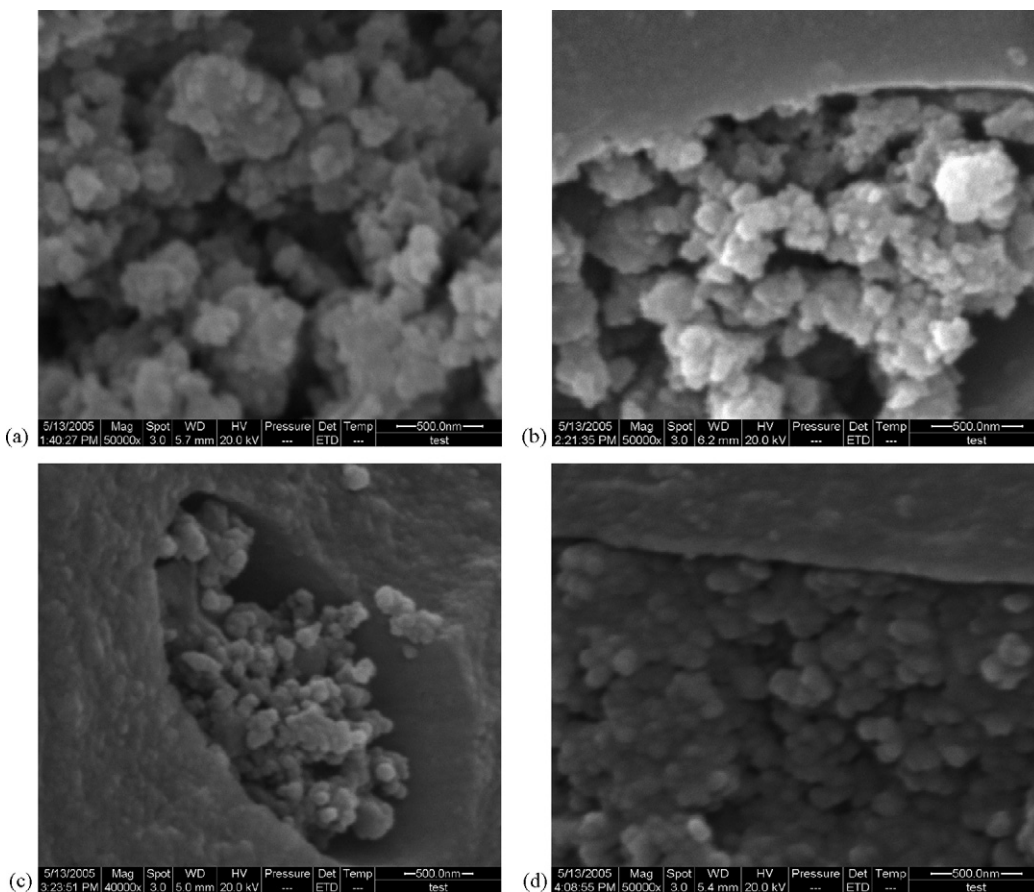


Fig. 2. SEM images of TiO₂ and TiO₂/xAC catalysts: (a) TiO₂, (b) TiO₂/2AC, (c) TiO₂/5AC, and (d) TiO₂/20AC.

Table 1
Crystallinity, aggregate size, and surface area of TiO₂/xAC

| | AC content (wt.%) | | | | |
|----------------------------------|-------------------|---------|---------|---------|------|
| | 0 | 2 | 5 | 20 | 100 |
| Phase structure | Anatase | Anatase | Anatase | Anatase | – |
| Crystallite size (nm) | 13.0 | 13.6 | 14.0 | 10.4 | – |
| Aggregate size (nm) | 14–300 | 15–200 | 15–30 | 20–50 | – |
| Surface area (m ² /g) | 58.37 | 67.56 | 96.97 | 296.35 | 1150 |

the size of TiO₂ aggregates decreased. The size range for TiO₂ aggregates was 15–300 nm for TiO₂, 15–200 nm for TiO₂/2AC, 15–30 nm for TiO₂/5AC and 20–50 nm for TiO₂/20AC.

FTIR spectra of the samples are shown in Fig. 3. The main absorption peaks are located at 3410, 1600 and 510–1060 cm⁻¹. The band at 3410 cm⁻¹ was assigned to –OH stretching and that at 1600 cm⁻¹ to –OH vibration. The band at 520 cm⁻¹ was assigned to the Ti–O stretching vibration [9,11]. No significant change in the stretching frequency and intensity for –OH groups was observed. However, with the addition of AC, a new peak located at 1060 cm⁻¹ appeared and the peak at 520 cm⁻¹ shifted to lower wave numbers. With increasing AC content, the width and intensity of the peak at 1060 cm⁻¹ increased. Thus, it can be concluded that the appearance of this peak was related to AC. Zhang et al. attributed a peak at 949 cm⁻¹ in the FTIR spectrum of titania–silica mixed oxide to a newly formed Ti–O–Si bond [19]. Considering the electron affinity of C and Si, the peak at 1060 cm⁻¹ should be attributed to Ti–O–C, suggesting a slight conjugation effect between bulk AC and Ti–O bonds.

The effect of carbon content on the band energy of TiO₂ was investigated by UV/DRS (Fig. 4). It can be observed that the light reflection of TiO₂/xAC catalysts in the range 400–600 nm decreased, which may be due to the black characteristic of AC. However, the adsorption edges of the TiO₂/xAC catalysts remained unchanged and no significant change in band energy was observed. This result suggests that the enhanced photocatalytic activity of the TiO₂/xAC catalysts was not due to a change in band energy.

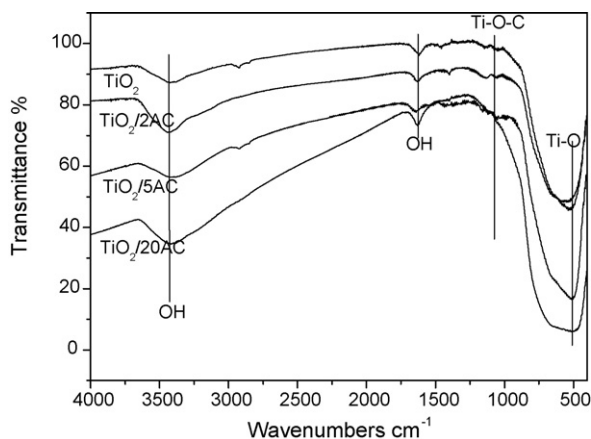


Fig. 3. FTIR spectra of TiO₂ and TiO₂/xAC catalysts.

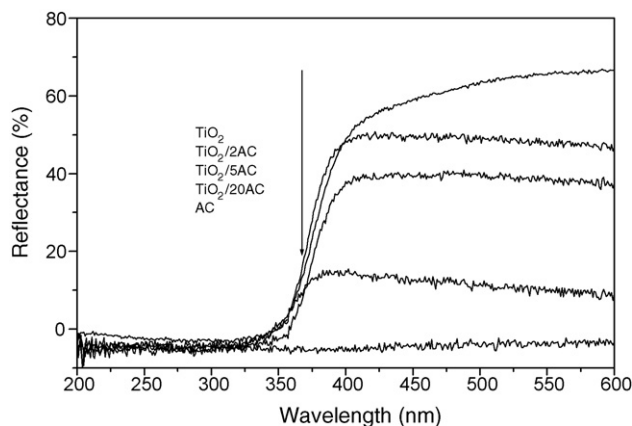


Fig. 4. Diffuse reflectance spectra of TiO₂ and TiO₂/xAC catalysts.

3.2. Photocatalytic performance

To evaluate the photocatalytic activity of the TiO₂/xAC samples, phenol was first used as a model organic substrate in the suspended TiO₂/xAC reaction system. The results for phenol degradation are shown in Fig. 5. It can be observed that the photocatalytic degradation rate of phenol on naked TiO₂ prepared in this work was almost the same as for P-25 in the initial 40 min, after which degradation on P-25 occurred remarkably faster than on naked TiO₂. However, on TiO₂/5AC, phenol degradation was more efficient than on P-25 and the other TiO₂/xAC. According to the kinetic analysis, photocatalytic phenol degradation fitted pseudo-first-order kinetics well. The first-order reaction rate constant (*k*) is shown in Table 2 and followed the sequence: TiO₂/5AC (*k*=0.0481) > TiO₂/P-25 (*k*=0.0327) > TiO₂/2AC (*k*=0.0248) > TiO₂ (*k*=0.0241) > TiO₂/20AC (*k*=0.0194). The optimum AC content in the TiO₂/xAC samples was found to be 5 wt.%.

Photocatalytic degradation of two other substrates, MO and Cr(VI), is shown in Figs. 6 and 7, respectively, and the kinetic data are listed in Table 2. It can be observed that the activity of TiO₂/5AC was much higher than for P-25 and naked TiO₂.

The photocatalytic activity of TiO₂ was strongly influenced by the pH of the reaction solution due to its amphoteric behavior. The surface charge properties of TiO₂ changed with pH. The

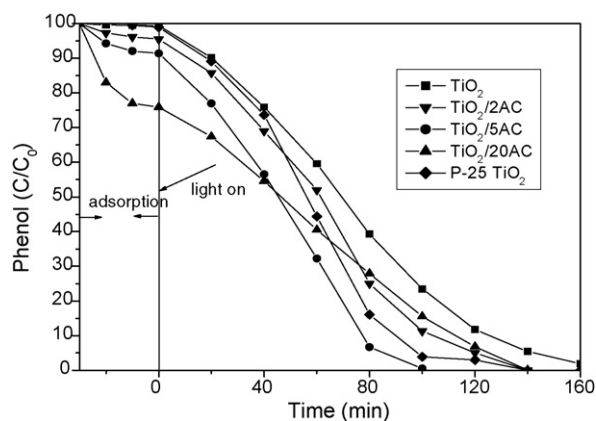


Fig. 5. Kinetics of photocatalytic phenol degradation over TiO₂ and TiO₂/xAC.

Table 2
Photocatalytic characteristics of TiO₂ and TiO₂/xAC

| AC content (wt.%) | Phenol | | | MO | | | Cr(VI) | | |
|-------------------|-------------------------------|-------------|----------|-------------------------------|-------------|----------|-------------------------------|-------------|----------|
| | <i>k</i> (min ⁻¹) | Removal (%) | <i>R</i> | <i>k</i> (min ⁻¹) | Removal (%) | <i>R</i> | <i>k</i> (min ⁻¹) | Removal (%) | <i>R</i> |
| 0 | 0.02412 | 76.3 | 0.953 | 0.00599 | 52.8 | 0.977 | 0.02169 | 74.5 | 0.9221 |
| 2 | 0.02485 | 88.7 | 0.955 | – | – | – | – | – | – |
| 5 | 0.04806 | 99.5 | 0.953 | 0.04981 | 100 | 0.902 | 0.05073 | 100 | 0.9268 |
| 20 | 0.01937 | 84.5 | 0.957 | – | – | – | – | – | – |
| 100 | 0.00139 | 38.9 | 0.932 | – | – | – | – | – | – |
| P-25 | 0.03273 | 96.2 | 0.952 | 0.00714 | 57.2 | 0.985 | 0.02370 | 91.4 | 0.9678 |

k is the reaction constant and removal was calculated for 100 min.

point of zero charge (pzc) for titanium dioxide is at pH ≈ 6.5. The TiO₂ surface is positively charged in acid solution (pH < pzc) and negatively charged in basic solution (pH > pzc) [20]. In an attempt to identify the effect of pH on the photocatalytic activity of TiO₂/xAC samples during phenol degradation, the TiO₂/5AC sample was selected, since it exhibited the highest activity. Fig. 8 shows the effect of pH on the photocatalytic activity. It can be observed that TiO₂/5AC remained active over a wide pH range, suggesting it has low sensitivity to pH changes. For comparison, phenol degradation on naked TiO₂ was also evaluated.

The results indicate that the activity of naked TiO₂ was pH-dependent and strongly influenced by pH. From pH 3 to 5, the activity increased remarkably, then decreased dramatically from pH 5 to 9.

To determine the deactivation of prepared catalysts, TiO₂ and TiO₂/5AC were used for several photocatalytic runs. After the first photocatalytic reaction, the catalyst was separated and used for further runs without any treatment. The results in Fig. 9 show that the activity of TiO₂ decreased greatly and significant deactivation occurred; only 55% of phenol could be removed

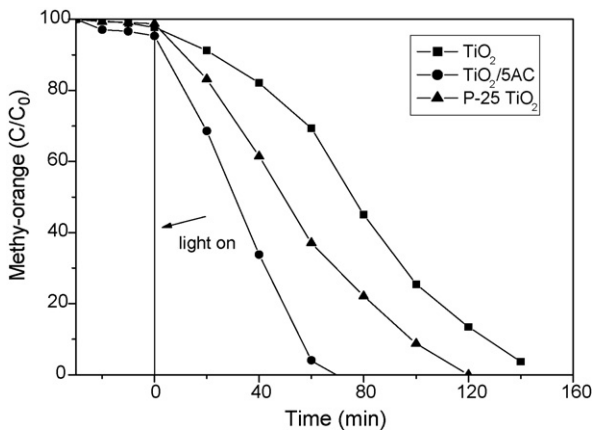


Fig. 6. Kinetics of photocatalytic MO degradation over TiO₂ and TiO₂/xAC.

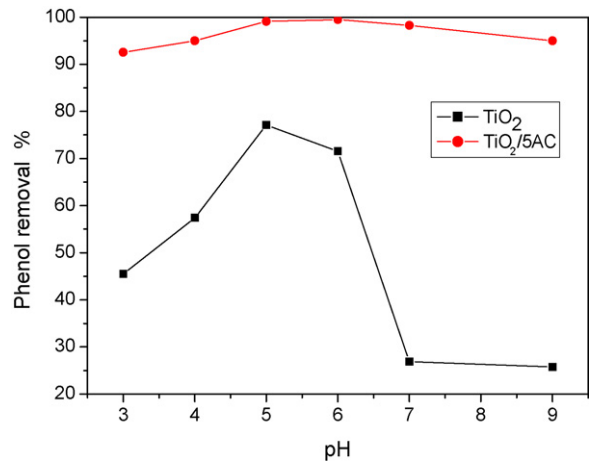


Fig. 8. Effect of pH on phenol degradation over TiO₂ and TiO₂/5AC.

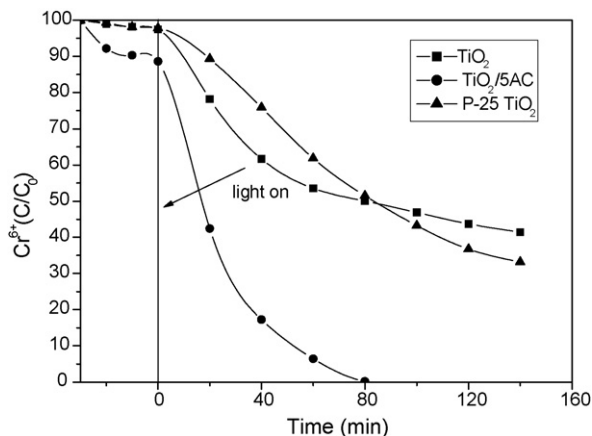


Fig. 7. Kinetics of photocatalytic Cr(VI) reduction over TiO₂ and TiO₂/xAC catalysts.

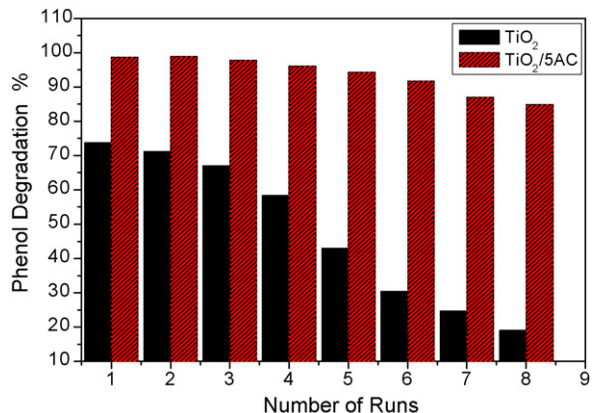


Fig. 9. Effect of number of runs on phenol degradation over TiO₂ and TiO₂/5AC.

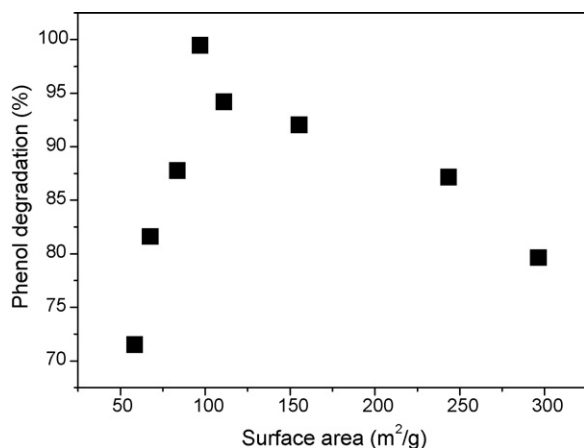


Fig. 10. Relationship between specific surface area and photocatalytic activity of $\text{TiO}_2/x\text{AC}$.

within 100 min after four runs. On the other hand, the activity of $\text{TiO}_2/5\text{AC}$ only slightly decreased and 95% phenol degradation was still achieved after eight runs; thus, $\text{TiO}_2/5\text{AC}$ retained almost the same activity as in the first run and almost no deactivation occurred.

Separation tests showed that the $\text{TiO}_2/x\text{AC}$ series can easily be separated by gravity sedimentation. All catalysts could settle on the bottom of a graduate cylinder within 5 min, whereas 20 min was needed for naked TiO_2 and 300 min for P-25. Considering the separation problem of nanosized TiO_2 , the easy separation and high activity of $\text{TiO}_2/5\text{AC}$ imply that it has great potential in practical applications.

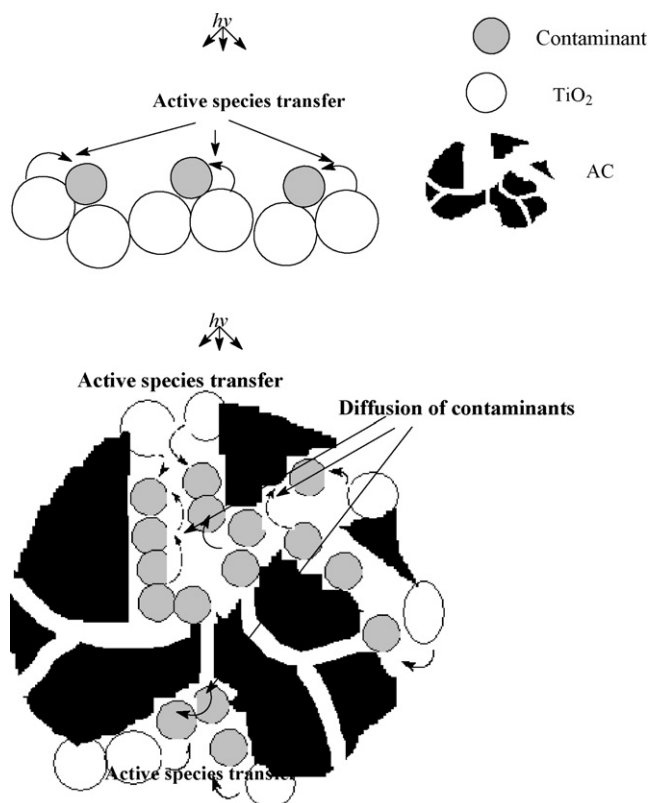


Fig. 11. The role of AC in the enhanced activity of TiO_2 .

3.3. Mechanism for the enhanced activity of $\text{TiO}_2/x\text{AC}$ samples

From Figs. 5–7, it can be observed that 5 wt.% AC remarkably enhanced catalyst activity in the photocatalytic degradation of phenol, MO and Cr(VI). Since, AC is highly adsorptive, and the photocatalytic experiments were performed under the same conditions, other than on naked TiO_2 samples, this enhanced activity could be related to the adsorption of AC. A plot of the specific surface area against $\text{TiO}_2/x\text{AC}$ activity is shown in Fig. 10.

Suitable adsorption capacity is crucial for high photocatalytic activity. An important step in the photocatalytic process is the adsorption of reacting substances onto the surface of the catalyst [21,22]. AC has a well-developed pore structure, very large surface area and strong adsorption capacity and is widely used as an adsorbent and catalyst support. AC in the $\text{TiO}_2/x\text{AC}$ catalysts can act as a center where organic molecules can adsorb before transferring to the decomposition center, illuminated TiO_2 , which is located on the AC surface, because of the concentration difference. However, strong adsorption of pollutant molecules may inhibit subsequent photocatalytic reactions. SEM revealed that TiO_2 particle aggregation was effectively inhibited when a suitable AC content was used, yielding better distribution of the TiO_2 nanoparticles. This may also contribute to the high activity. A mechanism for the enhanced activity of $\text{TiO}_2/5\text{AC}$ is shown in Fig. 11.

4. Conclusion

Highly active $\text{TiO}_2/x\text{AC}$ composite photocatalysts with the advantages of easy separation and low deactivation can be prepared using a hydrothermal method. When an optimal AC content (5 wt.%) is used, the photocatalytic oxidation activity of the prepared TiO_2 catalyst can be improved significantly, with less reduction in activity over time. Better TiO_2 distribution can also be achieved when an optimal AC content is used. The formed Ti–O–C bond suggesting the presence of a slight conjugation effect between the AC bulk and TiO_2 . There were no changes in the electronic bandgap or crystalline phase when AC was added. AC in the $\text{TiO}_2/x\text{AC}$ catalysts can act as a center where organic molecules can adsorb before transferring to the decomposition center, illuminated TiO_2 , which is located on the AC surface because of the concentration difference. Suitable adsorption capacity and better distribution of TiO_2 nanoparticles are the main reasons for the high activity.

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