Preparation of Nanocrystalline TiO₂/Activated Carbon Composite Catalyst for the Removal of Phenol in Aqueous Solution

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Abstract: The nanocrystalline TiO₂/activated carbon composite catalyst (TiO₂/AC) was prepared through sol-gel method in isopropanol mixed with activated carbon (AC) in order to remove phenol from aqueous solution. The prepared-TiO₂/AC was calcined at 400 °C and characterized by X-ray diffraction spectrometry (XRD), Transmission electron microscopy (TEM), Scanning electron microscopy (SEM) and nitrogen adsorption-desorption by Brunauer-Emmett-Teller (BET) method. The XRD pattern indicated that the TiO₂/AC was in Anatase phase. TEM image showed that the crystallite size of TiO₂/AC was in the range of 7-9 nm. The SEM image of TiO₂/AC showed that the activated carbon was homogeneity covered with TiO₂ particles and was coated with TiO₂-film spreading throughout the surface. The specific surface area from BET method was 441 m²/g and adsorption capacity determined from adsorption isotherm was 5.0×10⁴ mg/g. The TiO₂/AC calcined at 400 °C was used to remove phenol in aqueous solution under UV irradiation, which showed higher removal efficiency than TiO₂ (Degussa-P25) and AC. The percentage of removal of 100 ppm phenol by 0.4 g of TiO₂/AC in 4 h was 68.03%, due to both adsorption (54.14%) and photocatalytic degradation (13.88%) with rate constant of 0.1080 h⁻¹. The prepared TiO₂/AC can be reused for the treatment of phenol for at least 3 times with 76% efficiency compared to the first photocatalytic run.

Key words: Titanium dioxide, activated carbon, TiO₂/AC, photocatalyst, phenol.

1. Introduction

Titanium dioxide (TiO₂) is chemically and biologically inert, photoactive and inexpensive, which are the important reasons for the fact that this material is probably one of the most extensively used photocatalytic supports for solving environmental problems, especially in the purification of wastewater [1-3]. Titanium dioxide has three crystalline forms those are anatase, rutile and brookite. Anatase form possesses the best photocatalytic properties and is commonly used as photocatalyst. The photocatalytic mechanism involves irradiation of electron-hole pairs

in the valence band of TiO₂ by light of energy higher than that of the band gap (3.2 eV for anatase phase) [4]. Electrons (e⁻) are excited to the conduction band and holes (h⁺) still remain in the valence band. The holes perform as strong oxidizing agent reacting with water molecules or hydroxyl groups on the TiO₂ surface so as to generate hydroxyl radicals (•OH), which initiate the photodegradation. Moreover, the excited electrons can also react with oxygen molecules to form superoxide radicals (O₂•⁻), which can react with protons (H⁺) to provide hydroxyl radicals [3, 5].

In present, various methods are used to improve photocatalytic reaction such as doping, metal coating, surface sensitization and support [5]. Support is one of the effectively methods for improving photocatalytic

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reaction of TiO₂, for example, immobilize the TiO₂ photocatalyst, increase the illuminated specific catalyst area and increase the adsorption capacity and surface area of the photocatalyst. Previous works attempt to use the adsorbent such as silica [6, 7], alumina [8, 9], zeolite [10-12] and activated carbon [13-15]. Recent works, TiO₂ supported activated carbon (TiO₂/AC) has been reported that it exhibits synergistic effect between the TiO₂ and activated carbon [15-18].

Phenol is a phenolic compound contaminated in natural aquatic resource. The main source of phenol is the discharge from various chemical process industries. Phenol in environment is considered as a major aquatic pollution because it easily contaminates in water. Furthermore, it has been reported that even low concentration of phenol is carcinogenic to humans [15].

In this work, nanocrystalline TiO₂/activated carbon composite catalyst (TiO₂/AC) was prepared by sol-gel method to get anatase phase and characterized. The removal efficiency of phenol by the prepared catalyst has been studied in term of both adsorption activity and photodegradation activity under UV irradiation. The recyclability of the prepared TiO₂/AC was also investigated.

2. Materials and Methods

2.1 Catalyst Preparation and Characterization

Titanium dioxide supported activated carbon (TiO₂/AC) was prepared from Titanium (IV) tetraisopropoxide (Lab Grade, ACROS, New Jersey, USA) by sol-gel method in the presence of activated carbon (AC, AR Grade, Fluka, Steinheim, Switzerland). Activated carbon (1 g) was suspended in titanium (IV) tetraisopropoxide (2 mL) under stirring condition. Isopropyl alcohol (20 mL, AR Grade, Sentmenat, Spain) was subsequently added and was stirred of the mixture for 1 h. TiO₂/AC was collected by incubation at 120 °C for 1 h and then it was calcined at 400 °C for 1 h.

Samples for X-ray powder diffraction (XRD) analysis were deposited on a silicon wafer sample holder and characterized using a Phillips Pw 1830

X-ray diffractometer (CuK α , 1.5418 Å). Sample for transmission electron microscopy (TEM; JEOL 1200EX, 120 keV) was deposited on carbon-coated 3 mm-diameter, electron microscope grids. Scanning electron microscope image was acquired by using a JEOL JSE-5600Lv scanning electron microscope, operating at 15 kV. Each powdered sample was spread on carbon tape mounted on a SEM stub and needed to be coated with Pt/Pd particles prior to SEM operation. Specific surface area was calculated according to the Brunauer-Emmett-Teller (BET) method by using nitrogen adsorption-desorption data from the Autosorb-1 Quanta Chrome.

2.2 Adsorption Isotherm

In general, the sample (50 mg) was added into 25 mL of various concentration of phenol (50-500 ppm), and each sample was kept in an isothermal shaker for 4-6 h to ensure the equilibrium of the adsorption by each adsorbent which varies from 1-3 h. The samples were removed and analysed for concentration of phenol by UV-vis spectrophotometer (JASCO 7800) at 270 nm.

2.3 Photocatalytic Activity

Photocatalytic activity of the catalyst (TiO₂/AC) was determined by phenol degradation in aqueous solution under UV irradiation. Degradation efficiency of phenol was measured spectrophotometrically using a UV-Vis spectrometer (JASCO 7800). Photodegradation of phenol with/without catalysts under UV light was monitored by changes in absorption at 270 nm (A_{270}) associated with phenol residue. Changes in A_{270} with time were converted to relative concentration of phenol (C/C_0). Stock solution of 100 ppm phenol in distilled water was prepared freshly prior to undertaking the reaction. Typically, the reaction was carried out at 30 °C in a 250 mL-flask, using a mixture consisting of 200 mL of 100 ppm phenol and 0.4 g of catalyst. The reaction mixture was stirred under dark condition for 1 h. Sequentially, the UV lamps (120 W of Hg lamps) were turn on to irradiate samples and then the samples

were collected every 30 min for 3 h to measure the absorbance at 270 nm. Each experiment was done in three replicates. The recyclability of the TiO₂/AC was also determined for three photocatalytic runs. After each run the used catalyst was sonicated in distilled water, air dried, before reused in the next run.

3. Results and Discussion

3.1 Characterization of Catalyst

The XRD patterns as shown in Fig. 1 indicate that the TiO₂/AC changes from amorphous to anatase phase by the elevation of calcination temperature up to 400 °C. Anatase phase is identified at 2θ of 25.4°, 38.1°, 48.2°, 53.9° and 55.1° (JCPDS file No. 21-1272). Besides, TiO₂/AC changed from black to gray color when temperature was higher than 400 °C due to the oxidation of the charcoal. Therefore, TiO₂/AC calcined at 400 °C was selected to use for the removal of phenol in aqueous solution.

In addition, crystallite sizes of TiO₂/AC calculated by Scherrer's equation [19] are in the range of 7-9 nm which are confirmed by TEM image as shown in Fig. 2. The SEM image of TiO₂/AC as shown in Fig. 3 shows that the activated carbon was homogeneity covered with TiO₂ particles and was coated with TiO₂-film spreading throughout the surface.

3.2 Adsorption Isotherm

The maximum capacity of adsorption (b) and adsorption constant (Q) can be calculated using the Langmuir isotherm by the plot between C_e/q_e versus C_e as followed:

$$C_e/q_e = 1/bQ + C_e/Q \quad (1)$$

where C_e is liquid phase concentration of phenol at equilibrium (mg/L), q_e is equilibrium of solid phase absorbed concentration (mg/g), b is absorption constant of Langmuir isotherm (L/mg), Q is maximum surface coverage (monolayer) (mg/g).

The constants b , Q and correlation coefficient (r^2), which calculated from the Langmuir adsorption isotherms of AC, AC-400, TiO₂/AC and TiO₂ (Degussa-P25)

Fig. 1 XRD patterns of TiO₂/AC calcined at 500 °C (A), 400 °C (B), 300 °C (C) and without calcination (D).

Fig. 2 TEM micrographs of TiO₂/AC calcined at 400 °C.

Fig. 3 SEM micrographs of TiO₂/AC calcined at 400 °C.

are shown in Table 1. The calculated Langmuir constant of AC and AC-400 which indicate the thermodynamic stability of the adsorption toward phenol are 34.9×10^{-2} and 11.7×10^{-2} L/mg respectively, with similar maximum adsorption capacity (Q) of 1.4×10^5 mg/g. These results implied that the calcination at 400 °C caused decreasing adsorption activity of AC-400 due to the lost of some functional

Table 1 Langmuir adsorption isotherm constants of the samples obtained from experiments.

Sample	b (L/mg)	Q (mg/g)	r ²
AC	34.96×10 ⁻²	1.43×10 ⁵	0.9967
AC-400	11.67×10 ⁻²	1.43×10 ⁵	0.9987
TiO ₂ /AC	5.0×10 ⁻²	5.0×10 ⁴	0.9935
TiO ₂ -P25	3.31×10 ⁻⁴	3.14×10 ³	0.9900

groups at the surface of AC by the increasing of calcination temperature, but still had adsorption capacity as before calcination [20]. The AC-400 was used as a reference comparing with the TiO₂/AC catalyst. Besides, the Langmuir constant of TiO₂/AC is higher than Degussa-P25, it can be indicated that TiO₂/AC has higher thermodynamic stability for phenol than Degussa-P25.

Regarding the surface area, the BET surface area of AC, AC-400 and TiO₂/AC were 1110, 1056 and 441 m²/g, respectively. The trend of surface area from BET method was similar to the estimated surface area that was calculated from Q-value of the Langmuir adsorption isotherm.

3.3 Photocatalytic Activity

As shown in Fig. 4, percentage of phenol removal of TiO₂/AC, AC, P25 TiO₂ and the prepared-TiO₂ are 68.03%, 57.01%, 18.95% and 8.60%, respectively. The initial removal rate of TiO₂/AC is similar to AC, but after 60 min, the TiO₂/AC still has ability to remove phenol at similar degradation rate of pure TiO₂. The TiO₂/AC has the highest phenol removal efficiency with the rate constant of 0.1080 h⁻¹ (Table 2). The removal of phenol by AC may be due to the adsorption of phenol unlike TiO₂/AC, which composes of both adsorption by AC and photocatalytic activity by TiO₂.

Nevertheless, the TiO₂/AC calcined at 300 °C and without calcination that was still amorphous phase show only adsorption activity (Fig. 5 and Table 3). The TiO₂/AC calcined at 500 °C shows only photodegradation activity because all of activated carbon was oxidized completely. Accordingly, the TiO₂/AC calcined at 400 °C has more removal efficiency than others because of adsorption (first 60

Fig. 4 Phenol removal efficiency of TiO₂/AC calcined at 400 °C compared with AC, TiO₂-syn and Degussa-P25.**Table 2** The phenol removal efficiency by various samples and rate constant.

Catalysts	% Removal	Rate constant (h ⁻¹)
Prepared-TiO ₂	8.60	0.0233 (r ² = 0.9876)
P25 TiO ₂	18.95	0.0520 (r ² = 0.9876)
AC-400	57.01	-* (r ² = -*)
TiO ₂ /AC	68.03	0.1080 (r ² = 0.9876)

* No photodegradation occur.

Fig. 5 Phenol removal efficiency of TiO₂/AC with various calcination temperatures and without calcination.**Table 3** The percentage of phenol removal and rate constant by using TiO₂/AC.

Catalyst	% Removal			Rate constant (h ⁻¹)
	Adsorption	Degradation	Total	
w/o	67.55	4.48	72.03	0.0345 (r ² = 0.9524)
300 °C	68.36	3.78	72.15	0.0507 (r ² = 0.9840)
400 °C	54.14	13.88	68.03	0.1080 (r ² = 0.9292)
500 °C	8.15	10.83	18.98	0.0388 (r ² = 0.9154)

min) and photocatalytic degradation.

There are two possible degradation pathways of phenol by radical species ([•]OH). Firstly, the para- and meta-position of phenol molecule was reduced by [•]OH radical, which would be able to provide two possible intermediates that were hydroquinone and catechol,

respectively. Then both intermediates were reduced by •OH radical again, followed by ring opening of intermediates in accordance with the previous study by G. Sivilingam et al. [21].

The recyclability of the TiO₂/AC calcined at 400 °C was determined for three photocatalytic runs. Table 4 shows the %removal of phenol for each run. It can be seen that the %removal of phenol was decreased when the TiO₂/AC was repeatedly used in photocatalytic runs. This may be because the TiO₂/AC was deactivated by two reasons. First, the generation of reaction residues (by-products or intermediates) might be adsorbed onto the catalyst and block the active sites, which as a result reduced the adsorption and the photocatalytic reaction [22]. Second, the dirtiness (dust or impure particles) might change the catalyst surface by blocking pore [23]. However, the removal efficiency was reduced to 96% on the second run and 76% on the first run compared to the first photocatalytic run.

4. Conclusions

TiO₂/AC has been prepared using a simple and effective sol-gel method involving a titania tetraisopropoxide precursor and isopropanol. XRD diffractograms show that the TiO₂ undergoes the amorphous-to-anatase phase transformation when increase calcination temperature. TiO₂/AC calcined at 400 °C performs the synergistic effect of adsorption and photodegradation under UV light effectively, it provides 68.03% phenol adsorption, which 54.14% is from adsorption and 13.88% is from photocatalytic degradation with rate constant of 0.1080 h⁻¹. The phenol removal efficiency of the TiO₂/AC was reduced to 96% and 76% after the second and third photocatalytic

Table 4 The recyclability of TiO₂/AC on the removal of phenol.

Cycle	Average removal of phenol (%)		
	Adsorption	Degradation	Total
First run	54.20	13.90	61.10
Second run	48.96	9.45	58.41
Third run	41.03	6.15	46.19

run. In order to get the higher efficiency of the reused catalysts, the washing procedure should be further investigated.

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