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Removal of Phenol in Aqueous Solution by Nanocrystalline TiO_2/Activated Carbon Composite Catalyst

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ABSTRACT

A nanocrystalline TiO_2/activated carbon composite catalyst (TiO_2/AC) was prepared by the sol-gel method in isopropanol mixed with activated carbon (AC). The preparation of TiO_2/AC was calcined at 400°C and characterized. The X-ray diffraction (XRD) pattern indicated that the TiO_2/AC was in the anatase phase. The transmission electron microscopy (TEM) image showed that the crystallite size of TiO_2/AC was in the range of 7-9 nm. The specific surface area from the Brunauer, Emmett and Teller (BET) method was 441m^2/g and the adsorption capacity determined from the adsorption isotherm was 5.0×10^4 mg/g. The TiO_2/AC calcined at 400°C was used to remove phenol in aqueous solution under UV irradiation, which showed the highest removal efficiency when compared with TiO_2 (Degussa-P25) and AC. The percentage removal of 100 ppm phenol by 0.4 g of TiO_2/AC in 4 h was 68.03%, due to both adsorption (54.14%) and photocatalytic degradation (13.88%), with the highest rate constant being 0.1080 h^{-1}.

Keywords: titanium(IV) dioxide, activated carbon, TiO_2/AC, photocatalyst, phenol

INTRODUCTION

Titanium dioxide (TiO_2) is chemically and biologically inert, photoactive and inexpensive, which are important reasons why this is probably one of the most extensively used materials for photocatalytic support in solving environmental problems, especially in the purification of wastewater (Hoffman *et al*., 1995; Araña *et al*., 2003; Wendong *et al*., 2007). TiO_2 has three crystalline forms (anatase, rutile and brookite). The anatase form possesses the best photocatalytic properties and is commonly used as a photocatalyst. The photocatalytic mechanism involves irradiation of electron-hole pairs in the valence band of TiO_2 by light of energy higher than that of the band gap or 3.2 eV for the anatase phase (Choi *et al*., 2006). Electrons (e^-) are excited to the conduction band and holes (h^+) still remain in the valence band. The holes act as a strong oxidizing agent reacting with water molecules or hydroxyl groups on the TiO_2 surface to generate hydroxyl radicals ($OH^\bullet$), which initiate photodegradation. Moreover, the excited electrons can also react with oxygen molecules to form superoxide radicals ($O_2^{\bullet-}$), which can react with protons (H^+) to provide hydroxyl radicals (Hoffman *et al*., 1995; Carp *et al*., 2004).

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Currently, various methods are used to improve the photocatalytic reaction, such as doping, metal coating, surface sensitization and support (Carp *et al*., 2004). Support is one of the effective methods for improving the photocatalytic reaction of TiO_2, for example by immobilizing the TiO_2 photocatalyst, increasing the illuminated specific catalyst area and increasing the adsorption capacity and surface area of the photocatalyst.

Previous attempts have been made to use an adsorbent, such as silica (Sato, 1998; Hirano, 2004), alumina (Leem *et al*., 2001; Tanaka *et al*., 2002), zeolite (Yamashita *et al*., 1996; Xu and Langford, 1997) or activated carbon (Takeda *et al*.,1998; Nozawa *et al*., 2001; Tryba *et al*., 2003). In recent work, TiO_2-supported activated carbon (TiO_2/AC) has been reported to exhibit a synergistic effect between the TiO_2 and the activated carbon (Matos *et al*., 2001; Tryba *et al*., 2003a; Wang *et al*., 2005).

Phenol is a phenolic compound that contaminates the natural aquatic environment, and is sourced mainly from the waste discharge from various chemical processing industries. Phenol is considered a major source of aquatic pollution, because it is a ready contaminant of water. Furthermore, it has been reported that even low concentrations of phenol are carcinogenic to humans (Tryba *et al*., 2003b).

In the current work, a nanocrystalline TiO_2/activated carbon composite catalyst (TiO_2/AC) was prepared by the sol-gel method to produce the anatase phase and characterized. The prepared catalyst was investigated for its removal efficiency of phenol in terms of both adsorption activity and photodegradation activity under UV irradiation. In contrast, previous research has generally concentrated on the total removal efficiency.

MATERIALS AND METHODS

Catalyst preparation and characterization

Titanium dioxide-supported activated carbon (TiO_2/AC) was prepared from titanium (IV) tetraisopropoxide by the sol-gel method in the presence of activated carbon. Under constant stirring conditions, 1 g activated carbon (C, AR Grade, Fluka Chemika, Steinheim, Switzerland) was suspended in 2 mL titanium (IV) isopropoxide ($C_{12}H_{28}O_4Ti$, Lab Grade, ACROS, New Jersey, USA). Then, 20 mL isopropyl alcohol (C_3H_7OH, AR Grade, Sentmenat, Spain) was added and was stirred for 1 h. The TiO_2/AC was dried by incubation at 120°C for 1 h and then it was calcined at 400°C for 1 h.

Photocatalytic activity

The photocatalytic activity of the catalyst (TiO_2/AC) was determined by phenol degradation in aqueous solution under UV irradiation. The degradation efficiency of the phenol was measured spectrophotometrically using a UV-Vis spectrometer (JASCO 7800). Photodegradation of phenol with/without catalyst under UV light was monitored by the changes in absorption at 270 nm (A_{270}) associated with phenol residue. Changes in A_{270} with time were converted to a relative concentration of phenol (C/C_0). A 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 conditions for 1 h. Sequentially, the UV lamps (120 W of Hg lamps) were turned on to irradiate the mixture and then samples were collected every 30 min for 3 h to measure the absorbance at 270 nm.

Adsorption isotherm

In general, each sample (50 mg) was added into 25 mL of various concentrations 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 varied from 1-3 h. The sample was removed and analyzed for its phenol concentration by a UV-Vis spectrophotometer (JASCO 7800) at 270 nm.

RESULTS AND DISCUSSION

Characterization of catalyst

The XRD patterns (Figure 1) indicate that the TiO_2/AC was changed from the amorphous to the anatase phase by elevating the calcination temperature to 400°C. The anatase phase is identified at 2q of 25.4°, 38.1°, 48.2°, 53.9° and 55.1° (JCPDS file No. 21-1272). In addition, the color of the TiO_2/AC changed from black to gray when the temperature was higher than 400°C. Therefore, the TiO_2/AC that had been calcined at 400°C was selected for use in the removal of phenol in aqueous solution. In addition, the crystallite thickness of TiO_2/AC, as calculated by Scherrer's equation (Pomoni *et al.*, 2007) is in the range 7-9 nm, which was confirmed by transmission electron microscopy (TEM) images (Figure 2). The scanning electron microscope (SEM) image of TiO_2/AC in Figure 3 shows that

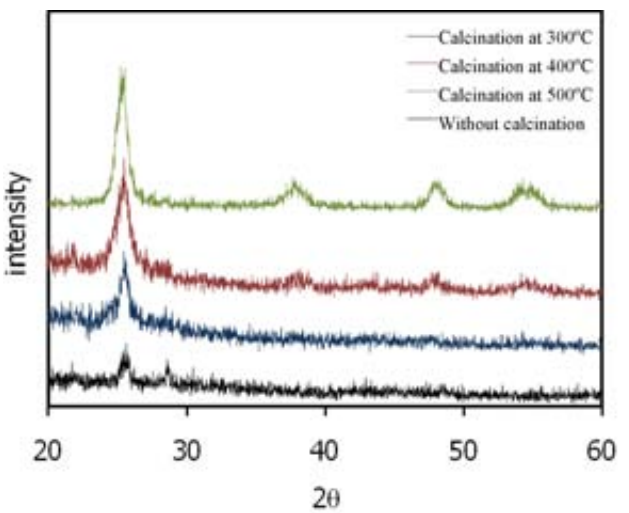

Figure 1 XRD patterns of TiO_2/AC calcined at various temperatures and without calcination.

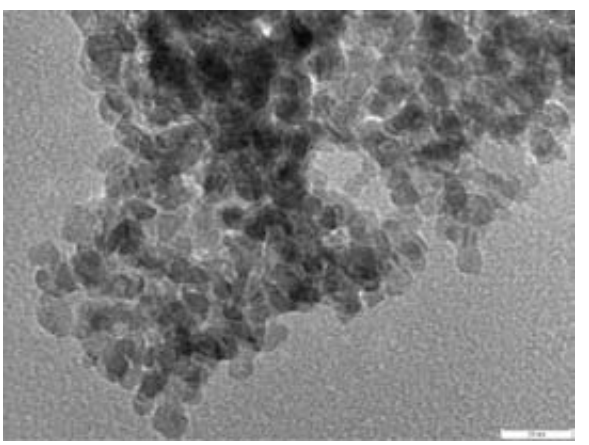

Figure 2 TEM image of TiO_2/AC calcined at 400°C.

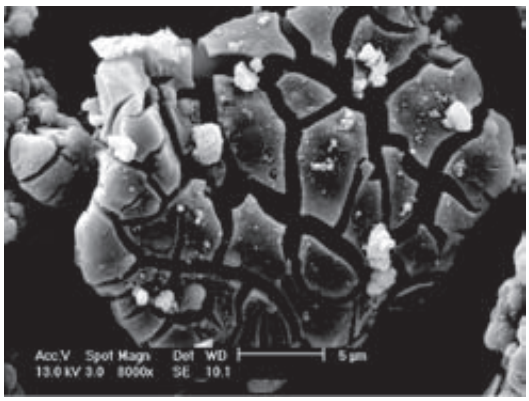

Figure 3 SEM micrograph of TiO_2/AC calcined at 400°C.

the activated carbon was homogeneously covered with TiO_2 particles and the surface was coated completely with the TiO_2 film.

Adsorption isotherm

Table 1 shows components of the Langmuir isotherm for AC, AC-400, TiO_2/AC and TiO_2 (Degussa-P25). The values of the Langmuir constant for AC and AC-400 indicate that the thermodynamic stability of adsorption occurs at 34.9×10^{-2} and 11.7×10^{-2} L/mg, respectively, with both having a similar maximum adsorption capacity (Q) of 1.4×10^{5} mg/g. These values implied that the calcination at 400°C caused decreasing adsorption activity of AC-400 due to the loss of some functional groups at the surface of the AC by the increase in the calcination temperature. However, the AC still had the same adsorption capacity as before calcination (Dabrowski *et al.*, 2005). The AC-400 was used as a reference compared with the TiO_2/AC photocatalyst. As the Langmuir constant of TiO_2/AC was higher than for P25, it can be deduced that TiO_2/AC has greater thermodynamic stability than P25. The maximum capacity of adsorption (Q), the adsorption constant (b) and r^2 can be calculated using Langmuir's isotherm (Equation 1):

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

where: C_e = liquid phase concentration of phenol at equilibrium (mg/L),

q_e = equilibrium of solid phase absorbed concentration (mg/g),

b = absorption constant of the Lamgmuir isotherm (L/mg)

Q = maximum surface coverage (monolayer) (mg/g).

The Brunauer, Emmett and Teller (BET) surface area of AC, AC-400 and TiO_2/AC was 1110, 1056 and 441 m^2/g, respectively. The trend in surface area from the BET calculation was similar to the estimated surface area that was calculated from the Q-value of Langmuir's isotherm.

Photocatalytic activity

As shown in Figure 4, the percentages of phenol removed by TiO_2/AC, AC, P25 TiO_2 and synthesized-TiO_2 were 68.03, 57.01, 18.95 and 8.60%, respectively. The initial removal rate of TiO_2/AC was similar to AC, but after 60 min, the

Table 1 Components of the Langmuir isotherm for samples obtained in the study.

Sample	b (L/mg)	Q (mg/g)	Equilibrium time (h)	r^2
AC	34.96×10^{-2}	1.43×10^{5}	3	0.9967
AC calcined at 400°C (AC-400)	11.67×10^{-2}	1.43×10^{5}	1	0.9987
TiO_2/AC	5.00×10^{-2}	5.00×10^{4}	1	0.9935
TiO_2-P25	3.31×10^{-4}	3.14×10^{3}	1	0.9900

TiO_2/AC was still able to remove phenol at a similar degradation rate as that of pure TiO_2. The TiO_2/AC had the highest phenol removal efficiency, with the highest rate constant of 0.1080 h^{-1} (Table 2). However, the removal of phenol by AC may have been due to the adsorption of phenol, unlike for TiO_2/AC, which combined the adsorption of AC and the photoactivity of TiO_2.

Nevertheless, the TiO_2/AC calcined at 300°C (and also without calcinations, but still in the amorphous phase) showed only adsorption activity (Figure 5 and Table 3). The TiO_2/AC

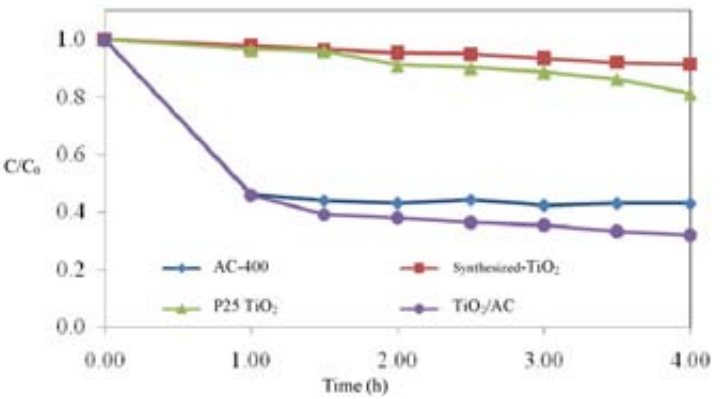

Figure 4 Phenol removal efficiency (measured as the relative concentration of phenol (C/C_0) over time) of TiO_2/AC calcined at 400°C compared with AC, synthesized-TiO_2 and Degussa-P25.

Table 2 Percentage phenol removal and rate constant for phenol removal by various catalysts.

Catalyst	% Removal	R^2	Rate constant (h^{-1})
Synthesized-TiO_2	8.60	0.9876	0.0233
P25 TiO_2	18.95	0.9340	0.0520
AC-400	57.01	-*	-*
TiO_2/AC	68.03	0.9292	0.1080

* No photodegradation occurred.

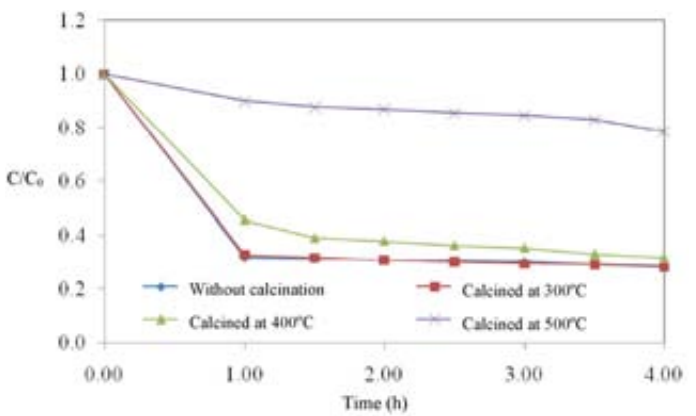

Figure 5 Phenol removal efficiency (measured as the relative concentration of phenol (C/C_0) over time) of TiO_2/AC with various calcination temperatures and without calcination.

Table 3 Percentage phenol removal and rate constant for phenol removal using TiO_2/AC.

Catalyst	% Removal			R^2	Rate constant
	Adsorption	Degradation	Total		(h^{-1})
Without calcination	67.55	4.48	72.03	0.9524	0.0345
Calcined at 300°C	68.36	3.78	72.15	0.9840	0.0507
Calcined at 400°C	54.14	13.88	68.03	0.9292	0.1080
Calcined at 500°C	8.15	10.83	18.98	0.9154	0.0388

calcined at 500°C showed only photodegradation activity, because the activated carbon had been oxidized completely. Accordingly, the TiO_2/AC calcined at 400°C had a greater removal efficiency than the other compounds, because of its adsorption (for the first 60 min) and photocatalytic degradation.

CONCLUSION

TiO_2/AC was prepared using a simple and effective sol-gel method involving a titanium tetraisopropoxide precursor and isopropanol. The XRD diffractograms showed that the TiO_2 undergoes the amorphous-to-anatase phase transformation when there is an increase in the calcination temperature. TiO_2/AC calcined at 400° C performed effectively the synergistic effect of adsorption and photodegradation under UV light, providing 68.03% phenol adsorption, which consisted of 54.14% from adsorption and 13.88% from photocatalytic degradation, with a rate constant of 0.1080 h^{-1}.

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