

Photocatalytic Degradation of Phenol Using TiO₂/Active Carbon

FARAH S. DAABOOL and FALAH H. HUSSEIN*

Chemistry Department, College of Science, Babylon University, Hilla, Iraq

*Corresponding author: E-mail: abohasan_hilla@yahoo.com

Received: 8 July 2015;

Accepted: 15 September 2015;

Published online: 3 November 2015;

AJC-17628

Photocatalytic degradation process was used to remove phenol from aqueous solution using pristine TiO₂ and dipping TiO₂ with activated carbon (AC). The 10 % AC/TiO₂ was prepared by simple evaporation and drying process. Different techniques were used to characterize the prepared materials, such as Raman spectroscopy, scanning electron microscopy and X-ray diffraction. All the characterized methods show the real interaction between activated carbon and TiO₂. The crystal sizes for prepared composite were calculated by using Scherrer equation from XRD data. The morphology of the prepared composite was studied using scanning electronic microscopy (SEM). From SEM image the particle size of the prepared materials was found to be equal 75 nm. The results show that 10 % of activated carbon was succeeding to increase the activity of TiO₂ to 18 % towards photocatalytic degradation of phenol by TiO₂.

Keywords: Water treatment, Phenol, TiO₂, Activated carbon, AC/TiO₂ composite, Date palms.

INTRODUCTION

In recent years, huge efforts has been taken in the development of advanced and more efficient techniques for wastewater treatments, by using classical technologies such as ion-exchange resins and adsorption in dealing with various kinds of compounds. Many challenges were shows limitation in used this techniques for example poor economic feasibility, limited applicability and effectiveness and reduces the abilities to use the same materials to remove this pollutants [1]. Different volatile organic compounds were emission from industrial activities and most of them as phenol are very harmful for human [2]. In addition, phenol is a common reagent in the preparation of a large variety of compounds. The major sources of phenol are: petroleum refineries, petro chemical, steel, synthetic resins, pharmaceutical, paints, plywood and wood processing industries, these are poisonous to aquatic life plants and humans [3].

United State Environmental Protection Agency (USEPA), European Union (EU) and World Health Organization (WHO) have been established for lowering phenol content in the wastewater to less than 0.5 mg/L [4]. The moderate techniques that used for this purpose was photocatalytic degradation by using semiconductors [5]. Titanium dioxide is simplest type of semiconductors, chemically and biologically inert, photoactive and inexpensive [6]. One of the important photocatalysts *i.e.*, TiO₂ is used, especially for the detoxification of water and air. Titanium dioxide is found in three crystallo-

graphic forms *i.e.*, anatase, rutile and brookite. Anatase and rutile forms are semiconductors with a high energy band gap (3.00 eV for rutile and 3.23 eV for anatase) [7]. Low surface area and easy recombination of the electron-hole pair these properties represent the most important reasons that causing limitation and reduction in activity of TiO₂ [8]. Many works were focused on the preparation as well as on the modification of TiO₂ such as doping, metal coating, surface sensitization and support [9]. The high ability of dispersion for TiO₂ in the reaction media and large surface area were favourable for high photocatalytic efficiency [10]. Thus carbon materials appear to play multiple and unique roles in TiO₂ photocatalysis [11-14]. Carbon materials represent by many traditional materials such as activated carbons (AC), graphite (GP), carbon nanofibers (CNF), single-walled carbon nanotubes and multi-walled carbon nanotubes (SWCNT and MWCNT, respectively). Activated carbon (AC) widely used to modify TiO₂ for many reasons such as low coast, easy to prepared, large surface area, high porosity, thermal stability in addition to abilities to modified it in simple conditions [10-31]. Hermann and co-workers [32] reported that the activated carbon succeeded to improve the activity of TiO₂ under UV irradiation when investigated influence of different activated carbons on the photocatalytic degradation of aqueous organic pollutants by UV-irradiated which shows a beneficial effect on the photocatalytic degradation of phenol, 4-chlorophenol and herbicide in dependence of the properties of activated carbon. Velasco *et al.* [33] reported that presence of carbon actually changes the catalytic activity

of TiO_2 which represent the main causes for a synergistic effect on the degradation kinetics. In the present study, activated carbon was prepared from date palm seeds activated by phosphoric acid. The TiO_2/AC composite was prepared by simple evaporation and drying process. The composite was characterized by Raman spectroscopy, X-ray diffraction (XRD) and scanning electron microscopy (SEM).

EXPERIMENTAL

Titanium dioxide was purchased from Degussa, Germany ($\text{TiO}_2\text{-P25}$) which consist of 80 % anatase and 20 % rutile, phosphoric acid within purity 85 % Merck, Germany and phenol within 99.5 % from GCC was used as adsorbate for the study.

Preparation of activated carbon: Khstawy date seeds were used to prepare the activated carbon (AC). The seeds were washed with hot distilled water to remove dust and other impurities, dried at 105 °C. Phosphoric acid (30 %) was added to it during the chemical activation process. The activation was completed by heating at temperature 700 °C for 1 h. After cooling, the activated carbon was washed with distilled water until the pH of the washing solution reached 6-6.5. The product

was dried at 105 °C for 2 h and kept in tightly closed plastic container.

Synthesis of composite: The AC/TiO_2 composite was prepared using a simple evaporation and drying process. That is, commercial titanium dioxide and activated carbon were dispersed into 100 and 20 mL, respectively of distilled water by ultrasonic for 0.5 h. The activated carbon solution was added to the TiO_2 suspension along with sonication. The suspension containing activated carbon and TiO_2 particles was heated to 80 °C to evaporate the water. After the water had evaporated, the composite was dried overnight in an oven at 100 °C. Fig. 1 shows the experimental procedure for preparation of the AC/TiO_2 composite by using simple evaporation and drying process.

Characterization methods: Scanning electron microscopy measurements were carried out on a JEOL JSM-6700F instrument, using a secondary electron detector (SE) at an accelerating voltage of 2.0 kV. Raman spectrum and X-ray diffraction were taken to studies the change in composition of titanium dioxide.

Photocatalytic tests were performed at 25 °C with 1 g TiO_2 and 0.1 g activated carbon under stirring in 200 mL of 60

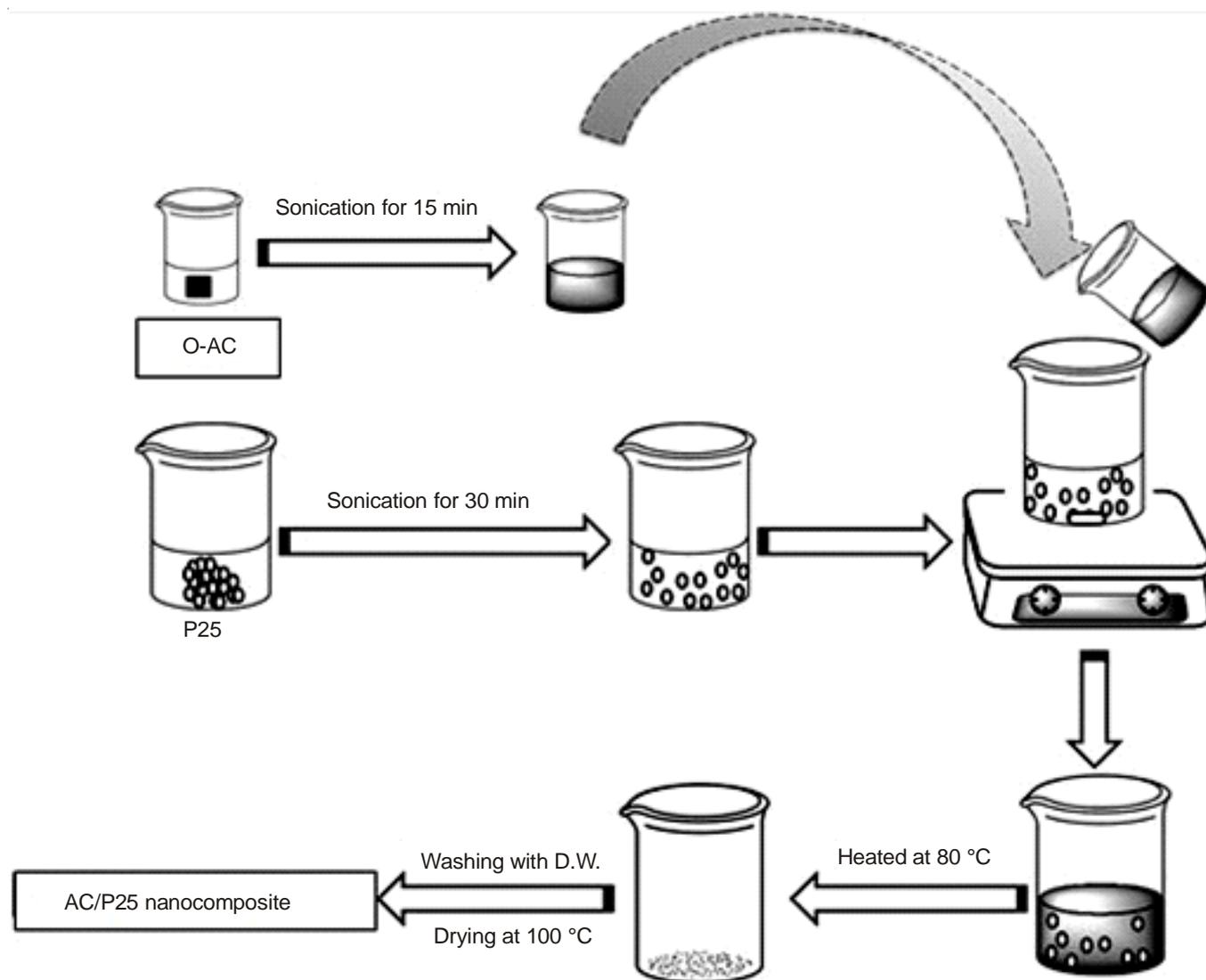


Fig. 1. Schematic diagram of the experimental procedure for the preparation of $\text{AC}/\text{P25}$ nanocomposite by using simple evaporation and drying process

ppm initial concentration of phenol. Samples were maintained in the dark for 1 h to complete adsorption at equilibrium prior UV irradiation and then the suspension was irradiated.

After centrifugation aliquots were analyzed by UV-spectrophotometer Perkin Elmer, Lambda. UV-visible lamp of Metal Halide was used for the photocatalytic tests.

Photocatalytic activity: The photocatalytic activity of AC/TiO₂ composite was determined using phenol decomposition in aqueous solution under an UV lamp (0.7 mW/cm²). The suspensions solutions were prepared by adding 0.175 g of nanocomposite catalysts to 100 mL of 60 ppm of aqueous solution of phenol. Prior to irradiation, the suspensions were stirred in darkness for 0.5 h using a magnetic stirrer to ensure adsorption equilibrium. During adsorption and irradiation, the suspensions were sampled at regular intervals. 3 mL of the reaction mixture was collected and centrifuged for 15 min. The clear solution was carefully removed using a syringe and centrifuged again at the same speed and the same period time. The second centrifuge was found necessary to remove fine particles of the catalyst. After the second centrifuge, the absorbance at the maximum wavelength of 269 nm of the phenol was measured with a UV-visible spectrophotometer.

RESULTS AND DISCUSSION

Characterization of the AC/TiO₂ composite: X-ray diffraction is used to measure of graphitization. Fig. 2 represented X-ray diffraction of the activated carbon. The pattern of the activated carbon shows two peaks at $2\theta = 25^\circ$ and 44° corresponding to the (002) and (100) reflections respectively. Fig. 3 shows the XRD patterns of the P25 compared with the AC/TiO₂ composite. The same peaks in TiO₂ and composite at 25.3° , 37.8° , 48.0° , 53.9° and 62.5° were the diffractions of (101), (004), (200), (211) and (204) planes of anatase, respectively and peaks at 27.4° , 36.1° , 41.2° and 54.3° belonging to the diffraction peaks of (110), (101), (111) and (211) planes of rutile, thus indicating that the P25 and the composite contain a mixed structure of anatase and rutile. When comparing the XRD patterns of the activated carbon and the AC/P25 composites, the characteristic peaks for the activated carbon at the positions of 25° and 44.0° might disappear or become thinner in the XRD pattern of the composites. The reason for this is that these peaks in the composites overlapped with the main peak of the anatase phase of the P25 at 25.3° . The average crystallite

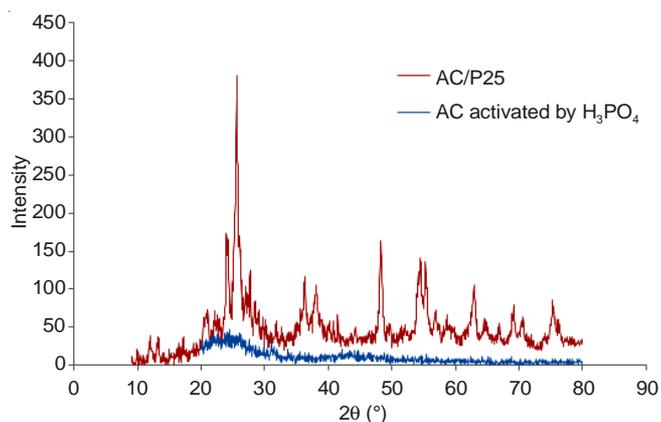


Fig. 2. XRD for activated carbon and AC/P25

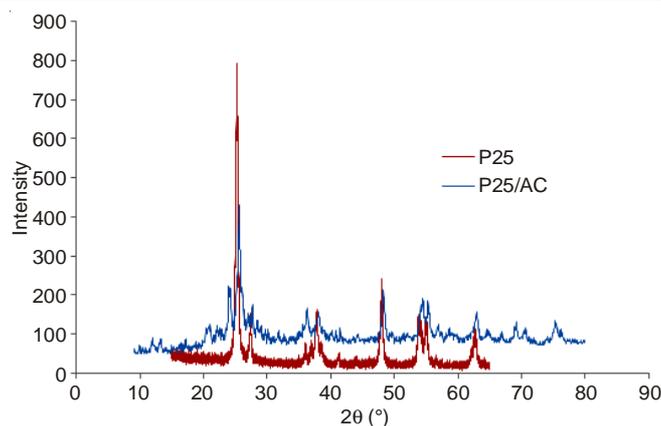


Fig. 3. X-ray diffraction for the P25 and AC/P25 composites

sizes of the TiO₂ and AC/TiO₂ composite were calculated by Debye-Scherrer formula. According to the calculation, the average crystallite sizes of the TiO₂ and composite AC/TiO₂ were 23 and 24.026 nm respectively and the average particle sizes of the composite AC/TiO₂ was 100 nm.

The morphology of the AC/P25 composite was measured by SEM, as shown in Fig. 4. The SEM images indicate that the AC/P25 and the activated carbon is homogeneously distributed throughout the P25 matrix with an apparent agglomeration of the P25 particles.

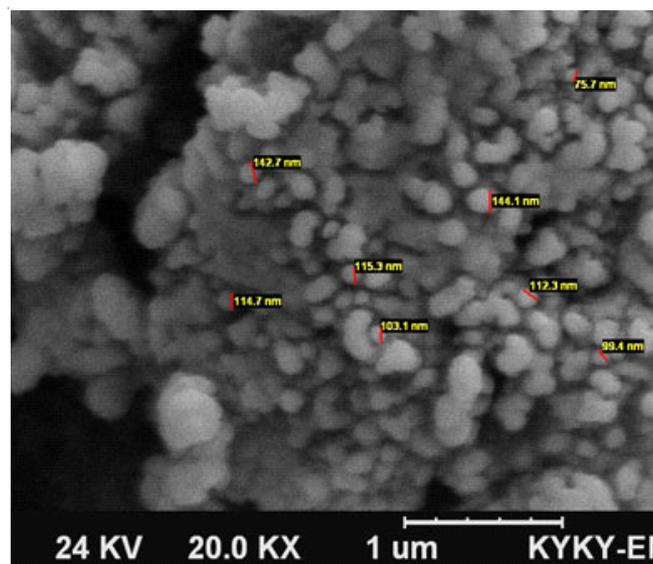


Fig. 4. SEM images of the AC/P25 composite

Photocatalytic activity of the AC/P25 composite: The UV light irradiation using a source for the photocatalytic removal of the phenol from aqueous solution. Fig. 5 indicates the changes in the relative concentration of the phenol in aqueous solution on UV irradiation times for the AC/P25 composite. The photocatalytic degradation of the phenol in aqueous suspension of the composite catalysts containing TiO₂ and AC/TiO₂ follows apparent first order kinetics. The kinetic plot is shown in Fig. 6.

Conclusion

The AC/P25 composite photocatalysts was prepared using simple evaporation and drying process. Composite characteri-

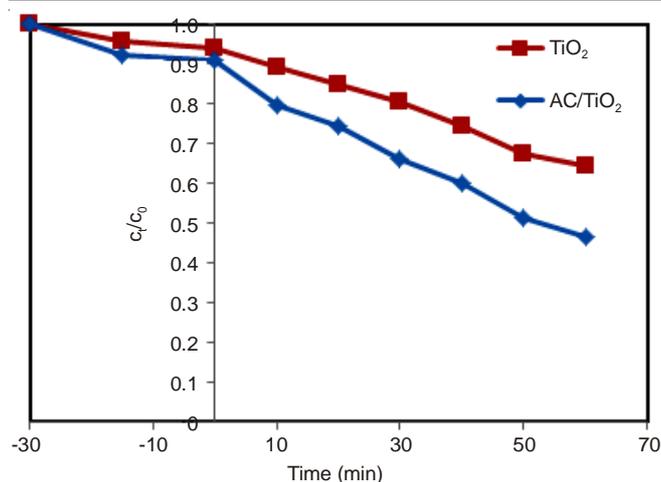
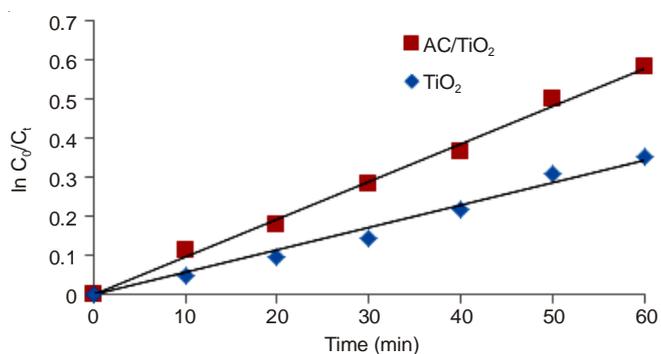


Fig. 5. Adsorption and irradiation of the AC/P25 composite

Fig. 6. Changes of $\ln C_0/C_t$ according to irradiation times at TiO₂ and the prepared AC/TiO₂ composite

zation indicates a relatively heterogeneous activated carbon dispersion in the P25 matrix. According to the results it could be suggested that all of the samples had a good photocatalytic activity for the phenol degradation. The rate constant for the photodegradation of phenol by the AC/TiO₂ increased by 1.7 times in the presence of the TiO₂. The enhanced photocatalytic efficiency of composite suggests that the activated carbon act as an adsorbent, dispersing agent and electron reservoir to trap electrons from the P25 particles due to UV irradiation and enhance hindering the electron-hole pair recombination.

REFERENCES

1. L.F. Velasco, J.B. Parra and C.O. Ania, *Adsorpt. Sci. Technol.*, **28**, 727 (2010).
2. O. Legrini, E. Oliveros and A.M. Braun, *Chem. Rev.*, **93**, 671 (1993).

3. N. Roostaei and F. Tezel, *J. Environ. Manage.*, **70**, 157 (2004).
4. G. Nirja, P. Prachi and P. Ajai, *Res. J. Chem. Sci.*, **2**, 6 (2012).
5. M.R. Hoffmann, T.S. Martin, W. Choi and D.W. Bahnemann, *Chem. Rev.*, **95**, 69 (1995).
6. C. Ngamsopasiriskun, S. Charnsethikul, S. Thachepan and A. Songsasen *Kasetsart J. (Nat. Sci.)*, **44**, 1176 (2010).
7. J. Yu, Q. Xiang and M. Zhou, *Appl. Catal. B*, **90**, 595 (2009).
8. L.M. Ahmed, I. Ivanova, F.H. Hussein and D.W. Bahnemann, *Int. J. Photoenergy*, Article ID 503516 (2014).
9. O. Carp, C.L. Huisman and A. Reller, *Prog. Solid State Chem.*, **32**, 33 (2004); J. Grzechulska and A.W. Morawski, *Appl. Catal. B*, **36**, 45 (2002).
10. B. Tryba, A.W. Morawski and M. Inagaki, *Appl. Catal. B*, **41**, 427 (2003).
11. H. Park, E. Bae, J.-J. Lee, J. Park and W. Choi, *J. Phys. Chem. B*, **110**, 8740 (2006).
12. H. Park, W. Choi and W.J. Phys. Chem. Br., **108**, 4086 (2004).
13. H. Park, W. Choi and M.R. Hoffmann, *J. Mater. Chem.*, **18**, 2379 (2008).
14. M.-J. Jung, E. Jeong, J.-S. Jang and Y.-S. Lee, *Carbon Lett.*, **11**, 28 (2010).
15. A. García and J. Matos, *The Open Mater. Sci. J.*, **4**, 2 (2010).
16. D.-N. Li and X.-J. Ma, *Wood Res.*, **59**, 77 (2014).
17. S.T. Hayle, *Am. J. Nanosci. Nanotechnol.*, **2**, 1 (2014).
18. Z. Zainal, C.S. Keng and A.H. Abdullah, *The Malaysian J. Anal. Sci.*, **12**, 111 (2008).
19. J. Matos, A. Garcia, J.-M. Chovelon and C. Ferronato, *The Open Mater. Sci. J.*, **4**, 23 (2010).
20. K. Zhang, Z. Meng and W.C. Oh, *Chin. J. Catal.*, **31**, 751 (2010).
21. W. Zhou, P. Zhang and W. Liu, *Int. J. Photoenergy*, **3**, 7 (2012).
22. N. Muchanyereyi, L. Chiripayi, D. Shasha and M. Mupa, *Maize Tassels*, **3**, 649 (2013).
23. G.G. Stavropoulos, P. Samaras and G.P. Sakellariopoulos, *J. Hazard. Mater.*, **151**, 414 (2008).
24. M. Ghauri, M. Tahir, T. Abbas and M. Khurram, *Sci. Int. (Lahore)*, **24**, 411 (2012).
25. J.R. Baseri, P.N. Palanisamy and P. Sivakumar, *Adv. Appl. Sci. Res.*, **3**, 377 (2012).
26. P.K. Chayande, S.P. Singh and M.K.N. Yenkie, *Chem. Sci. Trans.*, **2**, 835 (2013).
27. H. Nouri and A. Ouederni, *J. Chem. Eng. Process Technol.*, **4**, 153 (2013).
28. I.A. Bello, M.A. Oladipo, A.A. Giwa and D.O. Adeoye, *Int. J. Basic Appl. Sci.*, **2**, 79 (2013).
29. C.R. Girish and M.V. Ramachandra, *Int. Res. J. Environ. Sci.*, **2**, 96 (2013).
30. M.Z. Alam, S.A. Muyibi, M.F. Mansor and R. Wahid, *J. Environ. Sci. (China)*, **19**, 103 (2007).
31. V. Srihari, *Appl. Ecol. Environ. Res.*, **7**, 13 (2009).
32. J. Matos, J. Laine and J.M. Herrmann, *J. Mol. Catal.*, **200**, 10 (2001).
33. L.F. Velasco, J.B. Parra and C.O. Ania, *Appl. Surf. Sci.*, **256**, 5254 (2010).