

Characterization of TiO₂-activated carbon onto adsorption and photocatalytic properties and its application

Mark CHOBCHUN¹, Pasakorn JUTAKRIDSADA¹, Puttiporn THIAMINSANGWON², Pornnapa KASEMSIRI¹, Khanita KAMWILAISAK^{1,3*}, and Prinya CHINDAPRASIRT³

¹ Department of Chemical Engineering, Faculty of Engineering, Khon Kaen University, Khon Kaen, 40002, Thailand

² Department of Chemical and Material Engineering, Faculty of Engineering, Rajamangala University of Technology Thanyaburi, Pathum Thani 12110, Thailand

³ SIRDC-Sustainable Infrastructure Research and Development, Department of Civil Engineering, Faculty of Engineering, Khon Kaen University, Khon Kaen, 40002, Thailand

*Corresponding author e-mail: khanita@kku.ac.th

Received date:

7 May 2020

Revised date

21 September 2020

Accepted date:

22 September 2020

Keywords:

Titanium dioxide;
Activated carbon;
Nanocomposite;
Photocatalyst;
Synergic effect

Abstract

This study investigates the characterization of TiO₂ in conjunction with activated carbon (AC) on its adsorption and photocatalytic properties. TiO₂ in the absence and presence of AC were prepared by the sol-gel method. TiCl₄ was used as a precursor to reduce using acidic solution during preparation process. The effects of the amount of AC on the characteristics of composites were investigated. TGA technique was used to evaluate the amount of TiO₂ and AC in TiO₂/AC composite. The adsorption properties of TiO₂/AC were characterized using XRD, TEM, N₂ adsorption/desorption, FTIR and UV-Vis diffuse reflectance spectroscopy techniques. The photocatalytic activities of the composites were investigated by measuring the removal of acid dye. Results showed that the specific surface area of TiO₂/AC increased with increasing mass fraction of AC, while the energy band gap was reduced. It was clearly shown that TiO₂ in the presence of AC produced a synergistic effect of the composite and led to an increase in photocatalytic performance. Also, the reuse of TiO₂ with 20% AC nanocomposites for dye removal showed a high reuse efficiency above 90% in photocatalytic dye degradation.

1. Introduction

Recently, TiO₂ photocatalysis has been widely used in the environmental purification due to its being an inexpensive, strongly oxidizing and highly stable chemical [1]. It is also capable of the photo-oxidative destruction of most organics pollutants [1-5] to CO₂ and H₂O. However, the drawback of this catalyst is the difficulty in the separation and retrieval after the use in photocatalytic systems [6]. Although such problem has been solved by immobilizing the photo-catalyst on porous supports, such as porous alumina ceramic [7], carbon foam and cordierite foam [8], the advantage of recombination of materials is not adequately displayed on the photocatalytic degradation of pollutants [9].

It has been reported that TiO₂ when loaded with activated carbon (AC), can enhance the photocatalytic activity of TiO₂. This is because AC increases the adsorption of organic pollutant on TiO₂/AC, leading to a high organic concentration around TiO₂. While AC has no photocatalytic activity, the system exhibits synergism in which the adsorbed organic molecules on AC are transferred to TiO₂ where they are degraded [4,10-12]. Furthermore, the synergistic effect of adsorption by AC and TiO₂ particulates can have beneficial consequences in the photodegradation of a dye in aqueous media [13].

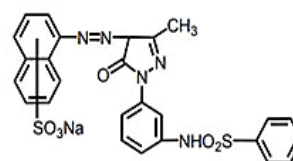
Due to the desirable properties described above, the TiO₂ with AC composites prepared by the sol-gel method to enhance the catalytic

properties was proposed. The effects of AC content on the physical and chemical properties of TiO₂/AC composites were investigated. The key objective was to evaluate the efficiency of dye degradation using TiO₂/AC in various experiment configurations. Besides, the reuse of TiO₂/AC nanocomposite for dye removal was determined.

2. Materials and method

2.1 Materials

Titanium tetrachloride (TiCl₄) from Merck Company (Germany); titanium dioxide (TiO₂) (COM-grade) Degussa P25 from Sigma-Aldrich Co. Ltd (Thailand); ammonium hydroxide (NH₄OH) from Ajax Finechem Company (Australia); activated charcoal (AR-grade) from Rankem (India) and yellow acid dyes (COM-grade) from Phua Kiam Seen Co. Ltd. were used in this work. For water, deionized water was used in all experiment.



Scheme 1. Yellow acid dye structure

2.2 TiO₂/AC composite catalyst preparation

TiO₂/AC composite was prepared by the sol-gel technique. Ten millilitres of titanium tetrachloride (TiCl₄) was slowly dropped into forty millilitres of deionized water at 4±1°C with continuous stirring. Titanium hydroxide (Ti(OH)₄) solution or sol was obtained. Various amounts of activated charcoal (0, 5, 10, 20, 25 and 30 wt% of AC) were put into the sol. A droplet of 30% v/v of ammonium hydroxide (NH₄OH) was continuously added until the gel was formed. The gel was then washed with distilled water and dried in the oven at 100°C for 4 h. The dried gel of TiO₂ and TiO₂/AC were heated in a nitrogen atmosphere to 500°C at heating rate of 10°C·min⁻¹. The sample was dried for further 4 h at 500°C. At 500°C, the anatase phase of TiO₂ can be formed. However, the slight decompose of AC was observed at 500°C about 5%. This value was in acceptable for using AC support for catalyst. The TiO₂/AC samples with various amounts of AC (0, 5, 10, 20, 25 and 30 wt%) were named TiO₂, TiO₂/5AC, TiO₂/10AC, TiO₂/20AC, TiO₂/25AC, and TiO₂/30AC.

2.3 Characterization

The thermal decomposition of the composite was determined by thermalgravimetric analysis (TGA) (TGA 50, Shimadzu, Japan). A 200 mg sample of prepared composites was heated in a range of 30-750°C with a heating rate of 10°C·min⁻¹ under a nitrogen flow. Crystalline structure and morphology of TiO₂/AC composite were examined by X-ray diffraction powder (a Bruker D8-Advance), and Transmission Electron Microscopy (TEM, model Tecnai™ G² 20, FBI, USA).

The specific surface area and pore volume of the composite were determined by Nitrogen adsorption-desorption isotherms measured by gas sorption analyzer (micromeritics ASAP 2010) [15]. Before the adsorption measurement, the samples were degassed at 110°C under vacuum (< 50 mmHg) for 12 h. The nitrogen adsorption/desorption isotherms were recorded at the liquid nitrogen temperature. The specific surface area, *S*_{BET}, was calculated using the Brunauer-Emmet-Teller (BET) method. The micropore volume, *V*_{mic}, was calculated using the Dubinin-Radushkevich (DR) equation. The total pore volume, *V*_T, was found from the amount of N₂ adsorbed at the relative pressure of 0.99. The mesopore and macropore volume, *V*_{meso+mac}, was obtained by subtraction of the micropore volume from the total pore volume. The average pore diameter, *D*_p, was calculated from $(4 \times V_T) / S_{BET}$.

The composites were examined by FTIR analysis on a VERTEX 70 spectrometer over the wave number of 3800-400 cm⁻¹ using KBr pellets for sample preparation. The UV-Vis diffuse reflectance spectra were recorded with a UV-3600 SHIMADZU (Japan) spectrometer in the wavelength of 800-200 nm. The absorption edge and bandgap energies of the as-prepared samples were determined by UV-Vis diffuse reflectance spectroscopy (Analytik Jena GmbH, Germany).

2.4 Photocatalytic activity test

Catalytic activity tests were conducted in a batch reactor (1000 mL) with magnetic stirrer running at 200 rpm. The 500 mL reaction mixture contained 1.0 g·L⁻¹ of TiO₂/AC with 70 mg·L⁻¹ of dye concentration.

The reaction mixture was kept in dark condition to reach an adsorption equilibrium for 15 min. The photocatalytic reaction was then carried out with 365 nm UV-light source (Haining Guanyi Electrical Co., Ltd). The sample was kept in the reactor for 0, 5, 10, 15, 30, 45, 60, 90, 120, 150 and 180 min. The concentration of dye solution was measured by UV-Vis Spectrophotometer at 396 nm. The percentage of dye removal was calculated by:

$$\%Dye\ removal = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (1)$$

where *C*₀ and *C*_{*t*} are acid dye concentrations (mg·L⁻¹) at time 0 and time *t*, respectively.

Langmuir-Hinshelwood model has been used to evaluate the kinetic order of dye photodegradation. This model could be modified to be a pseudo-first order rate equation that apparent rate constants (*k*_{app}) of the samples are calculated as follows [16]:

$$\ln \frac{C_t}{C_0} = k_{app} t \quad (2)$$

where *t* is the irradiation time.

3. Result and discussions

3.1 TGA analysis

TGA technique was used to evaluate the amount of TiO₂ and AC in TiO₂/AC composite. The results of TGA, as shown in Figure 1 showed that the AC thermally decomposed under N₂ condition from 520°C to 660°C. The weight loss of AC was approximately 99% at 660°C. On the other hand, TiO₂ was more thermal stable with a small weight loss of 2.06% from the start to 700°C. Thus, the weight fraction of TiO₂ to AC ratio was calculated. Figure 1 shows the weight fraction of TiO₂/AC composite. The ratios of TiO₂ to AC of TiO₂/5AC, TiO₂/10AC, TiO₂/20AC, TiO₂/25AC and TiO₂/30AC samples were 85:15, 83:17, 67:43, 18:82 and 15:85, respectively. The weight fraction of TiO₂ to AC was not the same as that of the initial preparation ratios due to the loss of Ti(OH)₄ during the preparation process.

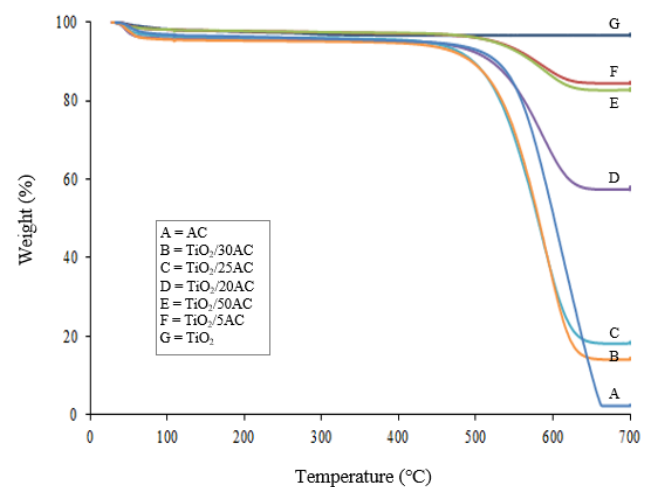


Figure 1. TGA of activated carbon (AC), Titanium dioxide (TiO₂), and TiO₂/AC composites.

3.2 XRD analysis

XRD patterns of AC, TiO₂ and TiO₂/AC are shown in Figure 2. TiO₂ and TiO₂/AC composites showed peaks of a nanocrystalline product of anatase (a form of TiO₂) as the only phase present. The highest peak was found at 25.29° as (101) plane. This was due to the heat treatment at 500°C, which is known to produce high anatase content [17]. Calcination at 500°C was used in this work because anatase has a better photocatalytic activity due to the higher electron-hole pair lifetime compared to rutile [18]. However, the sample TiO₂/25AC and TiO₂/20AC showed the presence of rutile peak at about 27°, it may be the presence of AC which could effect during phase transformation [19]. For AC sample, there was no peak in the XRD pattern. For TiO₂/AC composites, the peak intensity gradually decreased with an increasing amount of AC. The crystalline sizes of synthesized samples were in the range of 5-10 nm (supplementary data Table S.1) which was obtained from Scherrer's equation [20, 21].

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (3)$$

where λ (wavelength of X-Ray) = 0.15418 nm, β = full width and half maxima, θ = Bragg's angle ($2\theta = 25.15^\circ$). D = Crystallite size, K = Scherrer constant (0.089), and B = the line width at half-maximum height, after subtraction of equipment broadening.

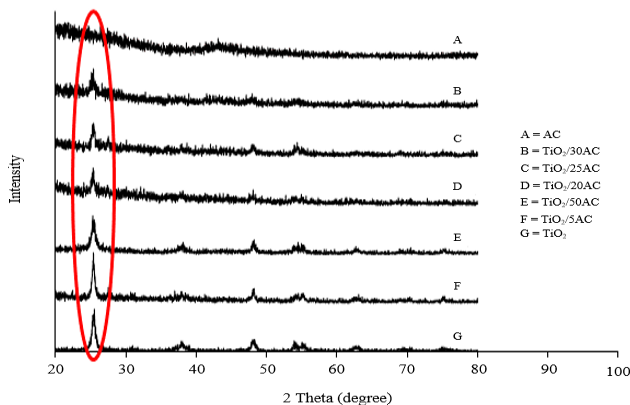


Figure 2. XRD pattern of activated carbon (AC), Titanium dioxide (TiO₂), and TiO₂/AC composites.

3.3 TEM analysis

Figure 3 shows a typical TEM image of TiO₂, AC and TiO₂AC

samples. The TiO₂ nanocrystals (Figure 3(a)) were tetragonal in shape, and the particle sizes were 10-15 nm in diameter, which are the characteristics of anatase structure [22]. Furthermore, from Figure 3 (b-d), all TiO₂/AC composites showed similar morphology to that of TiO₂ due to the same preparation conditions. The particle sizes obtained from TEM. were similar to those obtained from XRD.

3.4 BET analysis

Figure 4 shows the results of N₂ adsorption-desorption isotherms. The AC isotherm was the typical type I isotherm based on IUPAC (International Union of Pure and Applied Chemistry) classification and corresponded to unimolecular adsorption [23]. The isotherms rose sharply at the beginning of adsorption due to the micropore filling effect. After that, the adsorption of N₂ became constant. This result indicated the microporosity of the AC sample. The TiO₂ and TiO₂/AC isotherms are the typical type IV isotherm mostly found in mesoporosity materials of 2-50 nm in diameter [24]

However, the ratio of TiO₂ to AC had a considerable influence on the type of adsorption isotherm. The increased amount of AC tended to change the type IV isotherm to the typical type I isotherm. Table 1 gives a summary of the results of BET surface area (m²·g⁻¹), total pore volume (cm³·g⁻¹) and average pore diameter (Å) AC. The specific surface area, total pore volume and average pore diameter of TiO₂ were 56.09 m²·g⁻¹, 0.12 cm³·g⁻¹ and 85.26 Å, respectively and those of AC were 925.12 m²·g⁻¹, 0.61 cm³·g⁻¹ and 26.24 Å, respectively. The BET surface area and total pore volume increased significantly with an increasing amount of AC while the average pore diameter decreased sharply. However, it can be noticed that the average pore diameter of TiO₂/30AC was similar to AC, while the specific surface area of TiO₂/AC composite was related to the ratio of TiO₂ to AC.

The calculated specific surface area can be obtained from mass fraction and measured specific surface area of TiO₂ and AC from the following equation.

$$\text{Calculated specific surface area} = S_{BET,TiO_2}V_{TiO_2} + S_{BET,AC}V_{AC} \quad (4)$$

where S_{BET,TiO_2} and $S_{BET,AC}$ are specific surface areas of TiO₂ and AC measured from Nitrogen adsorption-desorption, and V_{TiO_2} and V_{AC} are mass fractions of TiO₂ and AC obtained from TGA analysis.

The calculated specific surface area of TiO₂/AC is also shown in Table 1. It can also be observed that the calculated specific surface area of TiO₂/AC was similar to the BET specific surface area due to the excellent distribution of TiO₂ in AC.

Table 1. Surface area, pore and energy band gap of TiO₂ (P25) TiO₂, AC and TiO₂/AC composite.

Materials	BET surface area (m ² ·g ⁻¹)	Calculated surface area (m ² ·g ⁻¹)	Total pore volume (cm ³ ·g ⁻¹)	Average pore diameter (Å)	Energy Band gap, Eg (eV)
TiO ₂ (P25)	-	-	-	-	2.96
TiO ₂	56.09	56.09	0.12	85.26	2.99
TiO ₂ /5AC	151.02	147.18	0.24	64.36	2.27
TiO ₂ /10AC	265.40	203.83	0.29	43.81	2.15
TiO ₂ /20AC	475.69	421.08	0.33	27.89	1.80
TiO ₂ /25AC	703.06	760.00	0.56	30.71	1.41
TiO ₂ /30AC	784.13	803.46	0.53	26.94	1.13
AC	925.12	925.12	0.61	26.23	1.03

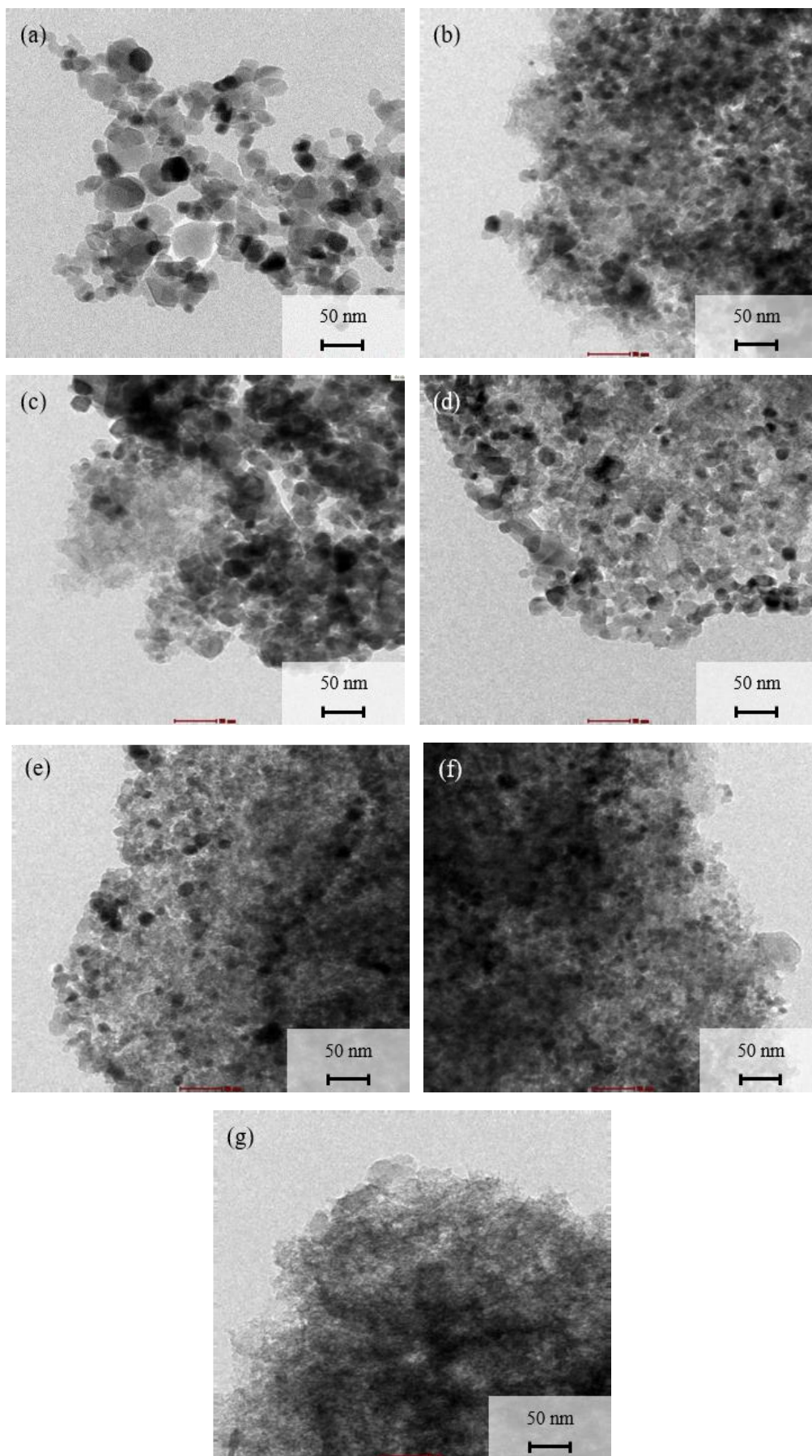


Figure 3. TEM image of (a) TiO_2 , (b) $TiO_2/5AC$, (c) $TiO_2/10AC$ (d), $TiO_2/20AC$ (e), $TiO_2/25AC$ (f), $TiO_2/30AC$, and (g) AC.

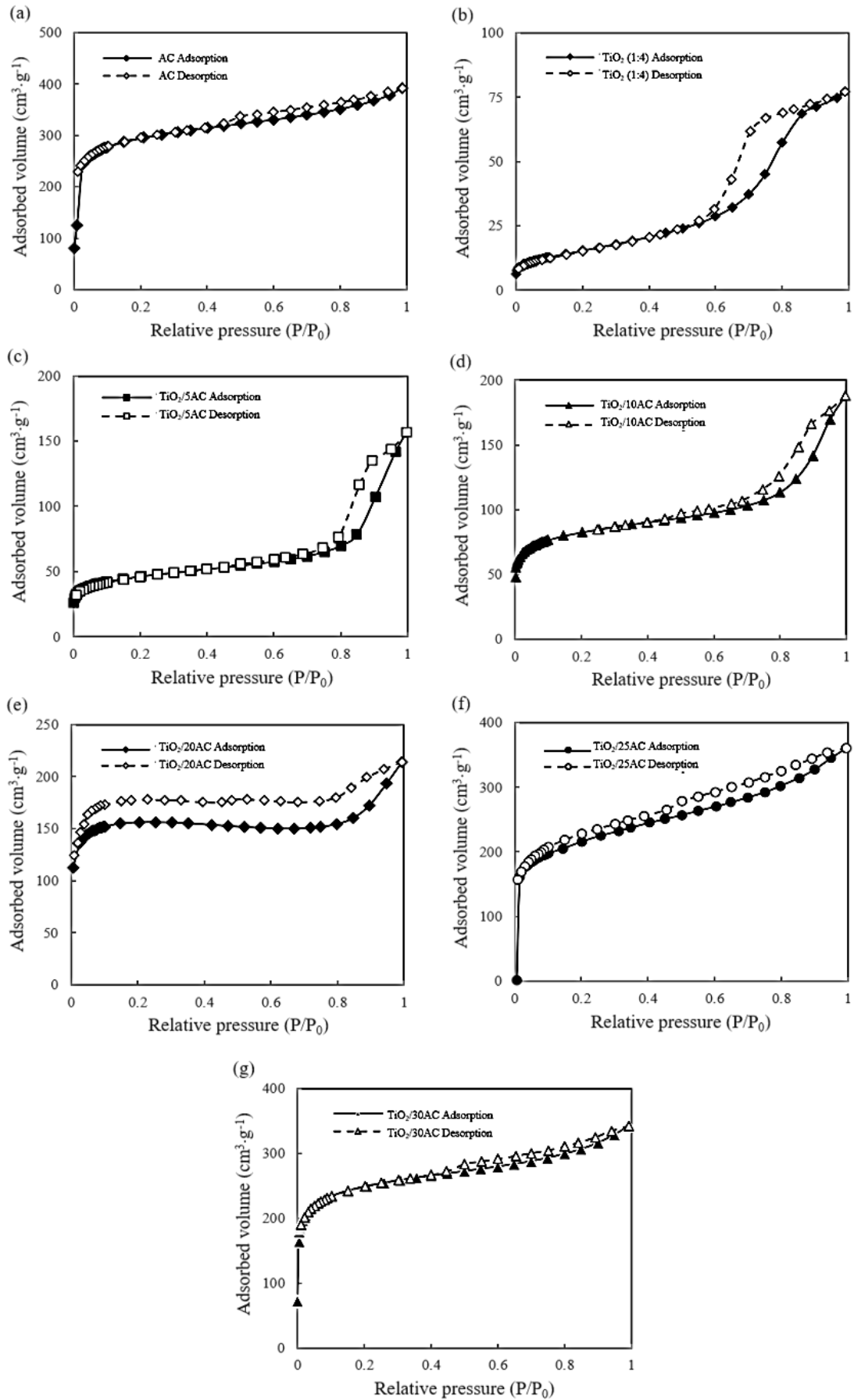


Figure 4. Adsorption/desorption isotherms of N_2 at 77 K of (a) AC, (b) TiO_2 , (c) $TiO_2/5AC$, (d) $TiO_2/10AC$, (e) $TiO_2/20AC$, (f) $TiO_2/25AC$, and (g) $TiO_2/30AC$.

3.5 FTIR analysis

Figure 5 shows FTIR spectra of TiO₂, AC and TiO₂/AC. The prominent absorption peaks were at 2632, 2378, 2111, 1994, 1885, 1031 and 667 cm⁻¹. The band at 2292 cm⁻¹ was assigned to -C≡C- alkynes stretching with and the band at 1250 cm⁻¹ to aliphatic C-N amines stretching. Furthermore, all TiO₂/AC showed peaks at 1046 cm⁻¹ corresponding to the Ti-O-C vibration band. The peak intensity increased with the increase in carbon contents. The result was similar to Liu *et al.* [10] and Perrin *et al.* [25] who reported that the electron affinity of C and Ti-O illustrated peak intensity in the range of 1038-1060 cm⁻¹. This was the evidence of carbon incorporating into the framework of titanium dioxide.

3.6 UV-vis-DRS analysis

Figure 6 shows the UV-Vis diffuse reflectance spectra of the TiO₂, AC, and TiO₂/AC composite. The TiO₂ (Degussa, P25), TiO₂, TiO₂/5AC, TiO₂/10AC and TiO₂/20AC spectra showed a characteristic absorbance around 320-420 nm indicating the existence of highly crystallized TiO₂. For the higher AC contents TiO₂/25AC, TiO₂/30AC

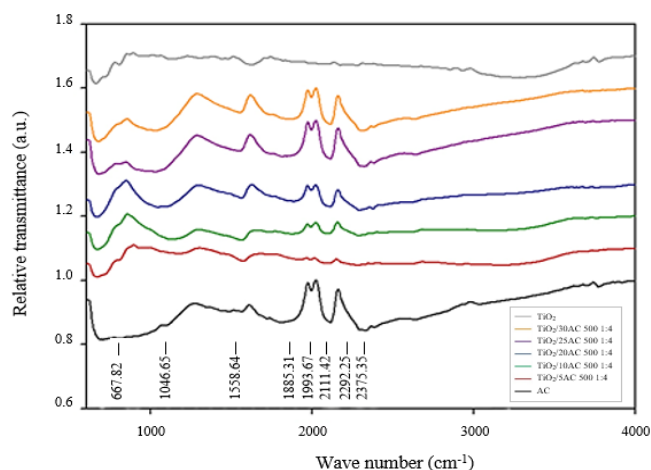


Figure 5. FTIR spectra of TiO₂, TiO₂/5AC, TiO₂/10AC, TiO₂/20AC, TiO₂/25AC, TiO₂/30AC and AC.

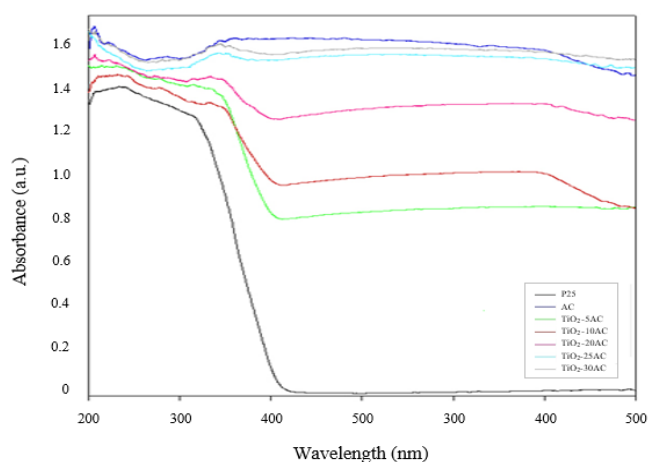


Figure 6. UV-Vis spectra of TiO₂, TiO₂/5AC, TiO₂/10AC, TiO₂/20AC, TiO₂/25AC, TiO₂/30AC and AC.

composites and AC, the spectra absorbance were relatively flat around 320-700 nm. This could be the effect of carbon molecules which would absorb in both UV and visible lights. An energy band gaps of the TiO₂ AC and TiO₂/AC nanocomposite were determined by graph plots of the Kubelka-Munk remission function for each nanocomposite (Figure S.1-S7.). The energy band gap is presented in Table 1. It can be seen that EG of TiO₂ prepared with the sol-gel technique was about 2.96 eV while Eg of TiO₂ (P25) was 2.99 eV. The bandgap of TiO₂/5AC, TiO₂/10AC, TiO₂/20AC, TiO₂/25AC TiO₂/30AC nanocomposites and AC were determined as 2.27, 2.15, 1.80, 1.41 1.13 and 1.03 eV, respectively. The reducing of bandgap could be attributed to the slight conjugation effect between Ti-O and carbon nanoparticle molecules (C). It can be noticed here that AC could enhance solar photocatalytic activity [26].

3.7 Dye removal

Figure 7 presents the percentage of dye removal by AC, TiO₂/5AC and TiO₂/10AC under UV-irradiation and dark condition. The percentage of dye removal was significantly increased with increasing time. The dye removal by AC reached 75% at 10 min and then remained constant, while those of TiO₂/5AC and TiO₂/10AC under dark condition were 52 and 72% at 180 min, respectively. The dye reduction by TiO₂/5AC and TiO₂/10AC in the presence of UV light was improved by 10 and 20% due to the photocatalytic reaction. TiO₂ in the presence of AC removed dye by adsorption up to approximately 30 min, and then the photocatalytic reaction phenomena occurred. Comparing the activity of AC, TiO₂, commercial TiO₂ (P25) and TiO₂/10AC, the fastest dye treatment was AC with 75% removal. It was known the physical treatment was fast and straightforward; however, the adsorption capacity depended on the quantity of adsorbent.

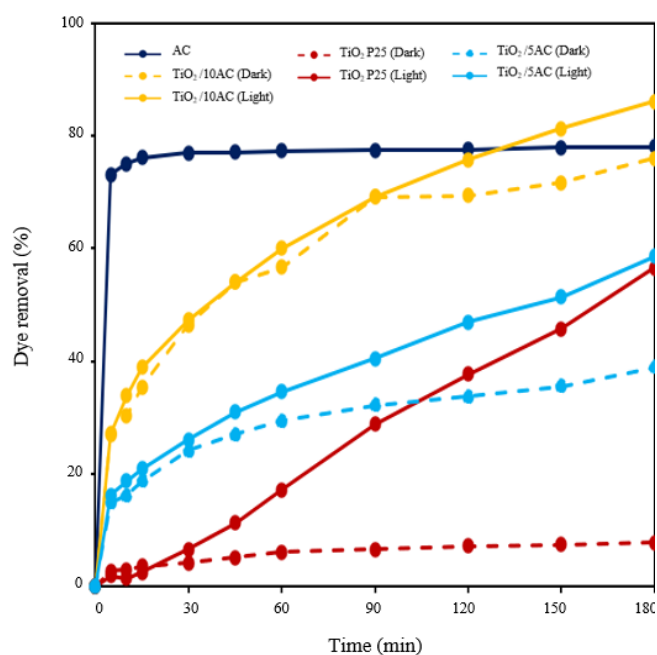
In case of TiO₂, the photocatalytic removal activity of TiO₂ (P25) was 57%, and that of as-prepared TiO₂ was 26% at reaction time 180 min. The better removal activity of TiO₂ P25 was primarily due to its smaller particle size than that of as-prepared TiO₂. The maximum dye removal of 88% was obtained with TiO₂/10AC under UV light. It was seen that TiO₂ in the presence of AC and UV light could significantly improve the dye removal. This confirmed the synergistic effect of TiO₂ and AC [27,28]. Furthermore, based on the literature, the physical mixture of the prepared TiO₂ and AC has been reported lower dye removal efficiency than that of the deposited TiO₂ on AC. This is because, in the physical mixture system, AC adsorbs dye and then desorbed, the photocatalytic reaction by TiO₂ begun to degrade dye from the bulk solution after absorption equilibrium, while in the deposited TiO₂/AC, the dye can be absorbed by AC and then directly reacted by TiO₂. This could be the benefit of the deposited TiO₂/AC in much faster photocatalytic rate and better performance [29].

3.8 Kinetic analysis of dye degradation

Based on equation (2), the straight-line relationship of $\ln \frac{C_t}{C_0}$ against reaction time was obtained, as shown in Figure S10 (supplement data). The apparent rate constants (k_{app}) and half-life time of each catalyst with an initial dye concentration of 75 mg·L⁻¹ was calculated from the slope of the plot. The kinetic values are presented in Table 2.

Table 2. Kinetic values of TiO₂ (P25) TiO₂, AC and TiO₂/AC composite for dye removal.

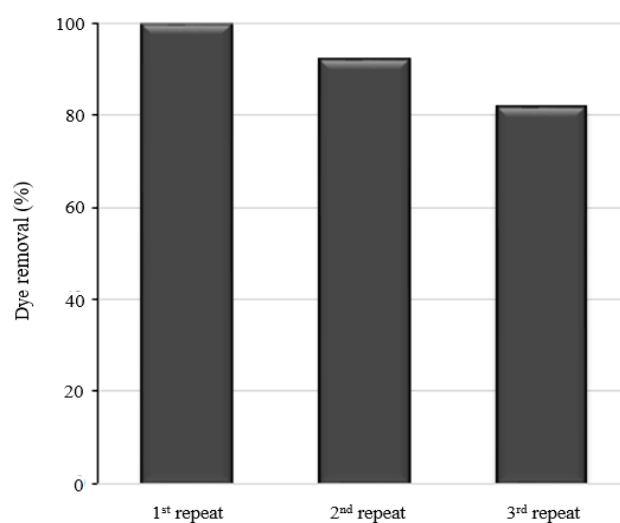
Sample	k_{app} (min ⁻¹)	$t_{1/2}$ (min)	Regression coefficient (R ²)
AC	0.0311	22.29	0.9789
TiO ₂ (P25)	0.0045	154.03	0.9838
TiO ₂	0.0015	462.10	0.9848
TiO ₂ /5AC	0.0041	169.06	0.9595
TiO ₂ /10AC	0.0096	72.20	0.9727
TiO ₂ /20AC	0.0889	7.80	0.9515
TiO ₂ /25AC	0.224	3.09	0.9525
TiO ₂ /30AC	0.2352	2.95	0.7987

**Figure 7.** Dye removal of AC, TiO₂ P25, TiO₂/5AC and TiO₂/10AC with optimal conditions (acid dye concentration 75 mg·L⁻¹ and catalytic loading 1.0 g·L⁻¹).

The R² of this was in the range of 0.7987-0.9848. The pseudo-first-order kinetics can be used to recognize the adsorption and photo-oxidation mechanisms taking place in the reactor. In case of AC TiO₂ P25 and TiO₂, k_{app} of AC is higher than that of TiO₂ P25 and TiO₂. The k_{app} of TiO₂ with various amounts of AC were significant increased with an increase of AC loading, while the half-life times were reduced. This is due to when the rate constant is increased, which lead to reduction of the reaction time. As mentioned in section 3.7, the adsorption and photocatalytic reaction are continuously reacted by the deposited TiO₂/AC, resulting in high k_{app} with low half life time. This result supported the synergistic effect phenomena of TiO₂ and AC. Similar results have been reported [16,30].

3.9 Reuse

The reuse of photocatalyst is a significant factor for its practical application in wastewater treatment. The stability of photocatalyst was investigated through recycling of the TiO₂/20AC, which possesses

**Figure 8.** Reusability of TiO₂/20AC in dye removal under UV-light with optimal conditions (acid dye concentration 75 mg·L⁻¹ reaction time 180 min and catalytic loading 5.0 g·L⁻¹).

optimal condition in this study. Figure 8 shows the dye removal efficiency with the number of recycling. The removal efficiency was slightly decreased with the number of recycling. At the second cycles, 92.05% of the initial dye was removed after the photocatalytic reaction of 180 min and dropped to 81.76% in the third cycle. The small reduction after each recycle indicates that the TiO₂/20AC is a relatively stable photocatalyst for the photocatalytic dye removal and could be developed into a commercial scale. In case of AC and TiO₂, the dye removal by AC reached 75% at 10 min while photocatalytic removal activity of TiO₂ (P25) was 57%, and that of as-prepared TiO₂ was 26%. In the case of AC, it may be used to remove the dye in only one cycle. For bare TiO₂, there were low dye removal efficiency compare to TiO₂/AC composite.

4. Conclusion

In the present study, photocatalyst TiO₂ with various amounts of AC composites (TiO₂/AC) were synthesized through the sol-gel method. TiCl₄ was used as a precursor to reduce using acidic solution during preparation process. Various amounts of AC were introduced as an assistant for a photocatalyst. The catalyst's characterization

showed an even distribution of TiO₂ over the AC surface. The specific surface area of TiO₂ with AC was increased with increasing of mass fraction of AC, while the energy band gap was reduced. The photo-reaction was more effective in the presence of AC than those of TiO₂ and AC alone. The efficiency of the TiO₂/10AC was optimal with 88% dye removal capacity compared with 75% of AC, 57% of TiO₂ (Degussa P25) and 26% of as-prepared TiO₂. The kinetic mechanism of acid dye via photocatalysis was a pseudo-first-order obtained using the Langmuir-Hinshelwood model. Furthermore, the test showed that the reuse of TiO₂/20% AC composite is quite significant, with over 90% efficiency in the recycle. The results thus showed the synergistic effect of TiO₂ and AC and the possibility for the commercial application.

Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.14456/jmmm.2020.48>.

Acknowledgement

This study was financially supported by Farm Engineering and Automatic Control Technology Research group (FEAT group), Applied Engineering for Important Crops of the North East Research group (AENE group), and Sustainable Infrastructure Research and Development Center, Khon Khaen University.

Reference

- [1] A. Fujishima, T. N. Rao, and D. A. Tryk, "Titanium dioxide photocatalysis," *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*, vol. 1(1), pp. 1-21, 2000/6/29 2000.
- [2] E. Bizani, Fytianos, K., Poulivos, I., and V. Tsiridis, "Photocatalytic decolorization and degradation of dye solutions and wastewaters in the presence of titanium dioxide," *Journal of Hazardous Materials, Selected Proceedings of the Seventh Biennial Protection and Restoration of the Environment International Conference*, vol. 136(1), pp. 85-94, 2006/8/10 2006.
- [3] H. G. Mobtaker, S. J. Ahmadi, S. M. Dehaghi, and T. Yousefi, "Coupling system application in photocatalytic degradation of methylorange by TiO₂, TiO₂/SiO₂ and TiO₂/SiO₂/Ag," *Rare Metals*, vol. 34(12), pp. 851-858, 2015.
- [4] A. C. Martins, A. L. Cazetta, O. Pezoti, J.R.B. Souza, T. Zhang, E. J. Pilau, T. Asefa, and V.C. Almeida, "Sol-gel synthesis of new TiO₂/activated carbon photocatalyst and its application for degradation of tetracycline," *Ceramics International*, vol. 43(5), pp. 4411-4418, 2017.
- [5] C. Telegang Chekem, V. Goetz, Y. Richardson, G. Plantard, and J. Blin, "Modelling of adsorption/photodegradation phenomena on AC-TiO₂ composite catalysts for water treatment detoxification," *Catalysis Today*, vol. 328, pp. 183-188, 2019.
- [6] Y. Li, S. Li, J. Wang, C. Ma, and L. Zhang, "Preparation and solarlight photocatalytic activity of TiO₂ composites: TiO₂/kaolin, TiO₂/diatomite, and TiO₂/zeolite," *Russian Journal of Physical Chemistry A*, vol. 88(13), pp. 2471-2475, 2014.
- [7] X. Zhang, Y. Shen, W. Shi, and X. Bao, "Ethanol fermentation with glucose and xylose by the recombinant industrial strain *Saccharomyces cerevisiae* NAN-127 and the effect of furfural on xylitol production," *Bioresource technology*, vol. 101(18), pp. 7093-7099, 2010.
- [8] M. Lorenzo, D. Moldes, S. R. Couto, and M. Sanromán, "Inhibition of laccase activity from *Trametes versicolor* by heavy metals and organic compounds," *Chemosphere*, vol. 60(8), pp. 1124-1128, 2005.
- [9] C. Adán, J. Carbajo, A. Bahamonde, and A. Martínez-Arias, "Phenol photodegradation with oxygen and hydrogen peroxide over TiO₂ and Fe-doped TiO₂," *Catalysis Today*, vol. 143(3), pp. 247-252, 2009.
- [10] S. X. Liu, X. Y. Chen, and X. Chen, "A TiO₂/AC composite photocatalyst with high activity and easy separation prepared by a hydrothermal method," *Journal of Hazardous Materials*, vol. 143(1), pp. 257-263, 2007.
- [11] L. Andronic, A. Enesca, C. Cazan, and M. Visa, "TiO₂-active carbon composites for wastewater photocatalysis," *Journal of Sol-Gel Science and Technology*, journal article vol. 71(3), pp. 396-405, 2014.
- [12] A. Nourbakhsh, S. Abbaspour, M. Masood, S. N. Mirsattari, A. Vahedi, and K. J. D. Mackenzie, "Photocatalytic properties of mesoporous TiO₂ nanocomposites modified with carbon nanotubes and copper," *Ceramics International*, vol. 42(10), pp. 11901-11906, 2016.
- [13] B. Gao, P. S. Yap, T. M. Lim, and T.-T. Lim, "Adsorption-photocatalytic degradation of Acid Red 88 by supported TiO₂: Effect of activated carbon support and aqueous anions," *Chemical Engineering Journal*, vol. 171(3), pp. 1098-1107, 2011.
- [14] K. Blus, "Synthesis and properties of acid dyes derived from 1-phenyl-3-methyl-5-pyrazolone," *Dyes and pigments*, vol. 20(1), pp. 53-65, 1992.
- [15] S.H. Madani, C. Hu, A. Silvestre-Albero, M.J. Biggs, F. Rodríguez-Reinoso, and P. Pendleton, "Pore size distributions derived from adsorption isotherms, immersion calorimetry, and isosteric heats: A comparative study," *Carbon*, vol. 96, pp. 1106-1113, 2016.
- [16] Y. Li, X. Li, J. Li, and J. Yin, "Photocatalytic degradation of methyl orange by TiO₂-coated activated carbon and kinetic study," *Water research*, vol. 40(6), pp. 1119-1126, 2006.
- [17] C. Adán, J. Carbajo, A. Bahamonde, and A. Martínez-Arias, "Phenol photodegradation with oxygen and hydrogen peroxide over TiO₂ and Fe-doped TiO₂," *Catalysis Today*, vol. 143, pp. 247-252, 2009.
- [18] J. Zhang, P. Zhou, J. Liu, and J. Yu, "New understanding of the difference of photocatalytic activity among anatase, rutile and brookite TiO₂," *Physical Chemistry Chemical Physics*, vol. 16(38), pp. 20382-20386, 2014.
- [19] S. Horikoshi, S. Sakamoto, and N. Serpone, "Formation and efficacy of TiO₂/AC composites prepared under microwave irradiation in the photoinduced transformation of the 2-propanol VOC pollutant in air," *Applied Catalysis B: Environmental*, vol. 140-141, pp. 646-651, 2013.
- [20] P. Scherrer and N.G.W. Gottingen, "Math-Pys. Kl.," no. 2, pp. 96-100, 1918.

- [21] A. W. Burton, K. Ong, T. Rea, and I. Y. Chan, "On the estimation of average crystallite size of zeolites from the Scherrer equation: A critical evaluation of its application to zeolites with one-dimensional pore systems," *Microporous and Mesoporous Materials*, vol. 117(1-2), pp. 75-90, 2009.
- [22] Z. Abbas, J. Perez-Holmberg, A-K Hellström, M. Hagström, J. Bergenholtz, M. Hassellöv, and E. Ahlberg, "Synthesis, characterization and particle size distribution of TiO₂ colloidal nanoparticles," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 384(1-3), pp. 254-261, 2011.
- [23] F. Rouquerol, J. Rouquerol, and K. Sing, "CHAPTER 1- Introduction," in *Adsorption by Powders and Porous Solids*, F. Rouquerol, J. Rouquerol, and K. Sing, Eds. London: Academic Press, 1999, pp. 1-26.
- [24] F.J. Sotomayor, K.A. Cychosz, and M. Thommes, "Characterization of micro/mesoporous materials by physisorption: concepts and case studies," *Accounts Material & Surface. Research*, vol. 3(2), pp. 36-37, 2018.
- [25] F. X. Perrin, V. Nguyen, and J. L. Vernet, "FT-IR Spectroscopy of acid-modified titanium alkoxides: investigations on the nature of carboxylate coordination and degree of complexation," *Journal of Sol-Gel Science and Technology*, vol. 28(2), pp. 205-215, 2003.
- [26] M. Gar Alalm, A. Tawfik, and S. Ookawara, "Solar photocatalytic degradation of phenol by TiO₂/AC prepared by temperature impregnation method," *Desalination and Water Treatment*, vol. 57(2), pp. 835-844, 2016.
- [27] H. Atout, A. Bouguettoucha, D. Chebli, J.M. Gatica, H. Vidal, M.P. Yeste, and A. Amrane, "Integration of adsorption and photocatalytic degradation of methylene blue using TiO₂ Supported on granular activated carbon," *Carbon*, vol. 16, pp. 123, 2016.
- [28] X.G. Zhao, and L.Q. Huang, "Iridium, carbon and nitrogen multiple-doped TiO₂ nanoparticles with enhanced photocatalytic activity," *Ceramics International*, vol. 43(5), pp. 3975-3980, 2017.
- [29] X. Wang, Z. Hu, Y. Chen, G. Zhao, Y. Liu, and Z. Wen, "A novel approach towards high-performance composite photocatalyst of TiO₂ deposited on activated carbon," *Applied Surface Science*, vol. 255(7), pp. 3953-3958, 2009.
- [30] M. Vishnuganth, N. Remya, M. Kumar, and N. Selvaraju, "Photocatalytic degradation of carbofuran by TiO₂-coated activated carbon: Model for kinetic, electrical energy per order and economic analysis," *Journal of environmental management*, vol. 181, pp. 201-207, 2016.