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TiO\textsubscript{2}/AC Composites for Adsorption-Photocatalytic of Methyl Orange

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Abstract. Herein, the adsorption-photocatalytic performance of composite titanium dioxide (TiO\textsubscript{2}) and Activated Carbon (AC) to decompose methyl orange was investigated systematically. This work demonstrated the synthesis of TiO\textsubscript{2}/AC composite via the sol-gel method. After getting the composite TiO\textsubscript{2}/AC under different ratios of AC, the prepared particles were then annealed at 500\degree C for 2 h. The presence of AC detected by Fourier transform infrared (FTIR) spectra at 1028 nm. Based on Brunauer–Emmett–Teller (BET) analysis, the result showed that the prepared particles specific surface area increased by increasing the AC ratio. The prepared photocatalyst was used to decompose methyl orange under UV light irradiation for 90 minutes. From the photocatalytic performance, the additional AC did not influence the adsorption process significantly under dark conditions. Interestingly, during the irradiation process, methyl orange could be decomposed until 62.5\%, which means 15\% higher than that of bare TiO\textsubscript{2}. The present result showed that an additional AC could enhance photocatalytic performance due to its ability as an electron transfer and avoid the recombination process between electrons and holes.

1. Introduction
More than 50\% of pollutant water contaminant consists of non-biodegradable organic pollutant produced from human activities. This hazardous pollutant is well thought-out as toxics to humans, including human hepatic dysfunction, carcinogenic, endocrine, etc. \cite{1}. Typical wastewater treatment technologies have been developed during the past decade, including biological and physical treatments to eliminate assorted types of contaminants \cite{2-4} effectively. Unfortunately, these techniques are cost-ineffective and lead to the production of secondary products or pollution. In this regard, non-destructive, green, and sustainable water treatment technology is highly desired.

Among the previous technologies, photocatalytic treatment has been considered one of the appealing options for wastewater treatment due to its ability to effectively decompose organic pollutants and harmful bacteria under appropriate photon energy \cite{5-6}. The abundance of solar energy with a high intensity as a renewable light source making photocatalytic treatment appropriate to be developed and applied. Theoretically, photocatalysis works based on the ability of photocatalyst
material in absorbing photon energy to create the pairs of electron (e-) and hole (h+)\[6\]. Here, the photon energy must be equal or higher than the band-gap energy of the photocatalyst material \[7\]. The numbers of e- and h+ are crucial in the oxidation-reduction reaction to produce the radical hydroxyl (OH*) or super anion (O_2^-) to decompose organic pollutants \[7\].

Compared to another photocatalyst material, Titanium dioxide (TiO_2) is the most effective and can potentially be applied due to its low-cost, simple preparation, and high stability \[8,9\]. Despite its merits, there are some drawbacks of TiO_2, including the wide bandgap and high charge recombination rate \[10\]. Given the wide bandgap, TiO_2 is active under UV radiation, which only accounts for 5% of the total solar light available in nature \[11\]. Extensive efforts have been devoted to improve the performance of TiO_2 as a catalyst \[10,12-13\]. However, the development of TiO_2 photocatalysts in terms of molecular structural variations so that they have high efficiency is still scarce. To increase the efficiency of TiO_2 nanostructuring (composite, hollow, porous, etc.) and functionalization (impurity doping, reduction, etc.) \[10, 14-18\] must be carried out. TiO_2 composites with activated carbon (AC) are effective ways to improve the photocatalyst performance.

Activated carbon (AC) has a large surface area with an internal pore structure of 25-100% of the weight of activated carbon \[19,20\]. AC can improve photocatalytic activity through the adsorption-catalytic process, which increases the contact between pollutants and the catalyst increasing the photodegradation rate \[19-23\]. Therefore, the research was carried out to synthesize TiO_2/AC composites via the sol-gel method to decompose waste organic compounds. To confirm, the fundamental reason for this catalytic improvement was the effect of TiO_2/AC ratio on crystallinity, particles structure, and surface area. In this study, the photocatalytic process was conducted under UV light irradiation.

2. Experimental method

TiO_2/AC composites were prepared by the sol-gel method. Titanium (IV) ethoxide (Sigma Aldrich, USA), activated carbon (Sigma Aldrich, USA), and ethanol (Merck, USA) were used as precursors without further purification. The composites were synthesized under different ratios of AC i.e. 1:1, 1:3, 1:5, 1:7. 5.24 mL of titanium (IV) ethoxide was dissolved in 20 ml of ethanol and stirred for 15 minutes. AC was added and stirred for 10 minutes. 10 mL of distilled water was added and followed by stirring for 1 hour until forming a gel. The gel is then oven for 12 hours at 100 °C. The obtained powder was annealed at 500 °C for 2 hours in a furnace.

To examine the crystallinity and crystal size of the TiO_2/AC composites, an X-ray diffraction (XRD; Rigaku Denki RINT 2000, Japan; using Cu Kα radiation and a 2θ scanning range of 20−80°). The prepared composites surface area was analyzed by using the Brunauer Emmett–Teller measurement (BET; BELSORP 28SA, Bel, Japan, nitrogen adsorption isotherms at 77.15 K). Fourier-transform infrared spectroscopy was used to determine the functional groups of the TiO_2 framework and UV-Vis Diffuse Reflectance spectrophotometer to determine the composites band gap energy.

The photocatalytic activity of the TiO_2/AC composites was assessed by mixing 0.2 g of the prepared composites with 4 ppm methyl orange (MO, Merck, USA). The mixed solution was introduced into the batch reactor equipped with a solar simulator system. 4 mL of the mixed solution sampled for several minutes. Prior to analysis, the sampled solution was then centrifuged at 12,000 rpm for 10 min. The MO concentration in the sample was measured using a UV–Vis spectrophotometer (UV3150; Shimadzu Corp., Japan) in the wavelength range of 200-700 nm.

3. Results and discussion

The structure and crystallite sizes of the TiO_2/AC composites were identified by XRD patterns, as depicted in Figure 1. The XRD patterns show that all prepared composites were consistent with the standard ICDD no. 04-014-8515. This number was indexed to the tetragonal structure of TiO_2 with orientation 101, 004, and 200. The crystallite sizes were determined from the broadening peak area by using the Scherrer method to be decreasing with an increase in AC content from 111.97 to 68.68 nm. This is because the AC has an amorphous structure, which affects the crystallinity of TiO_2. The phase
and pattern of the TiO$_2$ nanoparticles (NPs) and TiO$_2$/AC composites were similar, suggesting that AC did not induce a change in the structure of TiO$_2$ NPs.

Figure 1. XRD patterns of prepared TiO$_2$/AC composites
Figure 2 showed the FTIR spectrum of prepared TiO$_2$/AC composites with various compositions. The Ti-O-Ti bond was detected at a wavelength of 600 cm$^{-1}$, indicating the formation of TiO$_2$. The O-H group at a wavelength of 3369 cm$^{-1}$ and H-O-H group at wavelength 1630 cm$^{-1}$ indicate water absorption during the synthesis process. This result showed that the addition of AC particles only affects the presence of the Ti-O-C group at 1028 cm$^{-1}$.

Figure 3. Nitrogen adsorption of the prepared particles under various ratio composition

The surface area of the TiO$_2$/AC composites was determined using BET characterization. Figure 3 shows the nitrogen adsorption analysis of the prepared composites. The result showed that varying AC concentration influenced the specific surface area and porosity from 57.28 m$^2$/g to 103.42 m$^2$/g and
0.16 cm$^3$/g to 0.23 cm$^3$/g, respectively. The high specific surface area possibility produced a better photocatalyst.

The photocatalysis performance of the prepared TiO$_2$/AC composites to degrade 10 ppm methyl orange was examined. Figure 4 shows normalized MO concentrations (concerning the initial concentration) as a function of time. The photocatalytic experiments were conducted under varying the prepared composite TiO$_2$/AC. The solid line represents the pure TiO$_2$ particles, whereas the dotted line shows the TiO$_2$/AC ratio variation. The MO concentrations gradually decreased over time. Increases in the TiO$_2$/AC ratio from 1:1 to 1:7 for the synthesis of the catalyst resulted in an improvement in photocatalytic activity. From the photocatalytic performance, the additional AC did not influence the adsorption process significantly under dark conditions. However, the MO could be decomposed until 62.5%, which means 15% higher than that of bare TiO$_2$. This is showed that an additional AC could enhance photocatalytic performance due to its ability as an electron transfer and avoid the recombination process between electrons and holes. On the TiO$_2$/AC ratio of 1:1, the photocatalytic activity was not better than bare TiO$_2$ particles. This is due to the composite's surface area and porosity that smaller than that of bare TiO$_2$ particles. These results show that the addition of the AC particles, which is an adsorbent, improves the TiO$_2$ photocatalyst materials’ photocatalytic activity.

![Figure 4. Photodecomposition of Methyl Orange by the prepared particles over the time](image)

The effect of the composite ratio on the physical properties and photocatalytic performance is shown in figure 5. The diameter of the composite increased by increasing AC concentration. To evaluate the photocatalytic degradation rate ($k$), a simplified Langmuir-Hinshelwood kinetics model was used. As observed, the degradation rate of MO was dependent on the TiO$_2$/AC ratio. The highest photocatalytic rate was obtained using TiO$_2$/AC with a ratio of 1:3, whereas the lowest was obtained using the TiO$_2$/AC ratio with a ratio of 1:7.
4. Conclusion
The composites titanium dioxide (TiO$_2$) and Activated Carbon (AC) were successfully synthesized via the sol-gel method by varying the TiO$_2$/AC ratio. The adsorption-photocatalytic performance of prepared composite materials to decompose methyl orange was investigated systematically. After getting the composite TiO$_2$/AC under different ratios of AC, the prepared particles were then annealed at 500°C for 2 h. The result showed that the prepared particles' specific surface area and porosity increased by increasing the AC ratio. The prepared photocatalyst was used to decompose methyl orange under UV light irradiation for 90 minutes. From the photocatalytic performance, the additional AC did not influence the adsorption process significantly under dark conditions. Interestingly, during the irradiation process, methyl orange could be decomposed until 62.5%, which means 15% higher than that of bare TiO$_2$. The best photocatalytic performance was obtained using TiO$_2$/AC with a ratio of 1:3. The present result showed that an additional AC could enhance photocatalytic performance due to its ability as an electron transfer and avoid the recombination process between electrons and holes. The MO's degradation on the TiO$_2$/AC composite was facilitated by the synergistic relationship between surface adsorption characteristics and photocatalytic potential.
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