

Effect of TiO₂ Content in Activated Carbon-Supported TiO₂ for Paracetamol Degradation under Low Intensity UVC Light

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The current work describes the facile fabrication and characterization of activated carbon (AC)-supported titanium dioxide (TiO₂) photocatalysts for the degradation of paracetamol under low intensity UVC light. The synthesized photocatalysts were characterized using various techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM), photoluminescence (PL) and ultraviolet–visible, near-infrared (UV–vis NIR) spectrophotometry. The effect of varying TiO₂ content with different mass ratios of AC and TiO₂ on the catalytic activity was thoroughly examined. SEM images of the AC-TiO₂ composites exhibited rough surfaces with small, aggregated particles on top. XRD patterns of pure TiO₂ and AC-TiO₂ showed characteristics of anatase. Optical characterization results showed that the TiO₂ and AC-TiO₂ composite photocatalysts displayed a strong emission peak at 408 nm in PL analysis and reduced band gap energies for the AC-TiO₂ composites compared to pure TiO₂, in the range of 3.13–3.18 eV. The results indicate that the incorporation of up to 1.5 g of TiO₂ on AC significantly enhanced the degradation efficiency of paracetamol to a maximum of ~90 %. The rate constants k_1 and k_2 were 0.0165 and 0.8684 min⁻¹, respectively. The pseudo second-order model was shown to be the best-fitting model for the breakdown of paracetamol in aqueous solution. The electron-hole pairs were spatially separated due to strong and advantageous interactions between TiO₂ and AC, which inhibited charge recombination. This led to higher degradation percentages with increased TiO₂ content. The AC-TiO₂ composite photocatalysts exhibit promising potential for degrading pharmaceutical pollutants under environmentally relevant conditions.

Keywords: Activated carbon; paracetamol; photocatalysis; titanium dioxide; water recovery

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Concerns among scientists have been raised due to the penetration of pharmaceutical residues into the environment, particularly in water. Sewage and wastewater treatment facilities, veterinary usage, medical waste, and household waste are common ways that residues enter the water systems [1]. Pharmaceutical residues of over-the-counter medicines such as paracetamol have been found in water streams. Surface water has been found to contain paracetamol at values between 10 and 100 ng/L, while wastewater effluent has been found to contain amounts as high as 10 mg/L [2]. Due to the complicated molecular structure of this drug, it is non-biodegradable and persistent, making it challenging to remove using conventional water treatment methods. Paracetamol in water can cause serious negative impacts on human health. Long-term paracetamol use may result in endocrine disruption, cancer, antibiotic resistance, and several chronic disorders. The toxicity of paracetamol is well-evidenced in fish, algae, bacteria, protozoa, macrophytes, and other aquatic cultures. It has been reported to cause liver toxicity in zebrafish, as well

as morphological changes in zebrafish embryos and larvae upon exposure to this drug in water [3]. Thus, it is imperative to develop an efficient method for successfully removing paracetamol from polluted water.

Driven by these acute environmental concerns and a need for safe and clean water, the hunt for a sustainable solution to these challenges is generating significant attention. From this perspective, the use of stable semiconductor metal oxides has been regarded as a viable path for the abatement of contaminated water through a heterogeneous photocatalytic process. In this process, a semiconductor oxide is exposed to UV light to activate the material by overcoming the energy band gap. This phenomenon results in the excitation of electrons from the valence band (VB) to the conduction band (CB), creating electron-hole pairs (e⁻ and h⁺). Because the holes have a high oxidation potential, they can react with hydroxide ions (OH⁻) and/or water molecules to create hydroxyl radicals (•OH), which are involved in the degradation process.

Using a reductive process, the electrons in the CB can also generate superoxide radical anions ($\bullet\text{O}_2^-$), which possess the reduction potential to break down the organic pollutant molecules [3]. Titanium dioxide (TiO₂) photocatalysts have been investigated in depth as a promising technology for treating hazardous contaminants in water. For instance, Zyoud et al. investigated the efficiency of commercially available TiO₂ anatase and TiO₂ rutile phases in degrading acetaminophen under simulated solar light. The anatase form was revealed to exhibit 47 % degradation, 2.8 times higher than rutile [4]. Han et al. used Aeroxide P25 TiO₂ which consisted of anatase and rutile, which yielded almost complete estrone removal within 20 min of UVA irradiation [5]. These studies show that TiO₂ can be effectively used to remove pharmaceutical residues in water. However, utilizing TiO₂ alone has limitations that could lead to other issues including large band gap energies and photoexcited charge carrier recombination [6]. Interestingly, these limitations may be mitigated by adding activated carbon (AC) to the surface of TiO₂, which reduces the band gap for low-energy activation. Furthermore, AC may function as an electron-trapping agent to extend the lifetime of charge carriers and so prevent electron and hole recombination [7].

Several researchers have studied the viability of incorporating AC onto the surface of semiconductor metal oxides. This approach is seen as an effective strategy to improve the charge carrier's lifetime and light absorption, as well as narrowing the band gap energy simultaneously. Feng et al. investigated the photocatalytic performance of the core-shell structure of mesoporous carbon spheres coated with Fe/N co-doped nano-TiO₂ [8]. The results indicated that the composites exhibited smaller band gap energies in parallel with increased carbon sphere loading. The doping and interface of carbon spheres also influenced photocurrent density, contributing to the lower charge transfer resistance and good conductivity. This is necessary for rapid charge migration and to improve its performance. Meanwhile, Ye et al. introduced an ultrathin carbon layer onto the surface of CeO₂ nanorods and SnS₂ to form a ternary system [9]. The results revealed that the band gap increased towards the visible region. The carbon layer also acts as a superior electron acceptor and enables fast charge migration, as well as accelerating photocatalytic performance. Similarly, the incorporation of AC and Fe co-doped ZnO showed lower intensity photoluminescence spectra [10]. This behaviour

indicates that the dopants had a stronger capacity to capture photoexcited electrons and subsequently yielded higher separation of charge carriers for enhanced photoactivity.

The present study discusses the fabrication of AC-supported TiO₂ (AC-TiO₂) using a simple mixing process. Composites of various ratios were prepared by simply adjusting the TiO₂ content. The morphology, surface composition, structure, band gap energy, and recombination behaviour of the prepared composite photocatalysts were investigated using a variety of characterization approaches. The photocatalytic activity of the composites was tested against paracetamol in aqueous media using relatively low intensity UVC light (9 W). Pseudo first-order and pseudo second-order kinetics analyses were also compared to obtain a better understanding of the degradation mechanisms. It is hoped that this work provides an insight into developing enhanced photocatalysts with promising prospects for photocatalytic water recovery processes.

EXPERIMENTAL

Chemicals and Materials

Commercial activated carbon (AC) and titanium dioxide (TiO₂, 99 %) were supplied by R&M Chemicals and Sigma-Aldrich (Selangor, Malaysia), respectively. Paracetamol was obtained from a local pharmacy. All chemicals were used as received, without purification. Deionized water was utilized throughout the photocatalyst preparation and photocatalytic testing.

Preparation of AC-TiO₂ Composite Photocatalyst

The AC-TiO₂ composite photocatalyst was prepared via a facile chemical mixing technique. Briefly, 0.05 g of activated carbon and 1.0 g of TiO₂ were mixed in 50 mL of deionized water and continuously stirred for 1 h at room temperature. The process was continued by drying the slurry mixture in the oven at 90 °C overnight. Next, the dried sample was further ground to obtain a fine powder, which was labelled AC-TiO₂ (A). To investigate the synergistic effects between AC and TiO₂, different mass ratios of AC to TiO₂ (0.05:1.5, 0.05:2) were prepared under the same conditions (**Table 1**). Pure TiO₂ was used for comparison purposes.

Table 1. Preparation of different mass ratios of AC and TiO₂.

Mass of AC (g)	Mass of TiO ₂ (g)	Labelled as
0.05	1.0	AC-TiO ₂ (A)
0.05	1.5	AC-TiO ₂ (B)
0.05	2.0	AC-TiO ₂ (C)

Characterization Methods

A scanning electron microscope equipped with an energy dispersive X-ray analyser (SEM-EDX, TESCAN VEGA3) was used to analyse the surface morphology and composition of the AC-TiO₂ composites. An X-ray diffractometer (XRD, Philips PW 3040/60) was used to analyse the crystallinity and structure of the samples at $2\theta = 10 - 80^\circ$ ($\lambda = 1.54 \text{ \AA}$) and $5^\circ/\text{min}$ scanning speed. At room temperature, photoluminescence (PL, FP-8500, JASCO) spectra were captured at 325 nm. A UV-vis NIR spectrophotometer (UV-3101PC Shimadzu) was used to measure the energy gap values of the prepared composites.

Evaluation of Photocatalytic Testing and Kinetic Study

Photocatalytic testing was conducted using a 200 mL beaker. First, 0.2 g of the AC-TiO₂ composite was dispersed in a beaker containing 50 mL of 10 mg/L paracetamol solution (pH = 6.9). The paracetamol solution was stirred in the dark for 30 min to complete the adsorption/desorption equilibrium. The solution was then irradiated with a UVC lamp ($\lambda = 254 \text{ nm}$, 9 W) for 180 min, with continuous stirring. Samples of 5 mL were drawn at 30 min intervals throughout the experiment. The concentration of each sample was examined using a UV-vis spectrophotometer (PerkinElmer Lambda 35) at $\lambda_{\text{max}} = 243 \text{ nm}$, and the degradation percentage and amount were evaluated using Equations (1) and (2), respectively [11].

$$\text{Degradation percentage (\%)} = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (1)$$

$$\text{Amount of degradation (mg/g)} = \frac{(C_0 - C_t) \times \text{Volume}}{\text{mass of catalyst}} \quad (2)$$

where C_0 is the initial concentration of paracetamol and C_t is the final concentration at time t . The Langmuir-Hinshelwood (L-H) kinetic model was used to study the kinetics of paracetamol degradation by the prepared photocatalysts. The following linear form can be used to express the pseudo first-order kinetic model [12].

$$\ln\left(\frac{C_0}{C_t}\right) = k_1 t \quad (3)$$

The pseudo second-order kinetic model can be represented linearly as follows [13]:

$$\frac{t}{C_t} = \frac{1}{k_2 C_e^2} + \frac{1}{C_e} t \quad (4)$$

where k_1 and k_2 are the pseudo first-order (min^{-1}) and second-order ($\text{mg/L}^{-1} \text{ min}^{-1}$) rate constants, respectively, and C_0 and C_t are the concentrations (mg/L) of paracetamol initially and at different irradiation times, respectively.

RESULTS AND DISCUSSION

Analyses of Surface Morphology, Composition, and Structure

The morphology of the pure AC, pure TiO₂, and AC-TiO₂ composite photocatalysts were investigated using SEM and the results are displayed in **Figure 1**. Pure AC exhibited irregular flaky shapes with consistently smooth surfaces (Figure 1(a)), while pure TiO₂ (Figure 1(b)) seemed to consist of semi-spherical and spherical shapes with rough and porous surfaces. For AC-TiO₂ (A), the presence of flaky AC was seen on the surface along with the porous, less aggregated particles. Similarly, AC-TiO₂ (B) consisted of flaky AC but with slightly more aggregated particles and a rougher surface. AC-TiO₂ (C) had a denser and more packed surface with aggregated particles due to the higher TiO₂ content. The TiO₂ particles were observed to be homogeneous and well-distributed on the surfaces of all the composites as a consequence of the consistent mixing process (Figure 1(c)-(e)). The mapping images show good dispersion of the particles, which are represented by blue for Ti, green for O, and red for C, attributed to both AC and TiO₂ (Figure 1f(i)-(v)). The composition data showed the presence of Ti, O, and C, with Ti and O having the highest weight percentages on the photocatalyst surface at 53.09 % and 39.96 %, respectively, while C had only 6.95 %. The absence of other peaks in the EDX pattern and the Au peak's connection to the gold coating used for SEM image collection served to establish the samples' purity. The XRD patterns of the pure AC, pure TiO₂, and AC-TiO₂ composite photocatalysts are depicted in Figure 1(g). The peaks observed at 27.0° , 29.7° , 38.4° , 44.6° , 65.1° , and 78.2° are associated with well-defined porous AC (Figure 1g(i)). The peaks suggest that the structure of the AC sample was a mixture of crystalline and amorphous phases, while the stronger peak at 44.6° is associated with a more ordered carbon structure [14,15]. Nonetheless, upon incorporation of TiO₂ onto the AC surface, several peaks characteristic of anatase TiO₂ (JCPDS 00-021-1272) at 2θ of 25.34° (101), 37.82° (004), 48.06° (200), 53.91° (105), 55.08° (211), and 62.71° (204) were observed in pure TiO₂ and all of the composites (Figure 1g(ii)-(v)) [10]. The lack of discernible changes in the structure, peak intensities, and peak positions of TiO₂ in the XRD patterns may be attributed to the AC's mixed phase nature. It also proves that the native crystalline structure of TiO₂ was maintained after the composites were formed. The AC and TiO₂ were successfully incorporated into the tetragonal structure of the TiO₂ crystal as no impurities or secondary phases were observed in the XRD patterns of all the AC-TiO₂ composite photocatalysts. The characteristic peak of AC was not observed in the spectra of all the composite samples, possibly because of their low AC content (0.05 g) which was below the instrument's detection range.

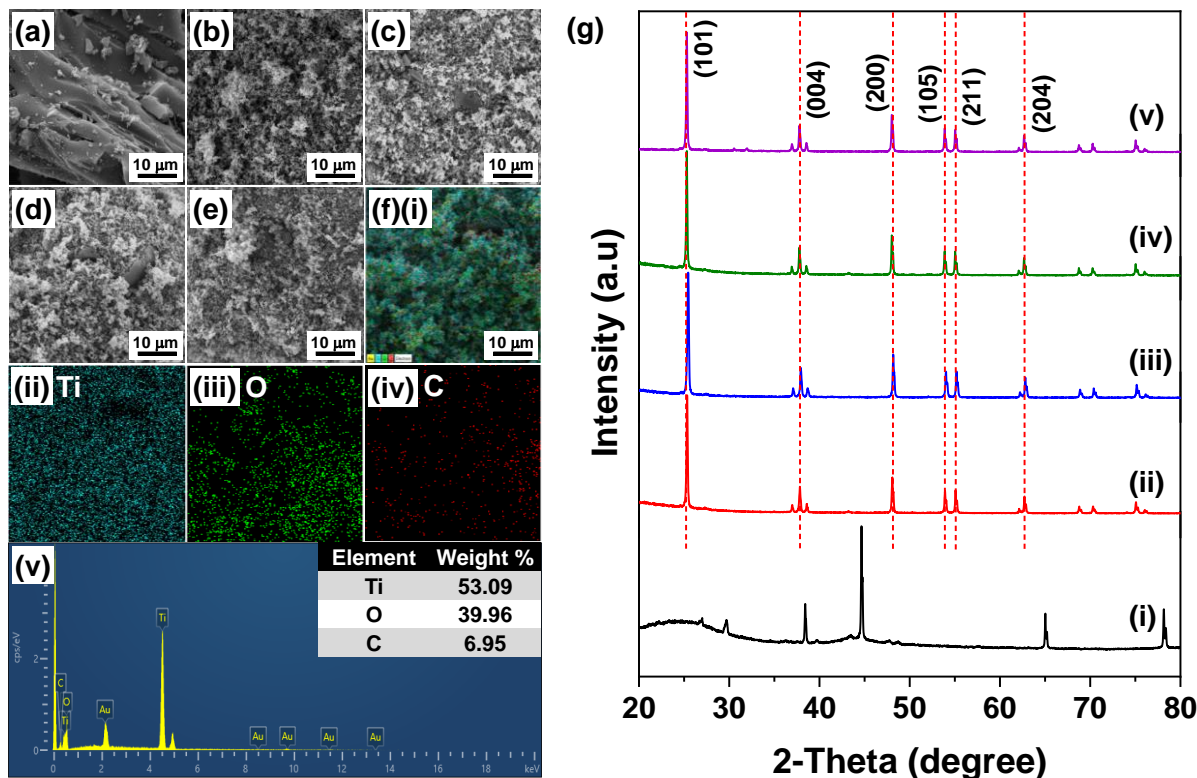


Figure 1. SEM images of (a) AC, (b) pure TiO₂, (c) AC-TiO₂ (A), (d) AC-TiO₂ (B), (e) AC-TiO₂ (C) at 3kx magnification; (f)(i–v) elemental mapping images of AC-TiO₂ (B); (g) XRD patterns of (i) pure AC, (ii) pure TiO₂, (iii) AC-TiO₂ (A), (iv) AC-TiO₂ (B), and (v) AC-TiO₂ (C).

Charge Carriers and Optical Analyses

The charge carrier behaviour and optical properties of the photocatalysts were observed via photoluminescence (PL) and UV-vis NIR analyses, respectively (**Figure 2**). In particular, PL analysis was employed to determine the separation efficiencies of the photoexcited electron-hole pairs in the photocatalytic materials. It has been noted that a lower PL emission intensity indicates higher separation efficiency and hence, results in enhanced photocatalytic performance [17]. Figure 2(a) shows that the PL spectra of both pure TiO₂ and the AC-TiO₂ composite photocatalysts had strong emission peaks at 408 nm, which is associated with the recombination behaviour of the photoexcited electron-hole of TiO₂. The PL intensities of all AC-TiO₂ composites reduced significantly in parallel with the increase in TiO₂ content from 1.0 to 2.0 g, and were lower than that of pure TiO₂. This shows that the presence of a constant amount of AC substantially reduced the recombination rate of electron-hole pairs for TiO₂.

Among the composite photocatalysts, a higher separation efficiency was observed with a higher TiO₂ content. Thus, the trend followed the ascending order of pure TiO₂ < AC-TiO₂ (A) < AC-TiO₂ (B) < AC-TiO₂ (C). The improved charge separation in the AC-TiO₂ composites was beneficial for enhanced photoactivity. Figure 2(b) shows the optical response of the AC-TiO₂ composite photocatalysts. The estimated value of the composites' band gap was determined from the tangent intercept at the x-axis of the Tauc's plot. The theoretical band gap of pure TiO₂ was reported to be 3.20 eV [18]. Interestingly, the composites demonstrated slightly reduced band gap energies compared to pure TiO₂, in the range of 3.13–3.18 eV. Previous research has indicated that by decreasing the band gap, the addition of AC to the surface of a semiconductor oxide may improve its ability to absorb light and its photocatalytic activity. The results demonstrated that under UVC irradiation, the AC-TiO₂ (B) composite with a band gap energy of 3.13 eV exhibited the strongest optical response and may thus be used as a potential UV-active photocatalyst at a lower intensity.

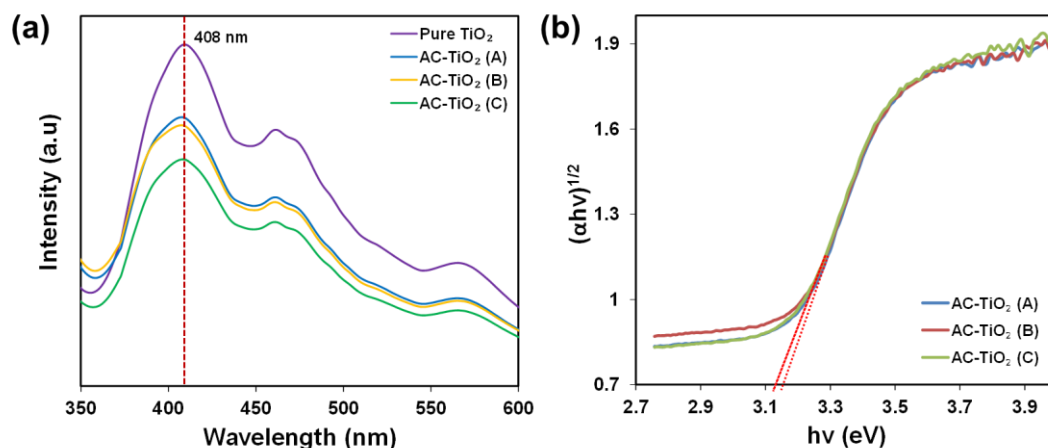


Figure 2. (a) Photoluminescence spectra of pure TiO₂ and AC-TiO₂ composite photocatalysts, and (b) optical response of AC-TiO₂ composite photocatalysts.

Evaluation of Photocatalytic Testing and Kinetics Study

The results of the photocatalytic testing and kinetics study of paracetamol degradation in aqueous media via pure TiO₂ and AC-TiO₂ composite photocatalysts with varied mass ratios is depicted in **Figure 3**. Paracetamol was found to be stable against UVC irradiation since no degradation was seen during the photolysis process. For the first 30 min of the adsorption process in the dark, the pure TiO₂ exhibited negligible paracetamol adsorption. However, the AC-TiO₂ composite photocatalysts made a very minimal contribution to the adsorption process. Even though a relatively small amount of AC was mixed with TiO₂, it may be explained by the greater surface area of AC (data not shown). Throughout the degradation process, pure TiO₂ showed positive degradation activity against paracetamol, of about 38 %. The percentage of paracetamol degradation increased to a maximum of ~90 % with the addition of 1.5 g of TiO₂ onto AC (AC-TiO₂ (B)). The degradation percentage gradually declined as the TiO₂ content increased further (Figure 3(a)). Using the composite photocatalysts, a significant amount of paracetamol was removed, indicating that photocatalysis was the

primary method of paracetamol removal. An increase in the number of active sites on the composite photocatalysts leads to greater degradation. The presence of AC in the composites leads to good photocatalytic efficiency due to its large specific surface area, pore size, and numerous active adsorption sites. From the previous study, the primary active sites identified on the carbon surface were functional groups like hydroxyl (-OH), carboxyl (-COOH), lactone (-COO), and carbonyl (C=O) [19]. Owing to its nucleophilicity, the electron acceptor C=O functions as a Lewis base site to produce a singlet molecular oxygen species (¹O₂), which has a potent degrading effect on electron-rich aromatic compounds such as paracetamol. Nonetheless, increasing the amount of TiO₂ up to 2 g caused aggregation of particles, which in turn reduced degradation. These findings are consistent with our results (Figure 3(b)), where the amount of TiO₂ that could be added to the AC without negatively impacting the reaction rate was limited. These outcomes are also in good agreement with the findings from a previously reported study [20], which found that aggregated particles may occur as a result of excessive photocatalyst dosage and hence, become resistant to light penetration.

Table 2. A comparative study of paracetamol removal using TiO₂-based photocatalysts from previously reported data.

Photocatalyst	Light source	Irradiation time (min)	Degradation (%)	Reference
ZSM-5/TiO ₂	14 W UV lamp	180	96.6	[27]
Pt/TiO ₂	1000 W Xenon lamp	180	> 95	[28]
Ag/TiO ₂			> 95	
Au/TiO ₂			> 90	
Carbon xerogel/TiO ₂	125 W Mercury lamp	240	96	[29]
Activated carbon/TiO ₂	9 W UVC lamp	180	~90	This work

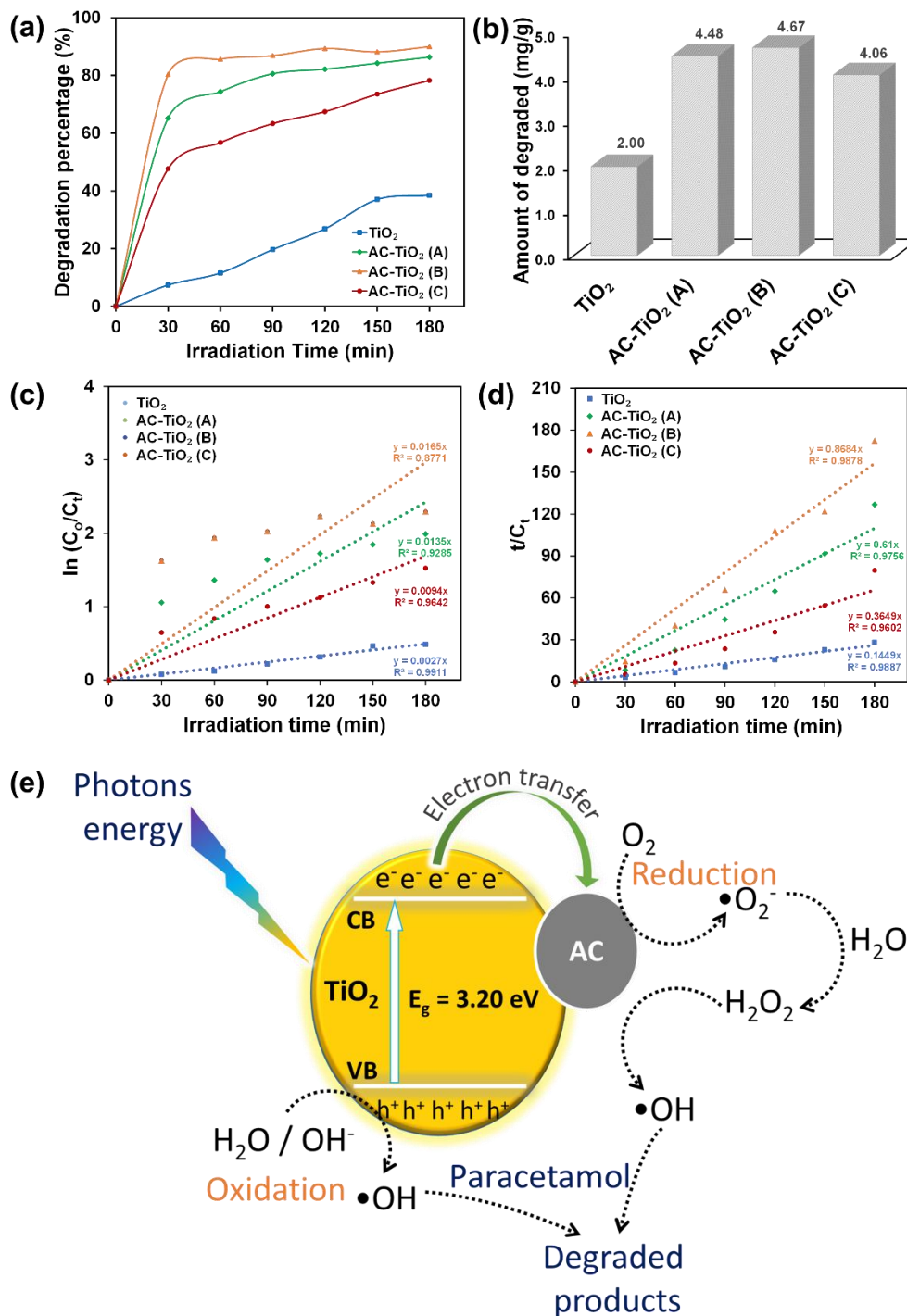


Figure 3. (a) Degradation percentage, (b) amount of degradation, (c) pseudo first-order kinetics, (d) pseudo second-order kinetics, and (e) plausible mechanism for photocatalytic degradation of paracetamol. [Paracetamol] = 10 mg/L, pH = 6.8, photocatalyst = 0.2 g.

For the pseudo first-order kinetics, the experimental data exhibited some nonlinearity and a low correlation coefficient ($R^2 = 0.8771$) (Figure 3(c)). The best rate constant for k_1 was found to be 0.0165 min^{-1} . However, the overall pseudo first-order kinetics did not suit the degrading process of the AC-TiO₂ composite photocatalysts well, as indicated by the comparatively low R^2 and rate constant values. In contrast, the pseudo second-order model produced

an R^2 value (0.9878) that was noticeably higher (Figure 3(d)), and a rate constant k_2 of 0.8684 min^{-1} . Therefore, the pseudo second-order model best described how paracetamol degrades in aqueous media. Modelling the degradation kinetics with a pseudo second-order model signifies that the rate constant of this system was time dependent due to the presence of different available active sites for the adsorption-photodegradation process (heterogeneous

surface), which involved sharing or exchanging electrons between photocatalyst and pollutant [14]. Comparatively, the pseudo second-order model could well describe the kinetic adsorption behaviour of paracetamol on the AC-TiO₂, suggesting a chemical bonding-related mechanism [22]. Some studies have also reported second-order kinetics mechanisms for photocatalytic processes [23, 24].

In theory, UVC light (photons with energies higher than the photocatalyst's band gap energy) activates the photocatalyst and excites electrons from the valence band (VB) to the conduction band (CB), producing electron-hole pairs (e⁻ and h⁺). The photoexcited electrons at the CB of TiO₂ will then transfer to AC since AC may act as both an electron mediator and capture [7]. The strong and synergistic interaction between TiO₂ and AC results in spatial separation of electron-hole pairs, thus avoiding charge recombination (Figure 3(e)). Through a series of redox reactions, more charge carriers such as •OH and •O₂⁻ radicals are produced for efficient paracetamol degradation [18]. The positive holes (h⁺) may also play a crucial role in paracetamol degradation by direct reaction with adsorbed water to produce •OH radicals. Interestingly, the use of UVC irradiation in this work also helped in the production of more •OH species by directly splitting hydrogen peroxide in the working solution. In comparison, UVA and UVB irradiation cannot decompose hydrogen peroxide to hydroxyl radicals. This observation was consistent with a previously reported study [26]. **Table 2** summarizes previous studies on photocatalytic reactions that used TiO₂-based photocatalysts to degrade paracetamol. In this study, the AC-TiO₂ composite degraded paracetamol with exceptional efficiency under low UVC light intensity, indicating enhanced photocatalytic activity against pharmaceutical residues in water.

CONCLUSION

This study successfully demonstrated the facile fabrication and characterization of AC-supported TiO₂ photocatalysts for the degradation of paracetamol under low intensity light conditions. Through systematic characterization techniques including XRD, SEM, PL, and UV-vis NIR, the synthesized photocatalysts were thoroughly analysed, revealing the presence of anatase TiO₂ nanoparticles uniformly dispersed on activated carbon substrates. Varying the mass ratios of activated carbon and TiO₂ provided valuable insights into the optimization of catalytic activity. SEM images showed similar surface morphologies with small, aggregated TiO₂ particles on top, while XRD patterns confirmed the presence of an anatase TiO₂ phase. PL and UV-vis NIR analyses indicated higher emissions and reduced band gap energies for the AC-TiO₂ composites compared to pure TiO₂, suggesting enhanced photocatalytic activity. The photocatalytic degradation of paracetamol

was found to be significantly improved with the incorporation of TiO₂ onto activated carbon, reaching a maximum degradation efficiency of approximately 90 % for the AC-TiO₂ (B) composite with 1.5 g TiO₂. The kinetic model that best suited paracetamol degradation was pseudo second-order. Because of the strong and beneficial contacts between TiO₂ and AC which prevented charge recombination, the electron-hole pairs were spatially separated. The AC-TiO₂ photocatalyst demonstrated excellent potential, making it suitable as an effective, environmentally friendly photocatalyst in real-world water recovery processes.

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