

Determination of photocatalytic process parameters on phenol degradation using TiO₂-MWCNT (cocoPAS) composite

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International Journal of Science and Research Archive, 2021, 03 (02), 070–077

Publication history: Received on 14 August 2021; revised on 19 September 2021; accepted on 21 September 2021

Article DOI: <https://doi.org/10.30574/ijrsra.2021.3.2.0132>

Abstract

Multi-walled carbon nanotubes (MWCNT) were prepared by treatment of cocoPas and titanium dioxide nanocomposites TiO₂ – MWCNT (cocoPAS) prepared by stirring and mixing method was used as a photocatalyst for the degradation of phenol in water under light irradiation. The morphology and microstructure of the composites were characterized with SEM, FT-IR, BET, XRD and UV-visible spectrophotometer. The purpose of this study were synthesize TiO₂-MWCNT (cocoPAS) composite and evaluate its performance for photodegradation phenol. It was found that the degree of photodegradation of phenol under UV light was highly dependent on the concentration of phenol and the degradation temperature. The presence of MWCNT worked as the adsorbent and electron acceptor to efficiently enhance the phenol photodegradation. The as-prepared nanotubes, with surfactant contents, showed high-photocatalytic activities with increase degradation. These results indicate that TiO₂ – MWCNT (cocoPAS) composites using cocoPAS can be used to enhance degradation and can expand potential applications for the degradation of organic pollutants.

Keywords: TiO₂; MWCNT; Photocatalyst; Phenol; Degradation; cocoPAS (surfactant)

1. Introduction

Various organic pollutants in wastewaters are highly toxic and non-biodegradable nature, one of which is phenol. Phenols are broadly used in textile, pesticides, paper and petrochemical industries [1]. Treating wastewater containing phenol has been proposed by various technologies such as adsorption, activated carbon, chemical oxidation, and biological treatment. However, these common technologies required time-consuming, high operation cost, and also possible production of toxic by-product [2]. Heterogeneous photocatalysis, which is an Advanced Oxidation Process (AOP) is a potential technology to degrade phenol. These techniques produce and use highly reactive radical like hydroxyl radical (OH•) that degrade the organic pollutants to carbon dioxide and water, which is more environmentally friendly and biodegradable. Degrade organic pollutants with photocatalytic process also known as photodegradation [3].

The heterogeneous photocatalysis process is a phenomenon in which a semiconductor photocatalyst are irradiated by photons from light source. The energy of photon must be equal or higher than semiconductor photocatalyst's band gap. In this process, the electrons of photocatalyst (e⁻) are excited from valence band to conduction band and leaving holes (h⁺) behind in the valence band. Electrons and holes respectively will react to produce hydroxyl radical (OH•) [4]. Photocatalytic performance of several semiconductor compounds has been studied. TiO₂ or titanium dioxide has been regarded as an excellent photocatalyst due to its long-term stability against photo and chemical corrosion, strong oxidizing power, high reactivity, inexpensive, and non-toxicity [5]. But, high degree of electron-hole recombination at the surface or in the bulk is a major limiting factor in controlling its photocatalytic efficiency. Electrons and holes must

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be separated so that each can react to form hydroxyl radical (OH•) [6]. Combining TiO₂ with support materials into a composite is one of the treatments that can enhance performance of TiO₂ photocatalysts.

The physical and chemical properties of support materials strongly affect the functions of composite [7]. The carbon materials are used in various ways in the composites such as supports, adsorbent agent, and dispersant to increase the surface area of functional materials. Compared with the other carbon material, Multiwalled Carbon Nanotubes (MWCNT) usage is greater and its integration into the semiconductor is advantageous for effective photocatalytic process due to unique thermal, electrical and physical properties and large surface area. Having the large electron-storage capacity, the MWCNT can act as electron-trapper to hindering the electron-hole recombination [8]. However, MWCNT is hydrophobic and prone to aggregation due to their strong van der Waals interaction, thus causing MWCNT not to be well dispersed on TiO₂ photocatalyst. This can inhibit the benefit of CNT to composites [9]. Therefore, the surface modification of the MWCNT must be modified before it is compiled with TiO₂, so that the MWCNT is evenly dispersed on the surface of TiO₂ and One of the functionalization to modify surface of MWCNT is non-covalent functionalization using surfactants. Their hydrophilic part imparts aqueous solubility while hydrophobic part adsorbs to the MWCNT's surface via non-covalent interactions such as van der Waals, charge transfer function and interaction of $\pi - \pi$. Based on the change of their head group, surfactants can be categorized as cationic, anionic, and nonionic [11]. Sodium dodecyl sulfate (SDS) is one of the anionic synthetic surfactants used as a MWCNT dispersing agent [12]. Interaction between MWCNT and SDS through hydrophobic interactions and electrostatic forces cause higher steric repulsion and negative charge on the surface of the MWCNT, thereby increasing MWCNT dispersion [13]. To maintain environmental conditions, surfactants derived from natural resources that are biodegradable as a substitute for synthetic surfactants such as cocoPAS surfactant made from coconut oil. Coconut oil based on primary alkyl sulfate (cocoPAS) surfactant is SDS derivatives that has a wide, linear chain length distribution between C₈ and C₁₈ where C₁₂ and C₁₄ chains comprise ca. 66 wt.% [14]. Based on this approach, in this study, synthesis of TiO₂-MWCNT composites was carried out with cocoPAS surfactant as MWCNT dispersing agent.

2. Material and methods

2.1. Materials

MWCNT were purchased from Dong Yang (HK) Int'l Group Limited of diameter 10-30 nm, length of 5-15 μ m, and purity of 99%, TiO₂-P25, cocoPas surfactant, HNO₃, phenol and aquades.

2.2. MWCNT Surface Modification using cocoPAS Surfactant

About 1 g of MWCNT and 0,5 g cocoPAS surfactant was suspended in 100 mL of aquades. The suspension was sonicated in a water bath for 1 hrs at room temperature to unlocked the agglomeration of the nanotubes. MWCNT (cocoPAS) solids contained in the suspension were separated using a vacuum device circuit and then were dried at 110°C for 1-2 hours to evaporate the water.

2.3. Synthesis of TiO₂-MWCNT (cocoPAS) Composite

Composite was prepared by simple mixing, evaporation and drying process. First, approximately 15 mg MWCNT (cocoPAS) were dispersed in 100 mL of aquades and sonicated for 30 minutes. Then, about 1 g TiO₂-P25 was added to the suspension and and sonicated for 30 minutes. To adjust the pH of the suspension to acidic (pH = 3), a few drops of 1 M HNO₃ were dropped on the solution until its pH is 3. Suspension in an acidic atmosphere can strengthen the composite bond [15]. The suspension was stirred with magnetic stirrer for 3 hours at 300 rpm and then were dried overnight in an oven at 110°C. The resultant solids were calcined with fixed bed reactor for 2 hours at 400°C.

2.4. Photodegradation Phenol with TiO₂-MWCNT (cocoPAS) Composite

Riau local application of Riau local suspension *B. bassiana* was carried out using a 100 ml sprayer. Each red chili plant is sprayed evenly according to the volume of spray. The application of Riau local suspension *B. bassiana* was carried out in the afternoon at 18.00 WIB The performance of the synthesized photocatalyst, TiO₂-MWCNT (cocoPAS) composite was evaluated by photodegradation experiments. All experiments were conducted in photodegradation reactor (40 cm x 50 cm x 60 cm) under six of UV Blacklight Blue (UV BLB) lamp (@10 W) irradiation for a period of 240 minute (after keeping in dark for 30 minutes in each run to reach equilibrium state). Phenol was prepared in 300 mL aquades with various initial concentration (10, 20, and 30 ppm). Then, 0,3 g TiO₂-MWCNT (cocoPAS) composite was added to phenol solution. The solution contents were kept uniformly distributed by using a magnetic stirrer in 300 rpm. Effect of degradation temperature was carried out at 30, 40, and 50°C respectively. Sample was drawn 5 mL every 30 minute

and separated from solids with centrifuge. The samples were analysed for the initial and residual concentrations of phenol by UV-visible spectrophotometer.

3. Results

3.1. Characterization of TiO₂-MWCNT (cocoPAS) Composite

Figure 1. shown morphology of TiO₂, MWCNT (cocoPAS) and TiO₂-MWCNT (cocoPAS) composite were characterized using SEM. MWCNT (cocoPAS) in the form of long tubular/cylindrical branches on TiO₂ surface. Morphology of TiO₂ is in the form of agglomerate. Figure 1 showed that the MWCNT (cocoPAS) are homogenously dispersed throughout the TiO₂ matrix [16]. So it was considered that the TiO₂-MWCNT (cocoPAS). composite could show a better photocatalytic performance.

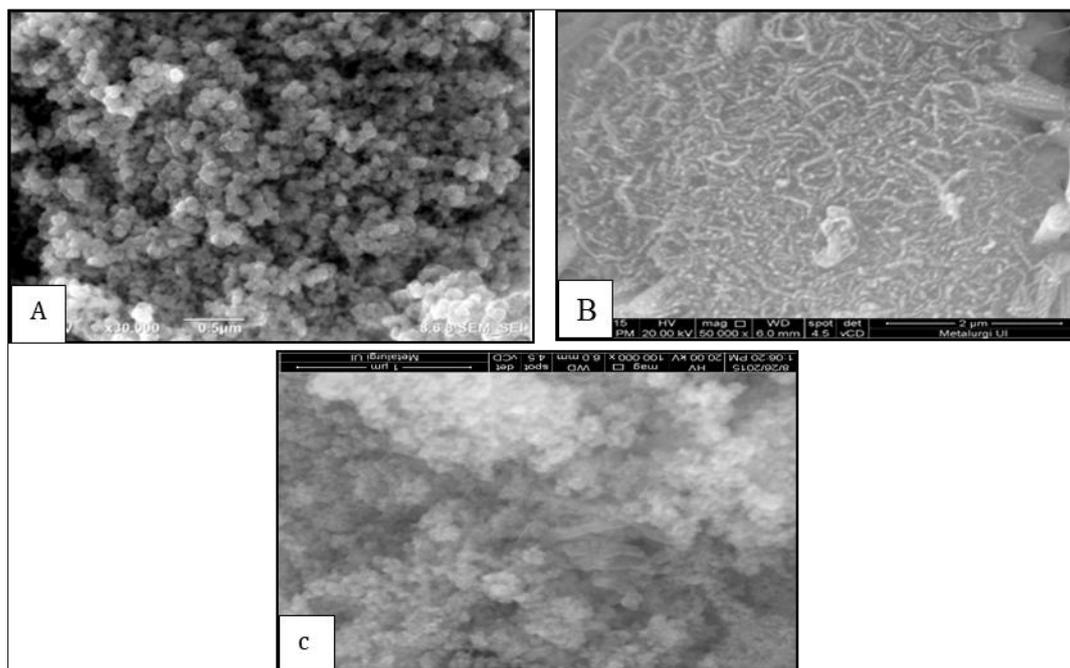


Figure 1 SEM Image of (A) TiO₂ (B) MWCNT (cocoPAS) (C) TiO₂-MWCNT (cocoPAS) Composite

FT-IR technique was applied to detect the changes in the characterized functional groups. Figure 2a shows the obtained spectrum for TiO₂ nanoparticles, in which there is an absorption band in the low frequency region (400-700 cm⁻¹), which is assigned to Ti-O and Ti-O-Ti stretching vibration of TiO₂. Other bands were observed at 1558,55 cm⁻¹ and 2339,75 cm⁻¹ which are related to Ti-OH and -OH stretch from strongly hydrogen-bonded, respectively [17]. The spectrum obtained for the carbon nanotubes (Figure 2c) show the presence of C=C stretching bonds at 1568,19 cm⁻¹, C-C at 2360,01 cm⁻¹, C=O at 1799,66 cm⁻¹, C-O at 1147,69 cm⁻¹, and C-H at 2978,92 cm⁻¹ [18]. Synthesis of TiO₂-MWCNT (cocoPAS) composite was confirmed by the existence of several carbon functional groups (C-H, C=C, and C=O) as shown in Figure 2b. A stretching of the Ti-O-C bond at 3129,64 cm⁻¹ is observed, confirming the bond of TiO₂ to the carbon nanotube structures [19].

Surface area of TiO₂ is a crucial factor in its use as photocatalyst, as all the chemical events take place at the surface. One of the benefits obtained from MWCNT doping on TiO₂ in order to expand the surface area of TiO₂ because the surface area of MWCNT is greater than TiO₂. The BET method was used to determine surface area of photocatalyst. Table 1 showed the BET data for TiO₂-MWCNT (cocoPAS) composite, TiO₂-P25, and MWCNT. The result revealed that surface area of TiO₂ was increase after being compiled with MWCNT (cocoPAS). The surface area of photocatalyst increases the photodegradation because the high surface area contains the greater number of active sites than the low surface area material. High surface area also can increase the adsorption ability of TiO₂ and expand the contact area between composite and organic compounds [20].

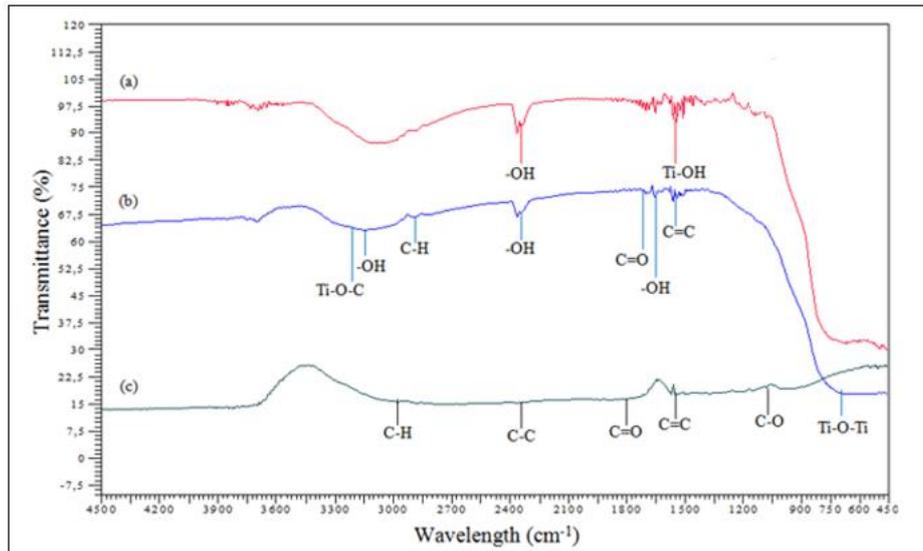


Figure 2 FT-IR Spectra of (a) (a) TiO₂ (b) TiO₂-MWCNT(cocoPAS) composite (c) MWCNT(cocoPAS)

Table 1 The BET Surface Area Data

Material	Surface Area (m ² /g)
TiO ₂	53,6 [21]
CNT	200 [21]
TiO ₂ -MWCNT (cocoPAS)	65,75

The crystalline phase of TiO₂ also influences the process of photocatalysis to degrade phenols. The mixture of anatase and rutile phases shows good photocatalytic activity [22]. The crystalline phase of TiO₂-MWCNT (cocoPAS) composite were analyzed by XRD measurements. The XRD pattern of TiO₂-MWCNT (cocoPAS) composite was shown in Figure 3 where A for anatase and R for rutile. Sharp peaks of composite in 2θ; 25,28°, 37,83°, 48,03°, 53,92°, dan 55,05° are observed that related to (101), (004), (200), (105), and (211) crystal plates in pure tetragonal anatase phase of TiO₂ (ICDD 01-072-7058). Peaks at 2θ; 27,4° belonging to the diffraction peak of (110) plane of rutile. Peak of MWCNT usually at 2θ; 26°, but carbon nanotube’s peak wasn’t shown in XRD pattern of composite may be because the low content and the low diffraction intensity of MWCNT compared to TiO₂. Therefore the main peak of anatase phase of TiO₂ at 25,28° can eliminate the main peak of a carbon nanotube at 26° [23].

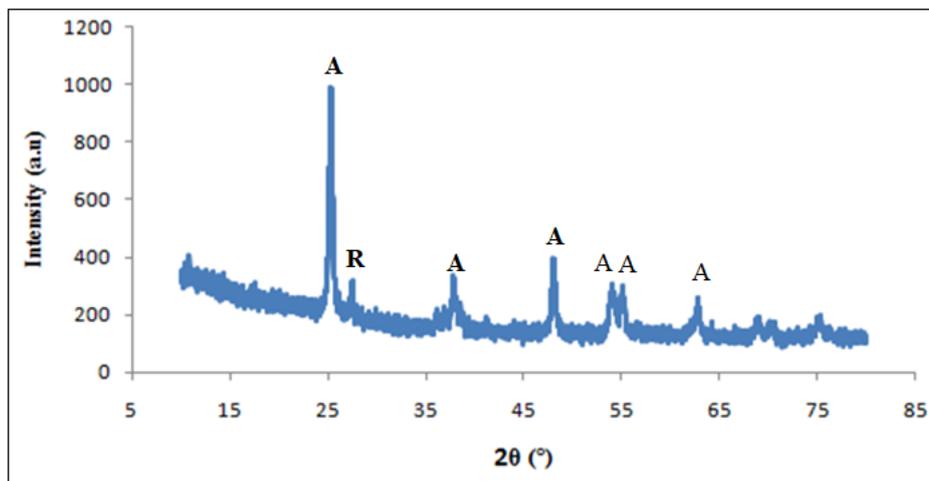


Figure 3 XRD Pattern of TiO₂-MWCNT (cocoPAS) Composite

The crystalline fraction can be determined by

$$X_R = \left(1 + 0,8 \frac{I_A}{I_R}\right)^{-1} \quad (1)$$

where X_R is rutile fraction; I_A is anatase intensity and I_R is rutile intensity that can be found in XRD results. Anatase fraction (X_A) can be determined by $X_A = 1 - X_R$. The anatase and rutile fraction of TiO_2 -MWCNT (cocoPAS) composite were 85,19% and 14,81% respectively. TiO_2 -P25 which is used for synthesise of composite contains 80% anatase and 20% rutile. Increasing anatase fraction in composite indicate that composite will have better photocatalytic performance because anatase having a higher surface adsorption capacity to hydroxyl group and lower charge carrier recombination rate than rutile [24]. However, anatase-rutile structure of TiO_2 -MWCNT (cocoPAS) composite promotes change-pair separation and inhibits recombination. The average size of crystal calculated by Scherrer equation,

$$D = \frac{k \lambda}{\beta \cos \theta} \quad (2)$$

where D is crystal size; k is a constant equal to 0,89; λ , the X-ray wavelength equal to 0,154056 nm; β , the full width at half maximum intensity (FWHM) and θ , the half-diffraction angle [25]. The average size of crystal for anatase and rutile were 18,82 nm and 26,15 nm, respectively. Smaller anatase crystal size makes anatase has a higher surface adsorption capacity than rutile.

3.2. Photodegradation of Phenol using TiO_2 -MWCNT (cocoPAS) Composite

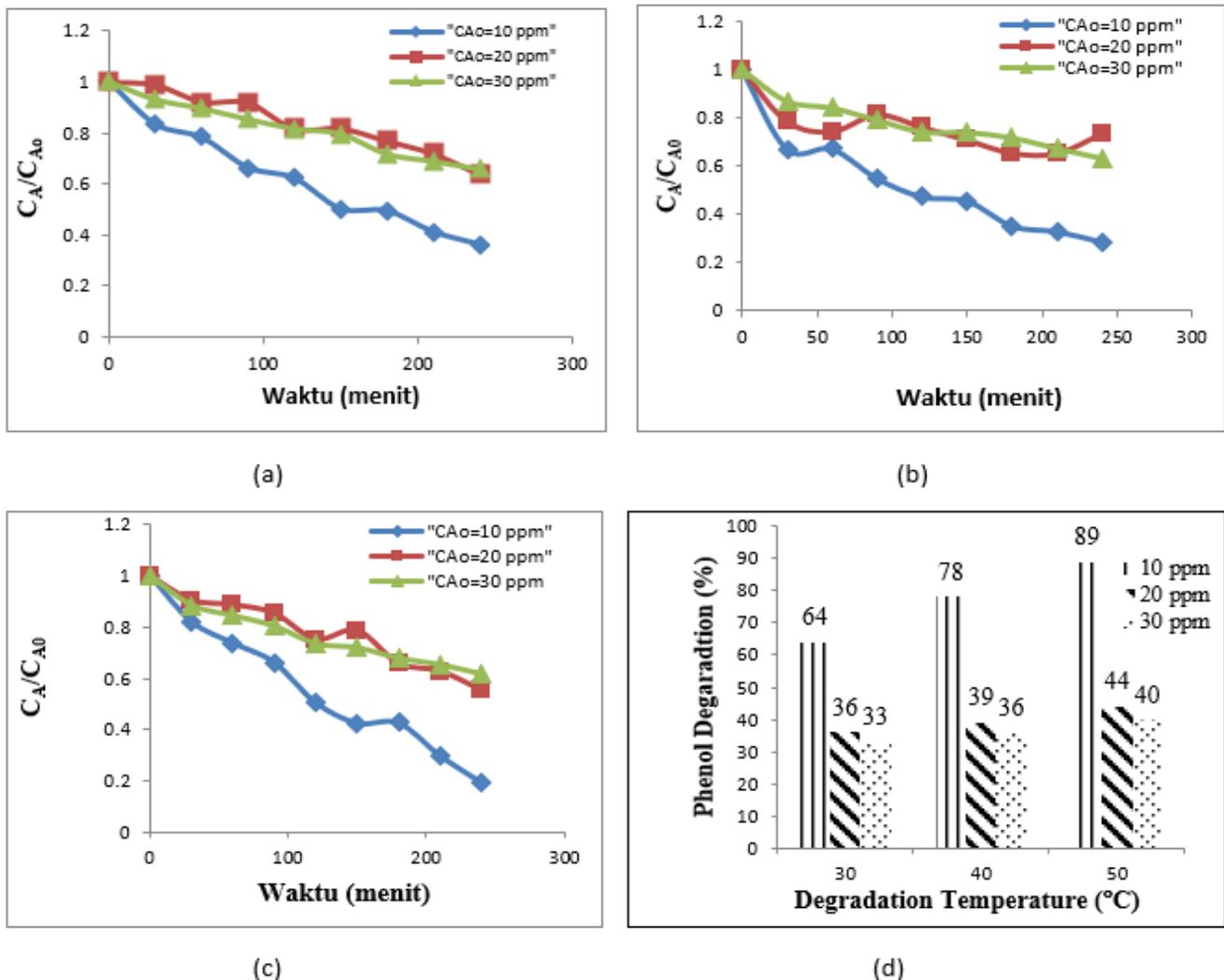


Figure 4 Effect of Initial Phenol Concentration and Degradation Temperature on Photodegradation Phenol using TiO_2 -MWCNT (cocoPAS) Composite of (a) 30 °C (b) 40 °C (c) 50 °C (d) Percent of degradation

Photocatalytic performance of TiO₂-MWCNT (cocoPAS) composite was evaluated with effect of initial phenol concentration (10, 20, and 30 ppm, respectively) and effect of degradation temperature (30, 40, and 50 °C, respectively). Figure 4 showed that increasing initial phenol concentration at constant temperature would decrease percent degradation of phenol. When the initial phenol concentration is high, the number of available active sites are decreased by phenol and major absorption of illuminated light by phenol molecules which reduced the photocatalytic performance of TiO₂-MWCNT (cocoPAS) composite. Since the intensity of irradiation light was constant, the hydroxyl radical formed on the surface of the photocatalyst were also constant, the attack of these radicals on the compound molecules decreased and simultaneously the photodegradation also decreases [26].

Figure 4 also showed that increasing degradation temperature at constant initial phenol concentration would increase percent degradation of phenol. This increase could be explained by the enhancement of the reaction rate that took place between the phenol molecules and the hydroxyl radical. Moreover, the enhancement of the degradation is probably due to the increasing collision frequency of phenol molecules [27]. Increasing temperature helps to speed up the velocity of both the hydroxyl radicals and the phenol molecules to interact with each other because the less energy of activation needed for a reaction to occur [28]. According to that explanation, the highest percentage of phenol degradation occurred at the lowest initial phenol concentration and the highest degradation temperature at the initial phenol concentration of 10 ppm and the degradation temperature at 50 °C, which was 89%.

4. Discussion

TiO₂-MWCNT (cocoPAS) composite has been synthesized with simple mixing, evaporation and drying process where MWCNT was modified with biodegradable surfactant cocoPAS. TiO₂-MWCNT (cocoPAS) composite have a larger surface area, smaller crystal size and greater anatase fraction compared to TiO₂ that caused its better performance.

The profile of variations in the initial concentration of phenol at each degradation temperature can be seen in Figure 4. The most significant decrease in phenol concentration occurred at the initial phenol concentration of 10 ppm while at the initial concentration of phenol 20 and 30 ppm there was only a slight decrease in phenol concentration. The higher the initial concentration of phenol, the lower the decrease in the concentration of phenol. This is due to the adsorption competition on the surface of TiO₂ between OH• which is formed from the OH group on the active site of TiO₂ with phenol molecules. As the initial concentration of phenol increases, the number of active sites containing OH groups on the TiO₂ surface decreases due to the adsorbed phenol [26].

TiO₂-MWCNT(cocoPAS) composite can reduce phenol concentration in various degradation temperatures. The most significant decrease in phenol concentration occurred at a degradation temperature of 50 °C. This is because the degradation temperature affects the reaction in the photocatalytic process. The decrease in the concentration of phenol which increases with increasing temperature is due to an increase in the rate of reaction between phenol and OH•. In addition, the increase in the percentage of degradation is also due to the increase in the frequency of collisions of phenol molecules as the degradation temperature increases [27].

The highest photocatalytic performance of the TiO₂-MWCNT (cocoPAS) composite was at an initial phenol concentration of 10 ppm and a degradation temperature of 50 °C, namely 89%.

5. Conclusion

We propose the determination of temperature and concentration in phenol degrading using photocatalyst of TiO₂-MWCNT (cocoPAS) composite to obtain the highest percentage of phenol degradation. The presence of MWCNT (cocoPAS) functions as an adsorbent and electron acceptor to enhance the photodegradation of phenol efficiently. The performance of the composite in degrading phenol related to the photocatalyst characteristics of the TiO₂-MWCNT (cocoPAS) composite gave a larger specific surface area. This shows that photocatalytic composites with TiO₂-MWCNT (cocoPAS) are promising for the degradation of wastewater, especially phenol. The highest photocatalytic performance from TiO₂-MWCNT (cocoPAS) composite were at 10 ppm of initial phenol concentration and 50 °C of degradation temperature is about 89% and the lowest were at 30 °C with the degradation is about 64%. This shows that the photocatalytic with the composite of TiO₂-MWCNT (cocoPAS) is promising for the degradation of wastewater.

Compliance with ethical standards

Acknowledgments

The authors would like to thank DRPM Universitas Riau and Directorate General of Higher Education (DGHE) Indonesian Ministry of National Education for the financial support of this research (Hibah) Penelitian Dasar, no. 482/UN.19.5.1.3/PT.01.03/2021.

Disclosure of conflict of interest

All authors declare there is no conflict of interest in this paper.

References

- [1] Rahmani A, Hadi R, Somayeh B. Photocatalytic degradation of phenolic compound (phenol, resorcinol and cresol) by titanium dioxide photocatalyst on ordered mesoporous carbon (CMK-3) support under UV irradiation Desalination and Water Treatment. 2019; (144): 224-32.
- [2] Moghaddam S, Zerafat MM, Sabbaghi S. Response surface methodology for optimization of phenol photocatalytic degradation using carbon-doped TiO₂ nano-photocatalyst International Journal Nano Dimension. 2018; (9): 89–103.
- [3] Safni, Mechy RW, Khoiriah, Yulizar Y. Photodegradation of phenol using N-doped TiO₂ catalyst Molekul. 2019; (14): 6-10.
- [4] Reti B, Karoly M, Andras D, Klara H. Substrate dependent photocatalytic performance of TiO₂/MWCNT photocatalysts Applied Catalysis A: General. 2014; (469): 153–8.
- [5] Wang X, Lasse S, Ren S, Stefan W, Peter H, Aref M. The influence of crystallite size and crystalinity of anatase nanoparticles on the photo-degradation of phenol Journal of Catalysis. 2014; (310): 100-8.
- [6] Shahbazi H, Alireza S, Saeed S. The effect of carbon nanotubes functionalization on the band-gap energy of TiO₂-CNT nanocomposites AIP Conference Proceedings. 2018; (1920): 0200401-4.
- [7] Kamegawa T, Ryota K, Daiki Y, Hiromi Y. Design of TiO₂-zeolite composites with enhanced photocatalytic performances under irradiation of UV and visible light Microporous and Mesoporous Material. 2013; (165): 142-7.
- [8] Gangu KK, Suresh M, Sreekantha BJ. A review on novel composites of MWCNTs mediated semiconducting materials as photocatalysts in water treatment Science of the Total Environment. 2019; (646): 1398-1412.
- [9] Li H, Yanhua Q. Dispersion, sedimentation and aggregation of multiwalled carbon nanotubes as affected by single and binary mixed surfactants Royal Society Open Science. 2019; (6): 1-9.
- [10] Kamil AM, Falah HH, Ahmed FH, Detlef WB. Preparation, characterization, and photocatalytic applications of MWCNTs/TiO₂ composite International Journal of Photoenergy. 2014; 1-8.
- [11] Lamprecht CJ, Torin H, Marina VI, Marianna F. Non-covalent functionalization of carbon nanotubes with surfactants for pharmaceutical applications- A critical mini review Drug Delivery Letters. 2011; 1: 45-57.
- [12] Zueva OS, Makshakova ON, Idiyatullin BZ, Faizullin DA. Structure and properties of aqueous dispersions of sodium dodecyl sulfate with carbon nanotubes. Russian Chemical Bulletin International Edition. 2016; (65): 1208-15.
- [13] Jiang L, Lian G. Fabrication and characterization of ZnO-coated multi-walled carbon nanotubes with enhanced photocatalytic activity Materials Chemistry and Physics. 2005; (91): 313-6.
- [14] Richards C, Mansur SM, Gordon JTT. Formulating liquid detergents with naturally derived surfactants-phase behaviour, crystallisation, and rheo-stability of primary alkyl sulfates based on coconut oil Colloids and Surfaces A: Physicochemical and Engineering Aspects. 2009; (338): 119-28.
- [15] Park K, En MJ, Hal BG, Sang ES, Chang KH. Effects of HNO₃ treatment of TiO₂ nanoparticles on the photovoltaic properties of dye-sensitized solar cells Material Letters. 2009; (63): 2208-11.
- [16] Huang X, Feng M, Liu X. Design of bristle-like TiO₂-MWCNT nanotubes to improve the dielectric and interfacial prooperties of polymer-based composite films RSC Advances. 2014; (4): 4985-92.

- [17] Shaban M, Abdallah MA, Mostafa RA. TiO₂ nanoribbons/carbon nanotubes composite with enhanced photocatalytic activity; fabrication, characterization, and application *Scientific Reports*. 2018; (8): 1-17.
- [18] Neto JOM, Carlos RB, Carlos HFS, Rene CS, Pablo AR. Synthesis, characterization and enhanced photocatalytic activity of iron oxide/carbon nanotube/Ag-doped TiO₂ nanocomposites *Journal Brazil Chemical Society*. 2017; (28): 2301-12.
- [19] Zabihi F, Mohamed RAY, Morteza E. Photocatalytic graphene-TiO₂ thin films fabricated by low-temperature ultrasonic vibration-assisted spin and spray coating in a sol-gel process *Catalysts*. 2017; (7): 1-16.
- [20] Lam S, Jin-Chung S, Abdul RM. Parameter effect on photocatalytic degradation of phenol using TiO₂-P25/Activated Carbon *Korean Journal Chemical Engineering*. 2010; (27): 1109-16.
- [21] Heltina D, Wulan PPKD, Slamet. Synthesis and characterization of titania nanotube-carbon nanotube composite for degradation of phenol *International Journal of Technology*. 2015; (6): 1137-45.
- [22] Luttrell T, Sandamali H, Janguang T, Alan K, Eli S, Matthias B. Why is anatase a better photocatalyst than rutile? – Model studies on epitaxial TiO₂ films *Scientific Reports*. 2014; (4): 1-9.
- [23] Askari MB, Zoha TB, Sahar S, AMajid S. Comparison of optical properties and photocatalytic behavior of TiO₂/MWCNT, CdS/MWCNT, and TiO₂/CdS/MWCNT *Optik*. 2018; (157): 230-9.
- [24] Zhang J, Peng Z, Jianjun L, Jiaguo Y. New understanding of the difference of photocatalytic activity among anatase, rutile and brookite TiO₂ *Physical Chemistry Chemical Physics*. 2014; (16): 20382-6.
- [25] Behanajady MA, Nasser M, Mohammad S, Hadi E, Arezoo Z. The effect of particle size and crystal structure of titanium dioxide nanoparticles on the photocatalytic properties *Journal of Environmental Science and Health Part A*. 2008; (43): 460-7.
- [26] Laofi NA, Tassalit D, Bentahar F. The degradation of phenol in water solution by TiO₂ photocatalysis in a helical reactor *Global NEST Journal*. 2008; (10): 404-18.
- [27] Shawabkeh RA, Omar AK, Gasan IB. Photocatalytic degradation of phenol using Fe-TiO₂ by different illumination sources *International Journal of Chemistry*. 2010; (2): 10-18.
- [28] Gajbhiye SB. Photocatalytic degradation study of methylene blue solutions and its application to dye industry effluent *International Journal of Modern Engineering Research*. 2012; (2): 1204-8.