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Performance of TiO₂/Al₂O₃/carbon nanotube nanocomposite on the photocatalytic degradation of metamifop

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Abstract. The photocatalyst of TiO₂/Al₂O₃/CNT nanocomposite was prepared by hydrothermal process. Its performance was evaluated based on the efficiency in degrading metamifop, an active ingredient in the commercial formulation herbicide. The effect of initial concentration metamifop, the dosage of photocatalyst used during photocatalytic degradation of metamifop and the effect of air flow rate were investigated for the evaluation of its performance. The highest percentage degradation of 10 mg/l metamifop obtained from this study was 95.0% using 20 mg of TiO₂/Al₂O₃/CNT nanocomposite photocatalyst with the air flow rate of 2 l/min. The prepared photocatalyst can be potentially used in environmental application.

1. Introduction

The molecular structure of metamifop (Figure 1) is one of the active ingredients in the herbicide formulation and widely used to control perennial and annual grass in a paddy field where it is able to control. Nevertheless, if the consumption of this herbicide is being used excessively along with the poor management in the agricultural system, it is indeed troubling the environment in the future. Metamifop persistence, hardly to be removed and may induce bioaccumulation where could end up in natural water body [1] through spray drift, surface run-off and by leaching from soil and vegetation [2]. Due to this it is a need to find a good treatment from remediation. Most of the conventional techniques (either to treat heavy metal, oil waste, or pesticide) such as biological treatment or phytoremediation [3] require a large system and very slow process whereas consumption of biosorbent or activated carbon [4-5] and chitosan [6] may requires a large amount of adsorbents. In order to degrade metamifop, Advanced Oxidation Process (AOP) can be a reliable treatment for solving water contamination issues and currently photocatalytic degradation with nanomaterials can be a promising method [7].

Titanium dioxide has been widely used as an efficient photocatalytic material in decomposing the pollutant in water body [8] and its usage in powder foam can contribute to the major drawback as it difficult to recover [9] after treatment thus in respond of this, immobilizing TiO₂ on supporter such as carbon nanotube (CNT) can be one of the solution. Furthermore it can reduce the band gap energy of



TiO₂ considerably from 3.2 to 2.65 eV [10]. CNT also a good reinforcement material for Al₂O₃ where some study stated that the use of Al₂O₃ could reduce the band gap of TiO₂ as well [11-12]. Moreover Al₂O₃ has high melting point, high thermal conductivity, and good thermal expansion hence can be potentially applied in environmental or high temperature application [11] Due to this the hydrothermal method is being used in the production of the TiO₂/Al₂O₃/CNT photocatalyst in this study and evaluate its performance in degrading metamifop. Furthermore hydrothermal method contributed more uniform distribution of particles and less agglomeration compared to the sol-gel method hence some study stated on the better photocatalytic activity [13].

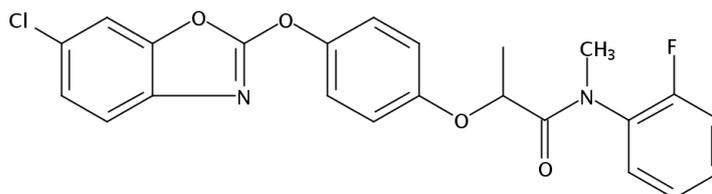


Figure 1. The molecular structure of metamifop

2. Experiment

2.1. Preparation of TiO₂/Al₂O₃/CNT nanocomposite

The raw materials used to prepare TiO₂/Al₂O₃/CNT were TiO₂ powder (>99.5% purity, average particle size > 21 nm) and Al₂O₃ powder (>99.9% purity, average particle size >20 μm) and carbon nanotube which bought from Sigma Aldrich. The composition ratio of TiO₂: Al₂O₃: CNT used in this study was 70:29:1. The mixture composition was then premixed using ball milling for an hour. Next, about 100 ml of NaOH (1 M) was added to the mixture and stirred for 30 minutes later proceed to the hydrothermal process at 200°C in an autoclave for 24 hours. Later, the photocatalyst was washed using 200 ml of 0.1 M HCl. The washing process was continued by distilled water until washing solution reached pH 7. The prepared photocatalyst was obtained and dried 24 hours in the oven at 80°C. The photocatalytic performance of TiO₂/Al₂O₃/CNT photocatalyst is evaluated in degrading metamifop solution.

2.2. Characterization of the prepared photocatalyst TiO₂/Al₂O₃/CNT nanocomposite

The prepared photocatalyst of TiO₂/Al₂O₃/CNT nanocomposite was characterized using XRD to determine the phase identification of TiO₂ doped Al₂O₃ and CNT nanocomposite. The XRD was performed using Bruker D2 Phaser with Cu Kα radiation (λ= 0.154 nm) with the step size was 0.02° and the range of 2θ angle was between 10° to 80°. The DIFFRAC.EVA software was used for the peak matching that refers to crystal structure and qualitative analysis.

2.3. Photocatalytic performance of TiO₂/Al₂O₃/CNT nanocomposite in degrading metamifop

The performance of TiO₂/Al₂O₃/CNT nanocomposite in degrading metamifop was studied. In each experiment, 250 ml solutions containing known concentration of metamifop (10 mg/l) with 10 mg of photocatalyst were added into the conical flask which contains a magnetic bar. The conical flask was placed on the magnetic stirrer and put in the chamber that contains a UV lamp. The chamber was then covered with aluminium foil to avoid UV light dissipation. The photocatalytic degradation process of metamifop was conducted for 3 hours and the samples were collected for every 30 minutes. The performances of the produced photocatalyst were tested on the effect of the initial concentration of the pollutant, photocatalyst loading and the flow rate of the air used. The collected samples were analyzed using UV-Vis spectrophotometer HACH DR6000 at the wavelength of 500 nm. All experiment was conducted without the usage of air whereas for the experiment on the effect of air flow rate, about 2

l/min of air flow was used. All experiments were repeated for three times and carried out under identical conditions.

3. Result and discussion

3.1. XRD result

According to the XRD result shown in Figure 2, the peak for TiO_2 powder showed three major peaks at 25.30° , 47.95° and 62.64° where all peaks were assigned to anatase TiO_2 and no peak of brookite or rutile of TiO_2 were visible in the XRD chromatogram. The crystal system for TiO_2 was tetragonal whereas for Al_2O_3 was hexagonal structure with identification peaks of Al_2O_3 were at 24.45° , 35.04° , 43.26° and 57.51° . The XRD pattern of photocatalyst $\text{TiO}_2/\text{Al}_2\text{O}_3/\text{CNT}$ nanocomposite shown in Figure 2(c) however revealed on the small shifting to the right indication on the TiO_2 structure changes when doping with Al_2O_3 .

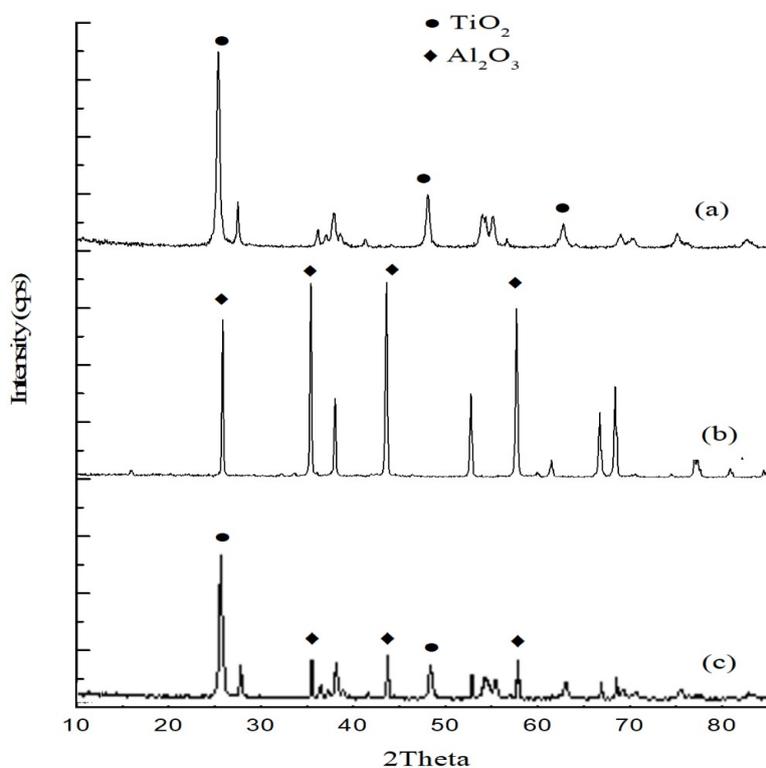


Figure 2. The XRD chromatogram of the (a) TiO_2 , (b) Al_2O_3 and (c) photocatalyst $\text{TiO}_2/\text{Al}_2\text{O}_3/\text{CNT}$ nanocomposite

3.2. The effect of initial concentration of metamifop

According to Figure 3, the degradation of metamifop (5 mg/l) under 3 hours UV irradiation was 84.5% in the presence 10 mg of $\text{TiO}_2/\text{Al}_2\text{O}_3/\text{CNT}$ nanocomposite photocatalyst. Once the initial concentration of metamifop was increased from 5 mg/l to 10 mg/l, the percentage degradation was slightly reduced to 83.6% and the value was not significant. The degradation of metamifop was decreased as the initial concentration of metamifop was increased from 5 to 10 mg/L. As the metamifop concentration was increased, the molecules of metamifop were adsorbed on the surface of the photocatalyst. This could result on the fewer active sites available hence reducing the production of $\bullet\text{OH}$ (hydroxyl radical) [14].

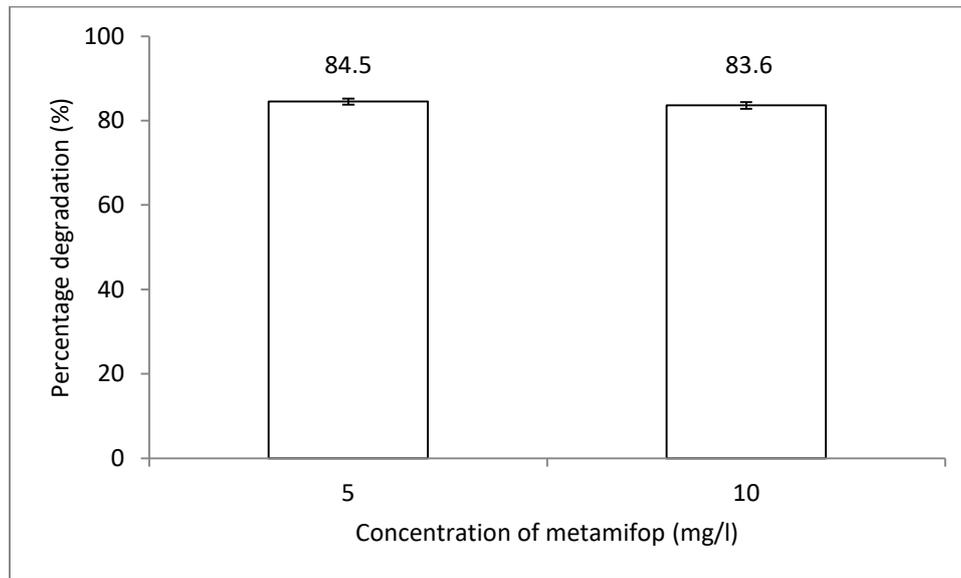
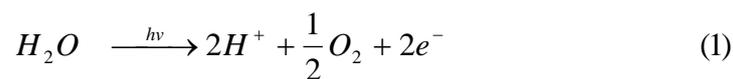


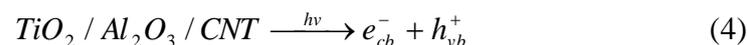
Figure 3. The photocatalytic degradation of 5 and 10 mg/l of metamifop in the presence of UV light

3.3. The effect of photocatalyst loading in degrading metamifop

The experiments were conducted using 10 and 20 mg of $\text{TiO}_2/\text{Al}_2\text{O}_3/\text{CNT}$ nanocomposite photocatalyst for 10 mg/l of metamifop solution as the working solution. The Figure 4 shown that 34.5% of percentage degradation occurred in the absence of photocatalyst. This due to the photolysis of water by UV light which shown in equation 1 producing electron. The produced electron later being consumed by oxygen generated from photolysis of metamifop (Figure 1) resulted on the production of superoxide radical anions (equation 2) and species such as $\bullet\text{HO}_2$ (equation 3). The presence of these radical species may be contributed to the one of the reasons for the obtained percentage degradation although no photocatalyst presence in the solution [7] [15].



The percentage degradation of 10 mg/l of metamifop with 10 mg of photocatalyst shown 83.6% and further increment occurred (86.0%) once the photocatalyst loading was increased to 20 mg. The generated hole-electron pairs (equation 4) increased as the loading of photocatalyst increased where this contributed to oxidation and reduction of metamifop in the solution [7].



The conducted experiment from previous researchers such as Shifu and Yunzhang [15] and Devipriya and Yesodharan [16] proved on the promotion of electron from valence band to the conduction band then created holes at the valence band. They also reported on that the $\bullet\text{OH}$ were formed from the hole and later reacting with the water or OH^- thus it is assumed that photocatalytic

degradation of metamifop in this study could be occurred on the surface of the $\text{TiO}_2/\text{Al}_2\text{O}_3/\text{CNT}$ [15-16].

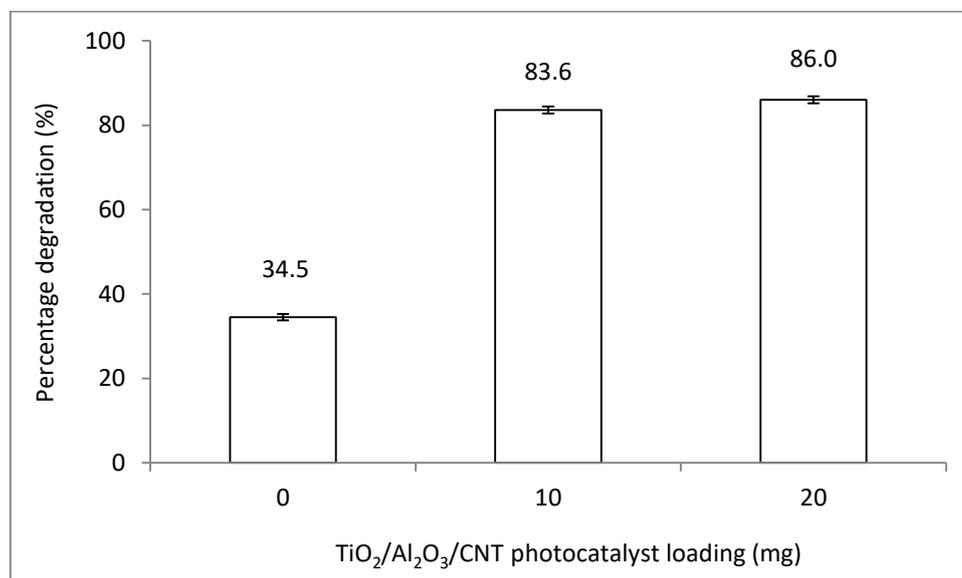


Figure 4. The photocatalytic degradation of 10 mg/l of metamifop using 10 and 20 mg of photocatalyst

3.4. The effect of air flow and photocatalyst loading in degrading metamifop

The usage of air flow instead of bubbling the solution (along the agitation by magnetic stirrer) it also enhanced the photocatalytic degradation process. The percentage degradation of 10 mg/l metamifop was increased to 91.5% and 95.0% once the air flow was supplied to the photoreactor (Figure 5). The increment was due to the formation of hydrogen peroxide (H_2O_2). The H_2O_2 was formed by reaction of $\bullet\text{O}_2^-$ (from equation 2) and $\bullet\text{HO}_2$ (from equation 3) and ultimately formed $\bullet\text{OH}$ and degraded the metamifop. Mineralization (CO_2 and H_2O products) was said to be achieved if 100% degradation obtained. This can be simplified by equation 5 - 7 [17-18].

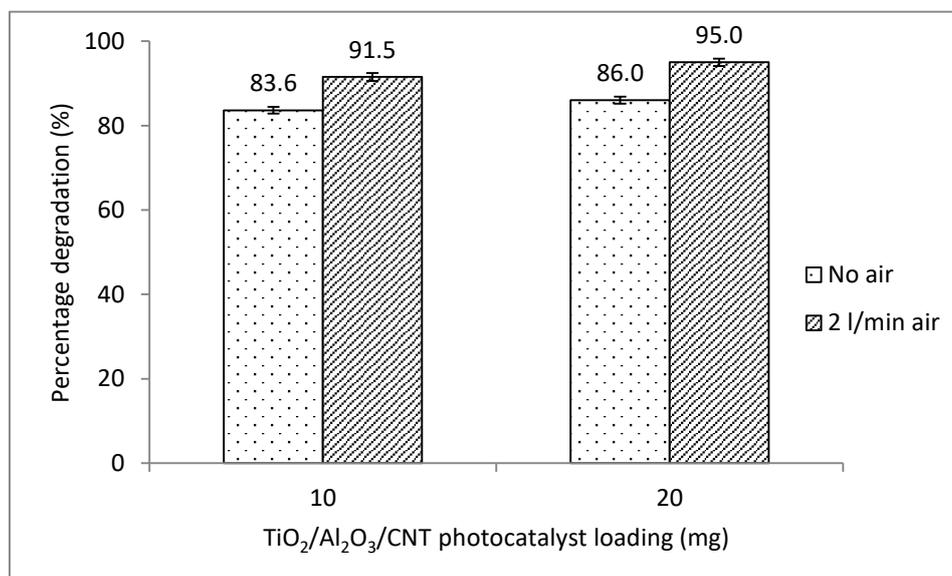
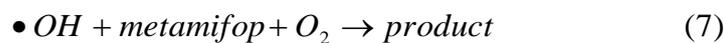
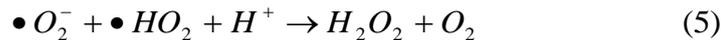


Figure 5. Photocatalytic degradation of 10 mg/l of metamifop using 10 and 20 mg of photocatalyst in the presence of 2 l/min of air flow

The air flow in the photoreactor during photocatalytic degradation also help in trapping the photoinduced e_{cb}^- on the photocatalyst surface which acting as electron acceptor as well resulted on another superoxide radical anions (equation 8) [7][9][15][18].



4. Conclusion

From this study, it can be concluded that the prepared TiO₂/Al₂O₃/CNT nanocomposite photocatalyst using hydrothermal method successfully been applied in treating metamifop. Its performance shown the degradation efficiency up to 95.0% when 20 mg of photocatalyst degraded 10 mg/l metamifop in the presence of 2 l/min air flow within 3 hours UV irradiation.

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References

- [1] Xia X *et al* 2016 Sci. Rep. **6** 34066
- [2] Suman S *et al* 2018 B. Environ. Contam. Tox. **100** 1
- [3] Najaa Syuhada M T *et al* 2019 J. Teknol. **81** 17-23
- [4] Voon M X and Mohd Ghazi R 2019 AIP Conference Proceedings **2068** 020038
- [5] Najaa Syuhada M T *et al* 2017 Malaysian J. Anal. Sci. **21** 1101-1100
- [6] Mohd Ghazi R and Zakaria Z 2011 *Bacteria in Environmental Biotechnology: The Malaysian Case Study-Analysis, Waste Utilization and Wastewater Remediation* ed Ahmad W A, Zakaria Z and Zakaria Z A (USA: Nova Science Publishers Inc.) chapter 4 pp 53- 69
- [7] Nik Yusof N R *et al* 2019 AIP Conference Proceedings **2068** 020034
- [8] Ali *et al* 2015 J. Mater. Res. Technol. **4** 126-132
- [9] Nik Yusoff N R 2013 *Photolytic degradation of acephate, glyphosate and malathion* PhD Thesis (London: Brunel University) chapter 2 pp 30
- [10] Taleshi F 2015 J. Appl. Spectrosc. **82** 303-306
- [11] Mohamad Isa N F *et al* 2018 IOP Conf. Series: Mater. Sci. Eng. **440** 012017
- [12] Barajas-Ledesma E *et al* 2010 Mater. Sci. Eng. B **174** 71-73
- [13] Koozegar Kaleji B and Gorgani M 2020 Int. J. Environ. An. Ch. **100** 1-16
- [14] Chung L W *et al* 2011 J. Nanotechnol. **2011** 1-9
- [15] Shifu C and Yunzhang L 2007 Chemosphere **67** 1010-1017
- [16] Devipriya S and Yesodharan S 2005 Sol. Energy Mater. Sol. Cells **86** 309-348
- [17] Rahman M A *et al* 2006 J. Adv. Oxid. Technol. **9** 103-1-9
- [18] Ahmed S *et al* 2011 J. Environ. Manage. **92** 311-330