Effect of photocatalyst dosage and air loading in photocatalytic degradation of metamifop

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Abstract. Excessive used of agrochemical product such as metamifop herbicide, besides having high crop yield production, it has resulted in runoff which later affected groundwater and give negative impact on the environment. Photocatalytic degradation is one of the Advanced Oxidation Process where it creates hydroxyl radicals (•OH) in the presence of UV light. Performance of TiO₂/Al₂O₃/carbon nanotube (CNT) (10 mg and 20 mg) which was produced through a hydrothermal process was applied to degrading 5 ppm and 10 ppm of metamifop. The performance of TiO₂/Al₂O₃/CNT to degrade metamifop was evaluated statistically via a two-way analysis of variance (ANOVA) followed by a post-hoc Turkey’s test. The average performance of photocatalytic degradation gave a significant result at confident level of 0.05 hence the null hypothesis (H₀) was rejected. The best performance was occurred in degrading 5 ppm of metamifop using 20 mg of TiO₂/Al₂O₃/CNT photocatalyst in the presence of air (2L/min) which resulted in 95.26% of percentage degradation. The addition of air assisted the photocatalytic degradation process from 84.54% to 92.44% and 83.62% to 91.47% when 10 mg of photocatalyst was used to degrade 5 ppm and 10 ppm of metamifop, respectively. When 20 mg of TiO₂/Al₂O₃/CNT photocatalyst was applied in degrading 5 ppm and 10 ppm metamifop, the percentage degradation increased from 86.94% to 95.26% and 85.88% to 94.62%, respectively when photocatalytic degradation was conducted in the absence of air to the presence of air. The inferential results show a significant difference in average performance of TiO₂/Al₂O₃/CNT photocatalyst and concentration of metamifop solution. However, there is no interaction effect between dosages of photocatalyst used with consumption of air in degrading metamifop. The study also proved that the produced photocatalyst was performed very well and suitable to be used in degrading metamifop herbicide.

1. Introduction

Metamifop is a herbicide that use to control the weeds and can bio-accumulates in crops and may leading to surface or groundwater contamination [1, 2]. Hence there is a concern to find a good treatment method for this kind of herbicide. Most of the technique such as phytoremediation [3], adsorption using activated carbon [4], consumption of zeolite [5], chemical coagulant [6] have been adopted. Some effective and some need to be paired with another treatment. Another promising and reliable method is using photocatalyst for solving water contamination issues. The application of titanium dioxide has been widely use and it is very powerful for generating hydroxyl radical (•OH), which responsible in
degrading any pollutants [7]. Nevertheless it is in the powder foam which later difficult to recover back. Hence, immobilization of TiO₂ on supporter such as alumina and carbon nanotube (CNT) is necessary. Hydrothermal method is a fast technique to produce photocatalyst. Moreover, it can control the morphology of the synthesized nanocomposite photocatalyst hence sustaining its performance in degrading pollutants. Furthermore, it is noticed that photocatalytic property of photocatalyst can be improved by changing morphologies and doping of element [8]. The experimental condition such as the photocatalyst dosage use, the presence of oxidant such as air, the irradiation time and the ultraviolet light intensity can significantly affect the performance of the produced photocatalyst [8, 9].

2. Materials and Methods

2.1 Preparation of TiO₂/Al₂O₃/CNT Nanocomposite Photocatalyst

The raw material used to prepare TiO₂/Al₂O₃/CNT nanocomposite photocatalyst were TiO₂ powder (>99.5% purity, average particle size > 21 nm), Al₂O₃ (>99.9% purity, average particle size >20 μm) and carbon nanotube were purchased from Sigma Aldrich. The photocatalyst nanocomposite was prepared similar to the previous study [2] but with a slight modification of the ratio, to wit, the ratio of TiO₂ to alumina and CNT was 70:29:1. Prior to conducting the hydrothermal method, the sample was premixed using ball milling for one hour. Then, 100 ml aqueous solution consisting of 1M NaOH and water were added to the mixture. The mixture was stirred for 30 minutes and subjected to hydrothermal treatment at 200°C for 24 h in an autoclave. Then, the sample was washed with both 200 ml HCl (0.1 M) and distilled water. The sample was dried in oven at 80°C for 24 hour duration.

2.2 Characterization of the Prepared Photocatalyst

The morphology of TiO₂/Al₂O₃/CNT nanocomposite was observed via optical microscope images, Jenoptik Metallurgical microscope model MT8100. A 20X magnification was used in this analysis. The software ProgRes® CT3 was used to analyze the morphology of the produce photocatalyst.

2.3 Photocatalytic Degradation Process

The performance of the produced photocatalyst, TiO₂/Al₂O₃/CNT nanocomposite on the degradation of metamifop was studied. The photocatalytic degradation process of metamifop solution was conducted under irradiation of UV light.

A photocatalytic degradation system was assembled by placing two conical flasks containing a known concentration of metamifop (5 ppm and 10 ppm) separately, in a laminar flow chamber containing UV lamp. The magnetic bar was placed in each conical flask to stir the solution. The chamber was covered with aluminium foil in order to concentrate the UV irradiation and to avoid dissipation. For the warm up phase, the UV lamp was turned on for 10 minutes preceding the experiment. Ten and 20 mg of TiO₂/Al₂O₃/CNT nanocomposite photocatalyst were used. The experiment was repeated for the effect of air loading where the flow rate of air was adjusted to 2 L/min which produced by air pump and was connected with a silicon tube to the sample solution. All experiments were performed in triplicate (n=3).

The concentrations of the degraded metamifop solution were measured using HACH DR6000 UV-Vis Spectrophotometer (USA) that was equipped with quartz cuvettes of 1 cm light path. The wavelength used was at 500 nm with the visible light source from a gas-filled tungsten and ultraviolet source from deuterium lamp.

3. Results and Discussion

3.1 Characterization of TiO₂/Al₂O₃/CNT nanocomposite photocatalyst

The produced photocatalyst was observed under optical microscope which shown in Figure 1. It was indicated that the hydrothermal process that involved in the photocatalyst production was successful.
3.2 Effect of photocatalyst loading

The performance of TiO$_2$/Al$_2$O$_3$/CNT photocatalyst in degrading 5 ppm and 10 ppm metamifop was shown in Figure 2. It showed that 54.3% and 34.5% of percentage degradation occurred in the absence of photocatalyst, respectively. This could be due to the presence of •O$_2^-$ and •HO$_2$ radicals resulted from photolysis of water by ultraviolet light [2, 10, 11] although no photocatalyst presence. As the addition of 10 mg of photocatalyst was added to each 5 ppm and 10 ppm of metamifop solution, the percentage degradation was increased to 84.5% and 83.6%, respectively. Further increment in percentage degradation was obtained when 20 mg of photocatalyst was used to degrade each 5 ppm and 10 ppm metamifop where the degradation values were 86.9% and 86.0%, respectively. The increment of percentage degradation value was occurred as the photocatalyst loading was increased where this being contributed through oxidation and reduction on the surface of the photocatalyst [12].

The result of two-way analysis of variance ANOVA has shown that the dosage of photocatalyst used and the concentration of metamifop solution has a significant interaction in the photocatalytic degradation treatment with F-value 76.494 as shown in Table 1. The presence of photocatalyst in the metamifop solution was greatly significant; however, the consumption either used 10 mg or 20 mg of photocatalyst in degrading metamifop was not significant at significance level 0.05 but can still be accepted at significance level 0.1 (Table 2).

Figure 1. The optical images of (a) TiO$_2$, (b) Al$_3$O$_3$, (c) CNT and (d) photocatalyst of TiO$_2$/Al$_2$O$_3$/CNT nanotube nanocomposite.
Figure 2. The effect of photocatalyst loading on the degradation of 5 ppm and 10 ppm metamifop under the irradiation of UV light.

Table 1. The Two-way ANOVA of photocatalyst-metamifop interaction.

| Source                      | Sum of Squares | degree of freedom | Mean Square | F       | P-value |
|-----------------------------|----------------|-------------------|-------------|---------|---------|
| Corrected Model             | 7269.701*      | 5                 | 1453.940    | 629.540 | .000    |
| Intercept                   | 92385.511      | 1                 | 92385.511   | 40001.905 | .000    |
| Photocatalyst               | 6679.697       | 2                 | 3339.849    | 1446.117 | .000    |
| Concentration               | 236.676        | 1                 | 236.676     | 102.478  | .000    |
| Photocatalyst * Concentration | 353.328     | 2                 | 176.664     | 76.494   | .000    |
| Error                       | 27.714         | 12                | 2.310       |         |         |
| Total                       | 99682.927      | 18                |             |         |         |
| Corrected Total             | 7297.416       | 17                |             |         |         |

a. R Squared = .996 (Adjusted R Squared = .995)
Table 2. The Turkey’s Test for post-hoc analysis to determine which specific usage of 10 mg and 20 mg of photocatalyst are given significant different.

| (I) photocatalyst | Mean Difference (I-J) | Std. Error | P-value | 95% Confidence Interval |
|-------------------|------------------------|------------|---------|-------------------------|
| UV + 0 mg photocatalyst | -39.6517*              | .87741     | .000    | -41.9925 -37.3109       |
| UV + 20 mg photocatalyst | -41.9783*              | .87741     | .000    | -44.3191 -39.6375       |
| UV + 10 mg photocatalyst | 39.6517*               | .87741     | .000    | 37.3109 41.9925         |
| UV + 20 mg photocatalyst | -2.3267                | .87741     | .051    | -4.6675 0.0141          |
| UV + 10 mg photocatalyst | 41.9783*               | .87741     | .000    | 39.6375 44.3191         |
| UV + 10 mg photocatalyst | 2.3267                 | .87741     | .051    | -0.0141 4.6675          |

*The mean difference is significant at the 0.05 level.

3.3 Effect of air loading
The assistance of 2 L/min of air flow in the photocatalytic degradation of metamifop was observed. It found that 10 mg of TiO$_2$/Al$_2$O$_3$/CNT was able to increase the degradation of 5 ppm and 10 ppm metamifop from 84.5% to 92.4% and 83.6% to 91.5%, respectively. Similar trend of increment also occurred when 20 mg of photocatalyst was applied (Figure 2). The highest percentage degradation was 95.0% when 5 ppm of metamifop was treated in the presence of air flow. The significant increment values were then being proof by using two-way analysis of variance, ANOVA and the result shows that there is no significant different in interaction of those mentioned factors on photocatalyst dosage used and air flow loading at the level of significance 0.05, however it significant different still can be accepted at significance level 0.1, as shown in Table 3.

Table 3. The Two-way ANOVA of photocatalyst-metamifop interaction.

| Source                  | Sum of Squares | degree of freedom | Mean Square | F       | P-value |
|-------------------------|----------------|------------------|-------------|---------|---------|
| Corrected Model         | 451.657*       | 7                | 64.522      | 52.833  | .000    |
| Intercept               | 191593.205     | 1                | 191593.205  | 156883.405 | .000   |
| Photocatalyst           | 446.717        | 3                | 148.906     | 121.929 | .000    |
| Concentration           | 4.797          | 1                | 4.797       | 3.928   | .065    |
| Photocatalyst *         | .143           | 3                | .048        | .039    | 989     |
| Concentration           | 19.540         | 16               | 1.221       |         |         |
| Total                   | 192064.402     | 24               |             |         |         |
| Corrected Total         | 471.197        | 23               |             |         |         |

a. R Squared = .996 (Adjusted R Squared = .995)
Figure 3. The effect of air loading on the photocatalytic degradation of 5 ppm and 10 ppm metamifop using 10 mg and 20 mg of TiO$_2$/Al$_2$O$_3$/CNT photocatalyst.

The presence of air flow in the photoreactor has helped in production of more hydroxyl radical (•OH) through superoxide radical anions. The more dosage of photocatalyst used has generated more electron-hole (equation (1)), hence the presence of air in the photoreactor trapped the photoinduced $e^{-}_{cb}$ on the photocatalyst surface which acting as electron acceptor. All these contributed to the photocatalytic degradation of metamifop which shown by the following equations [2, 10, 11, 13]:

$$TiO_2/Al_2O_3/CNT \xrightarrow{hv} e^{-}_{cb} + h^{+}_{vb}$$ (1)
$$O_2 + e^{-}_{cb} \rightarrow \bullet O_2^{-}$$ (2)
$$\bullet O_2^{-} + \bullet HO_2 + H^+ \rightarrow H_2O_2 + O_2$$ (3)
$$H_2O_2 \xrightarrow{hv} 2\bullet OH$$ (4)
$$\bullet OH + metamifop + O_2 \rightarrow product$$ (5)

4. Conclusion
The study shown that the TiO$_2$/Al$_2$O$_3$/CNT photocatalyst nanocomposite has been successfully produced using hydrothermal method. The best performance was occurred in degrading 5 ppm of metamifop using 20 mg of produced photocatalyst in the presence of air (2L/min) which resulted in 95.26% of percentage degradation.
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