

Photocatalytic degradation of glyphosate using TiO₂/Al₂O₃/CNT

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Abstract. Excessive use of glyphosate in agriculture has a negative impact on the environment because it causes runoff, which affects water sources and causes pollution. Advanced Oxidation Process (AOP) is the method for resolving water contamination concerns, and photocatalytic degradation using TiO₂/Al₂O₃/CNT nanocomposites has been observed to be a reliable solution for degrading glyphosate. The photocatalyst of TiO₂/Al₂O₃/CNT nanocomposite was prepared using various ratios which were 70:20:10, 70:29:1 and 70:30:0. These photocatalysts TiO₂/Al₂O₃/CNT were prepared using hydrothermal process. The prepared TiO₂/Al₂O₃/CNT photocatalyst nanocomposite has been applied to degrade glyphosate in order to assess its performance. Hence, the effect of initial glyphosate concentration and amount of photocatalyst used during photocatalytic degradation of glyphosate were investigated. This study found that 20 mg of 70:30:0 ratio TiO₂/Al₂O₃/CNT nanocomposite photocatalyst gave the highest percentage degradation of 5 mg/L of glyphosate which was 84.9%. The lowest degradation percentage for 5 mg/L of glyphosate was 68.2% using the 5 mg of ratio 70:20:10 TiO₂/Al₂O₃/CNT nanocomposite photocatalyst. Finally, the prepared photocatalyst was beneficial in degrading herbicide.

1 Introduction

Humans and aquatic wildlife will be impacted by the water contamination brought on by agrochemicals. Water that has been contaminated should not be consumed by anyone. Agrochemical runoff into water bodies can also contribute to eutrophication, a condition that develops when the body of water becomes overflowing with minerals like nitrogen and phosphorus that encourage the growth of algae [1]. Glyphosate is an active element in herbicide formulations used in this study to suppress weeds. It can bioaccumulate in crops and potentially contaminate surface or groundwater [2-3]. This raises the issue of finding an effective herbicide treatment strategy. Many techniques have been used including phytoremediation [4], chemical coagulant [5], consumption of biosorbents [6] and polymer-derived ceramic aerogels [7]. Water contamination problems may be resolved with the Advanced Oxidation Process (AOP) through photocatalytic degradation using nanomaterials.

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This was supported by our previous study on degrading another herbicide, metamifop using photocatalyst [2]. Although TiO_2 has been widely employed as a highly effective photocatalytic material in the degradation of pollutants in water bodies [8], its use in powder foam has the substantial drawback of being difficult to recover. Immobilising TiO_2 on a support such as a carbon nanotube (CNT) and alumina (Al_2O_3) may be one answer to this problem. Additionally, CNT serves as an excellent reinforcement material for Al_2O_3 besides, capable to reduce the band gap of TiO_2 [2]. The $\text{TiO}_2/\text{Al}_2\text{O}_3/\text{CNT}$ photocatalyst in this study is made using the hydrothermal approach because Al_2O_3 has a high melting point, strong thermal conductivity, and good thermal expansion properties [9]. It is anticipated that the hydrothermal approach will lessen aggregation for effective photocatalytic activity [10].

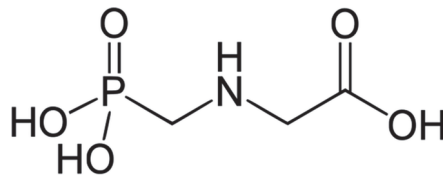


Fig. 1. Formula structure of glyphosate.

2 Experiment

2.1 Preparation of $\text{TiO}_2/\text{Al}_2\text{O}_3/\text{CNT}$ nanocomposite

The TiO_2 powder (>99.5% purity, average particle size > 21 nm), Al_2O_3 powder (>99.9% purity, average particle size >20 μm) and carbon nanotube were bought from Sigma Aldrich. The composition ratios of TiO_2 : Al_2O_3 : CNT used in this study were 70:30:0, 70:29:1 and 70:20:10. The ratios selection were based on our previous study [2]. Ball milling was used to combine the mixture components for an hour. After stirring the mixture for 30 minutes, 100 mL of NaOH (1 M) was added, and then the mixture underwent a 24-hour hydrothermal procedure at 200°C in an autoclave. Later, 200 ml of 0.1 M HCl was used to wash the photocatalyst. Until the washing solution reached pH 7, the washing process was continued using distilled water. The prepared photocatalyst was acquired and allowed to dry for 24 hours at 80°C in the oven. In order to degrade glyphosate solution, the photocatalytic efficacy of the generated photocatalyst is assessed. This methodology was used in our earlier investigation [2].

2.2 Photocatalytic performance of $\text{TiO}_2/\text{Al}_2\text{O}_3/\text{CNT}$ nanocomposite in degrading glyphosate

The performance of 70:30:0 ratio of $\text{TiO}_2/\text{Al}_2\text{O}_3/\text{CNT}$ nanocomposite in degrading glyphosate was studied. In each experiment, about 500 ml of 5 mg/L of glyphosate solution was poured into a beaker with a magnetic bar and placed on a magnetic stirrer. The experimental set was placed under a UV diode that located in a box chamber shown in Figure 2, so that the UV radiation was concentrated to the sample only. The glyphosate photocatalytic degradation process was carried out for three hours, with samples being taken every 30 minutes. The effects of the initial glyphosate concentration (5 mg/L and 10 mg/L) and the amount of photocatalyst utilised (10 mg, 15 mg, and 20 mg) during the photocatalytic degradation process were studied in terms of how well the produced photocatalyst performed. Using a UV-Vis spectrophotometer with a 290 nm wavelength, the obtained samples were examined. The conducted experiment was repeated for ratio 70:29:1 and 70:20:10. All

experiments were repeated for three times and carried out under identical conditions. The degradation of glyphosate was calculated using the formula [2]:

$$\eta\% = (C_0 - C_t)/C_0 \times 100 \quad (1)$$

where $\eta\%$ is the photodegradation efficiency of glyphosate; C_t is the amount of glyphosate in solution after UV irradiation and C_0 is the initial concentration of glyphosate before UV irradiation.

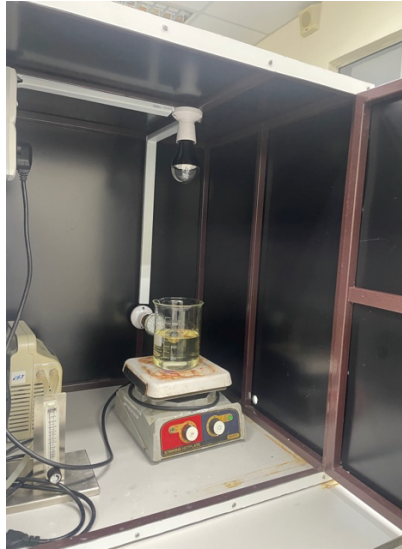


Fig. 2. The experimental set up in the box chamber.

3 Results and discussions

3.1 The effect on the different ratio of photocatalyst used.

Figure 3 shows the degradation of 5 and 10 mg/L glyphosate after 3 hours of UV irradiation in the presence of 5 mg of various ratio of $\text{TiO}_2/\text{Al}_2\text{O}_3/\text{CNT}$ nanocomposite photocatalyst. The highest percentage degradation shows 76.5% when 70:30:0 $\text{TiO}_2/\text{Al}_2\text{O}_3$ photocatalyst was used for degrading 10 mg/L of glyphosate concentration. However, the highest degradation in degrading 5 mg/L of glyphosate was achieved when $\text{TiO}_2/\text{Al}_2\text{O}_3/\text{CNT}$ photocatalyst's ratio of 70:29:01 was used (80.3%). The difference in percentage degradation between the two ratios could be attributed to the ratio's alterations in the presence of 1% CNT. Although the amount of CNT added was less, it nevertheless increased the exciting creation of electrons and decreased the rates of electron-hole recombination at the photocatalyst surface [11]. Furthermore, CNT extends the lifespan of excitons because the junction formed at the CNT- TiO_2 interface facilitates effective separation [12-13].

Additionally, CNT offers a significant amount of surface area for the adsorption of contaminants, concentrating them and bringing them closer to the TiO_2 active sites for photooxidation [14].

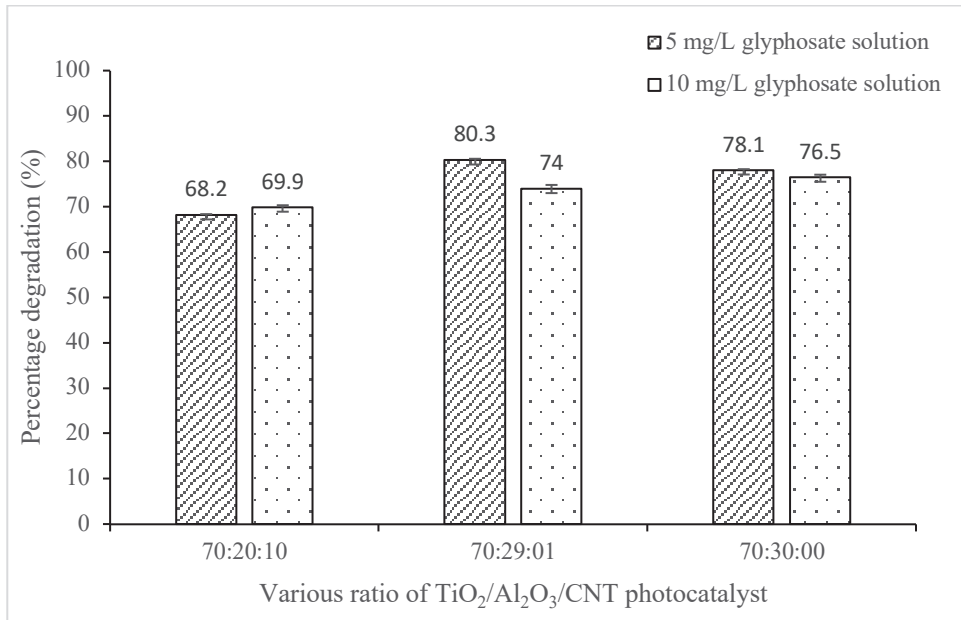
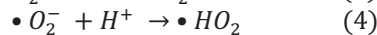
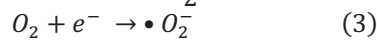
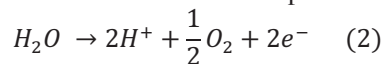


Fig. 3. Photocatalytic degradation of 5 and 10 mg/L of glyphosate using 5 mg of photocatalyst in the presence of UV light.

Additionally, CNT expands TiO₂'s light absorption to visible wavelengths by forming C-O-Ti chemical linkages that add additional band gap states [12, 15], increasing the material's band gap functionality. The following equations [11] illustrate how this caused water to be photolyzed, producing superoxide radical anions and species like •OH₂:



Besides, the adoption of Al₂O₃ also contributed to the increment of the surface area of photocatalyst. This supported by previous study where addition of Al₂O₃ to TiO₂ in degrading imazapyr has increased the percentage degradation [16]. The presence of Al₂O₃ and CNT particles in a titania-based composite influences its photocatalytic behaviour because both can influence its optical and electrical properties. The other previous study on photocatalytic degradation of 0.1 g/L and 5 mg/L imidacloprid using TiO₂ and CNT of Degussa (Evonik) P25, Aeroxide TiO₂ (alone) after 40 minutes of irradiation were approximately 32%, implying the necessity to adjust the photocatalyst by producing composites TiO₂/Al₂O₃/CNT. The composite has showed further increment (72%) indicating that the addition of crystalline solids into the titania lattice increased TiO₂ photocatalytic activity using the UV irradiation, proving the efficiency of this activity by TiO₂/Al₂O₃/CNT photocatalyst.

However, the application of 70:20:10 TiO₂/Al₂O₃/CNT photocatalyst has shown the lowest percentage degradation which were 68.2% and 69.9% when degrading 5 mg/L and 10 mg/L of glyphosate concentration, respectively. The adoption of 10% CNT has affected the performance of the produced photocatalyst. Previously addition of small amount of CNT has benefited the photocatalytic degradation process, however when the amount of CNT has increased to 10%, it has reduced the percentage degradation of both glyphosate concentration. Previous study also in agreement with this finding where the researcher Alonso et al. [17]

claimed that the $\text{TiO}_2/\text{Al}_2\text{O}_3/\text{CNT}$ composite had a lower light absorption intensity but an improved catalytic density when compared to $\text{TiO}_2/\text{Al}_2\text{O}_3$.

In summary, the results showed that incorporating Al_2O_3 and/or CNT into TiO_2 may affect the performance of the photocatalytic degradation of glyphosate.

3.2 The effect on the amount of 70:30 $\text{TiO}_2/\text{Al}_2\text{O}_3$ photocatalyst use for photocatalytic degradation of glyphosate.

To study the effect on the amount of photocatalyst used, only photocatalyst with ratio 70:30:0 (absence of CNT) was tested as this has been explained in last paragraph in section 3.1. Based on Figure 4, the percentage degradation shows further increment when the amount of photocatalyst used increased (5 mg, 10 mg, 15 mg, 20 mg). The increased amount of photocatalyst used resulted in a higher concentration of TiO_2 and Al_2O_3 , which increased the number of photons absorbed to generate electrons in the conduction band [18]. Electrons promoted from the valence to the conduction band created holes (h^+) in the valence band (equation (5)). The more active sites (electron-holes) accessible on the surface of the photocatalyst, the more glyphosate can be adsorbed onto the surface, allowing photocatalytic degradation to occur (equation (6)) [8].

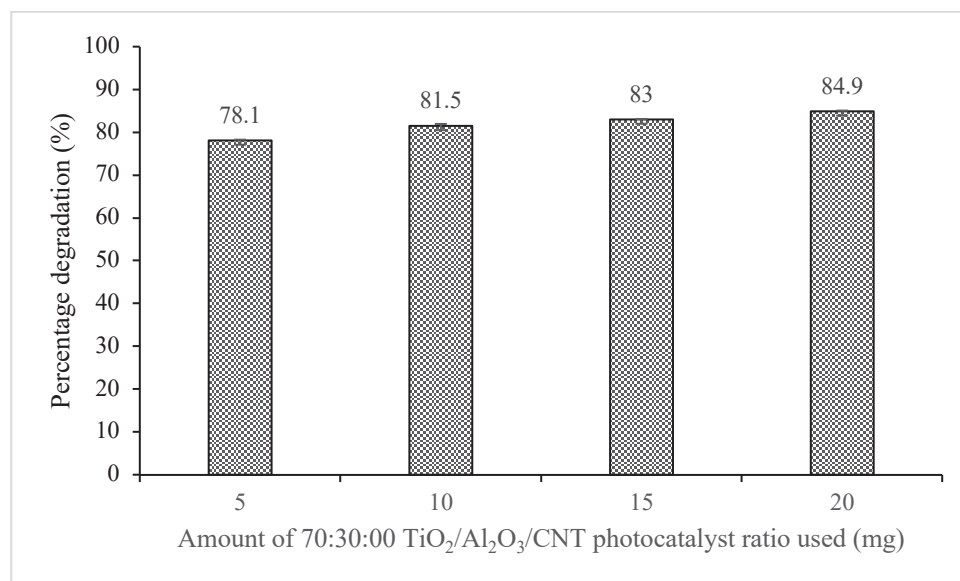


Fig. 4. Photocatalytic degradation of 5 mg/L of glyphosate solution using various amount of 70:30:0, $\text{TiO}_2/\text{Al}_2\text{O}_3$ photocatalyst in the presence of UV light.

The formation of the $\bullet\text{OH}$ radicals from the hole and their subsequent reaction with liquid or OH suggests that photocatalytic glyphosate degradation may have taken place on the surface of the TiO_2 and $\text{Al}_2\text{O}_3/\text{CNT}$ in this work. Even though the photocatalyst dosage was increased to 20 mg, this amount was still not excessive and did not retard the percentage of degradation. Further, it was discovered in a recent study that excess photocatalyst from optimum level may aggregate at high loads, decreasing the surface area for optical absorption, diminishing the effectiveness of photocatalysis, and led to non-uniform light intensity [19].

The previous study also showed that with the addition of TiO₂ and Al₂O₃, the strong linkage between the TiO₂ and Al₂O₃ were helpful to allow a smooth electron-hole pair separation and migration, which led to more availability of •OH and •O₂ radicals for photocatalytic degradation activities [20].

In another investigation of the photocatalytic degradation of diuron using TiO₂ and Al₂O₃, radical species were also involved in a photocatalytic process that was a schematization of the photodegradation reaction [21]. According to another study, Al₂O₃ possesses excellent textural, adsorbent, and photocatalytic capabilities in nanocomposite photocatalysts. By enhancing the contact surface between the TiO₂ semiconductor and Al₂O₃ and reducing the electron-hole pair separation, high specific surface area TiO₂ and Al₂O₃ can optimise photocatalytic activity [22]. In order to reduce recombination and produce a range of reactive oxidative species with increased photocatalytic performance, the electron is trapped by producing hole-Al³⁺ and surface adsorbed O₂ [22].

4 Conclusion

The results of this investigation concluded that the hydrothermally generated TiO₂/Al₂O₃/CNT nanocomposite photocatalyst has been successfully used in the treatment of glyphosate. About 20 mg of 70:30:0 ratio of TiO₂/Al₂O₃/CNT nanocomposite photocatalyst gave 84.9% of percentage degradation for 5 mg/L of glyphosate.

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