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Introduction and Objectives

The widespread use of pesticides in agricultural activity has led to problems related with pesticide waste management. The United Nations estimate that less than 1% of all pesticides used in agriculture actually reaches the crops. The remaining contaminates the land, the air and particularly the water [1]. These contaminants are in many cases toxic and non-biodegradable and they have the ability to accumulate in the environment with unpredictable consequences for the mid-term future [2].

Bentazone is a selective post-emergence herbicide (3-isopropyl-1H-2,1,3-benzothiadiazin-4-(3H)-one-2,2-dioxide, CAS No: 25057-89-0, Mr: 240.28), used to control many broadleaf weeds and sedges. Bentazone has the potential to contaminate both ground and surface water because of its low soil sorption and high water solubility. It is stable to hydrolysis and has a half-life of less than 24 h in water because it is readily broken down by sunlight [3].

Heterogeneous photocatalytic oxidation (TiO₂/UV-A) in the presence of artificial or solar light, has been effective for the degradation of a variety of toxic agrochemical substances, such as insecticides and pesticides [4]. Our current study investigates the effect of various operating conditions of heterogenous photocatalytic decomposition and mineralization of bentazone.

Materials and Methods

Materials

The catalysts used during heterogenous photocatalytic oxidation were TiO₂ P-25 (Degussa, anatase/rutile=3.6/1, BET: 50 m² g⁻¹, nonporous), TiO₂ UV 100 (Hombikat, 100% anatase, BET: 300 m² g⁻¹), TiO₂ Kronos 7000, TiO₂ Kronos 7500 (Kronos Worldwide, Inc., 100% anatase, BET: 250 m² g⁻¹) and ZnO (Merck, BET 10 m² g⁻¹).

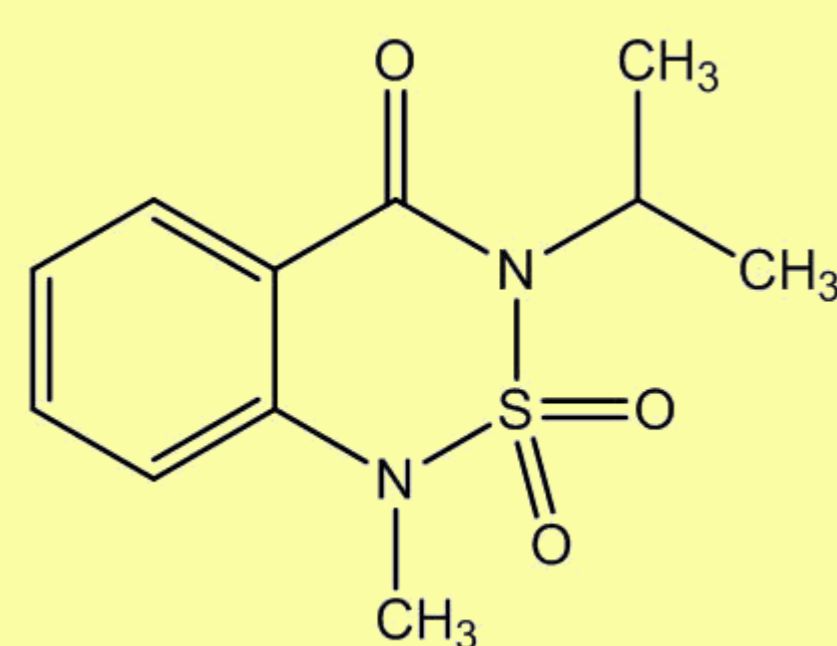


Figure 1: Bentazone (3-isopropyl-1H-2,1,3-benzothiadiazin-4-(3H)-one-2,2-dioxide, CAS No: 25057-89-0, Mr : 240.28)

Photocatalytic experiments

Experiments were performed in a closed Pyrex cell of 600 ml capacity. The reaction vessel was fitted with a central 9 W lamp and had inlet and outlet ports for bubbling CO₂ free air during the photocatalytic process. The spectral response of the UV-A irradiation source ranged between 350-400 (max: 366 nm), while that of the visible irradiation source ranged between 400-520 nm (max: 450 nm). Experiments were conducted at a working volume of 500 mL, under constant magnetic stirring. The catalyst/herbicide suspension was left for 30 minutes in the dark, to achieve maximum adsorption of the herbicide onto the semiconductor surface. Samples were filtered through a 0.45 μm filter. Heterogeneous photocatalytic experiments were carried out at the pH value of 6±0.2. The reaction temperature was kept constant at 25°C.

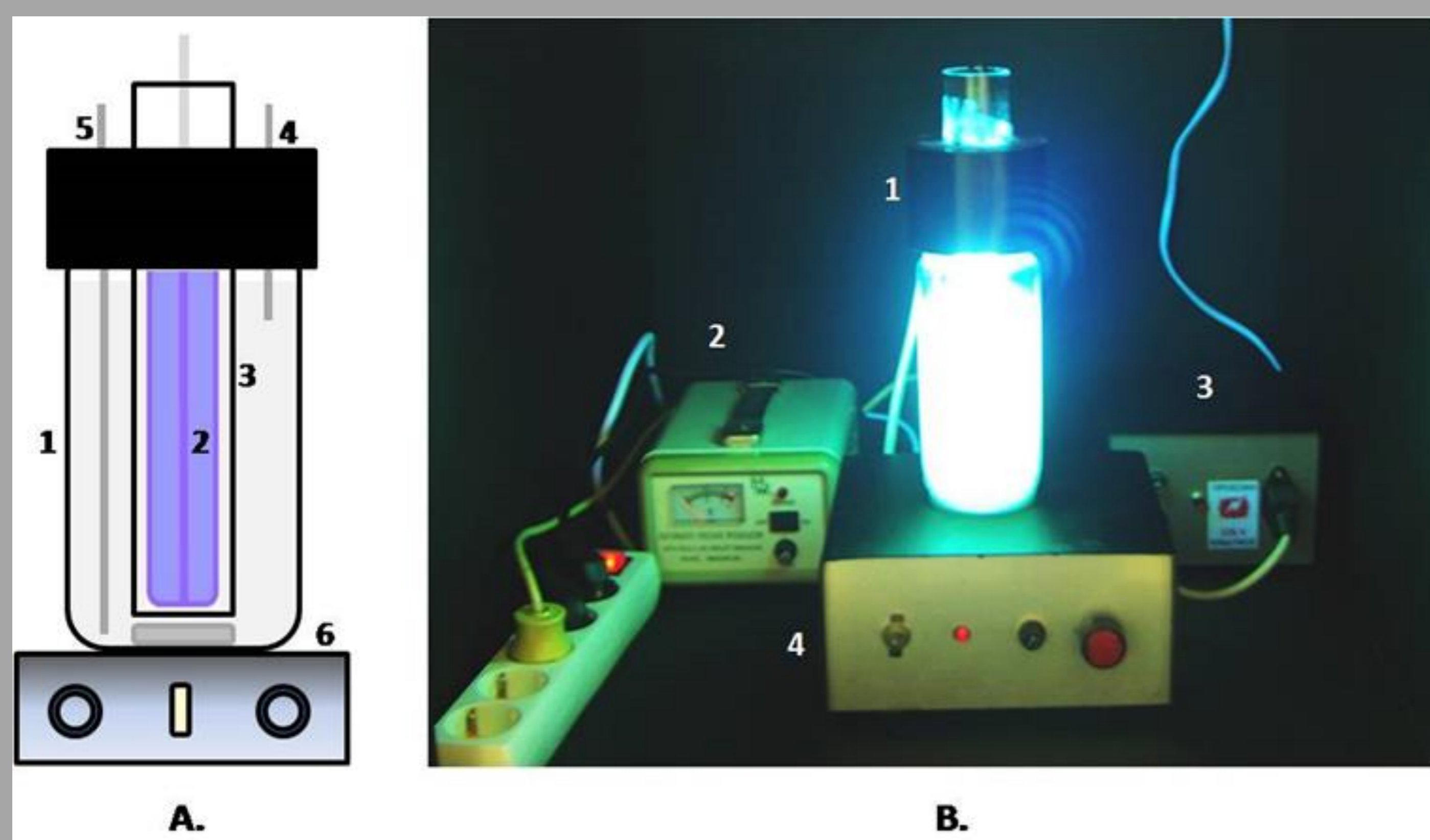


Figure 2: A: Sketch of the photocatalytic reactor employed in the photocatalytic oxidation of bentazone: 1. reaction vessel, 2. irradiation source, 3. borosilicate glass, 4. air inlet, 5. air outlet 6. stirrer. B: Photograph of the experimental setup: 1 photocatalytic reactor equipped with a black light irradiation source, 2. voltage regulator, 3. lamp power supply 4. stirrer.

Results

- The catalytic activity of TiO₂ P25, UV-100, Kronos 7000 and 7500 and ZnO under UV-A irradiation, was studied. Figure 3 shows concentration-time profiles during photocatalytic oxidation of 20 mg L⁻¹ Bentazone employing 0.5 g L⁻¹ of catalyst. Reactivity decreases in the order ZnO > TiO₂ P25 > Kronos 7000, with the degradation efficiency after 90 min illumination being 99, 87, 67% respectively.
- The effect of visible irradiation in the presence of Kronos 7000 (Fig. 4), leads to the photocatalytic degradation of BNZ. However, degradation rate appears to be reduced compared to that during the photocatalytic oxidation in the presence of Kronos 7000 and UV-A irradiation.
- As shown in Fig. 5 mineralization of BNZ during heterogeneous photocatalytic oxidation in the presence of 0.5 g L⁻¹ TiO₂ P25 and UV-A irradiation, is enhanced when H₂O₂ is added to the suspension.
- The release of the organic nitrogen in the molecule of BNZ is more effective in the presence of TiO₂ P25 compared to Kronos 7000, while the action of TiO₂ P25 is enhanced in the presence of H₂O₂.

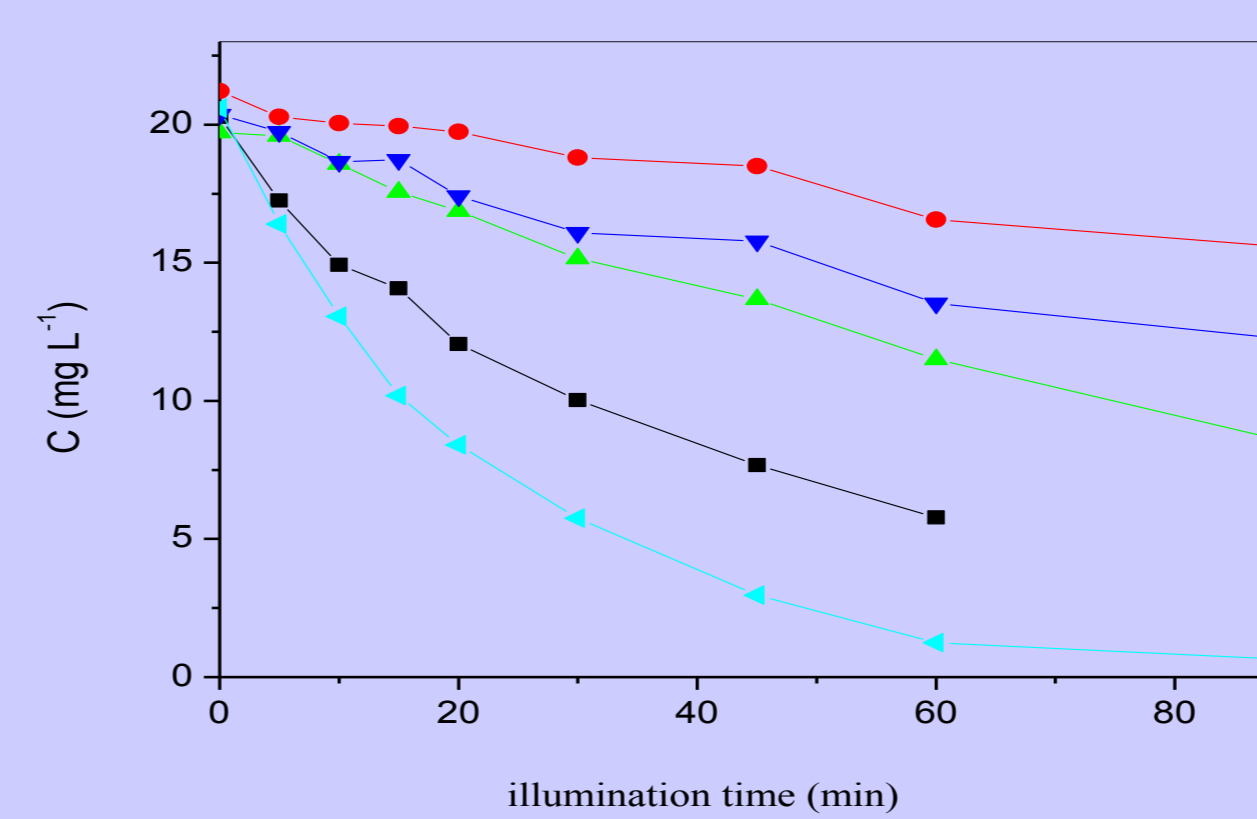


Figure 3: Photocatalytic degradation of 20 mg L⁻¹ of bentazone in the presence of 0.5 g L⁻¹ of photocatalyst and UV-A: [■] TiO₂ P25, (●) Kronos 7500, (▲) Kronos 7000, (▼) TiO₂ UV-100, (◄) ZnO.

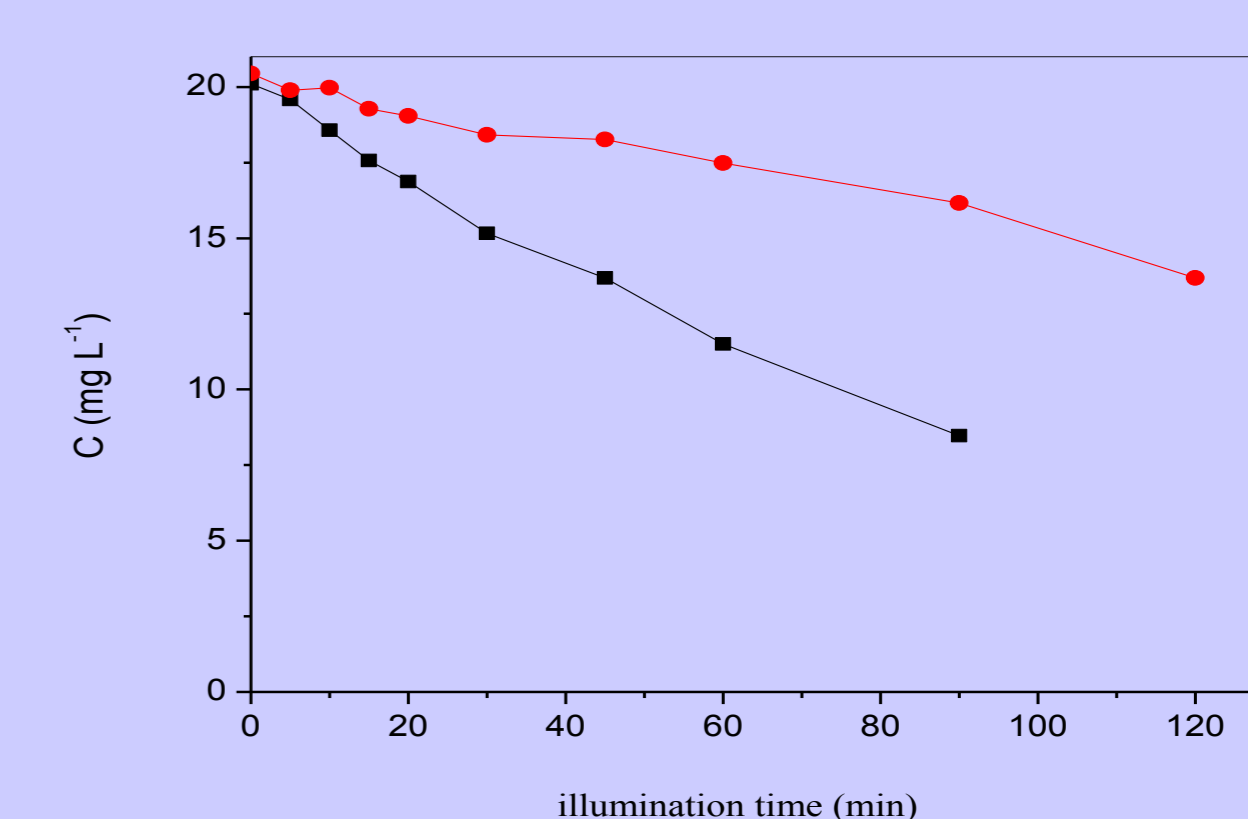


Figure 4: Photocatalytic degradation of 20 mg L⁻¹ of bentazone in the presence of 0.5 g L⁻¹ Kronos 7000 under: [■] UV-A irradiation, (●) Visible irradiation.

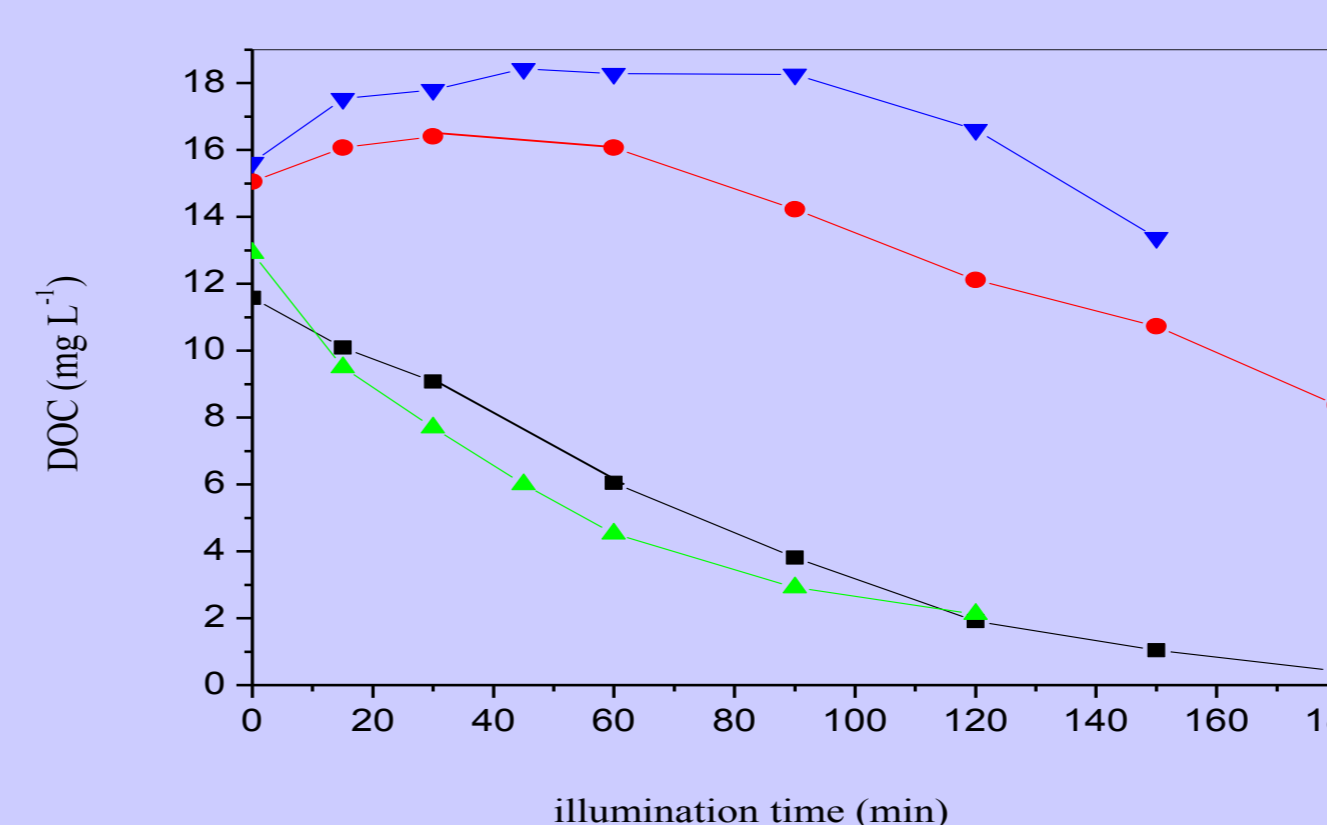


Figure 5: Photocatalytic mineralization of 20 mg L⁻¹ of bentazone in the presence of 0.5 g L⁻¹ of photocatalyst and UV-A: [■] TiO₂ P25, (●) Kronos 7000, (▲) TiO₂ P25 and 100 mg L⁻¹ H₂O₂, (▼) Kronos 7000 and 100 mg L⁻¹ H₂O₂.

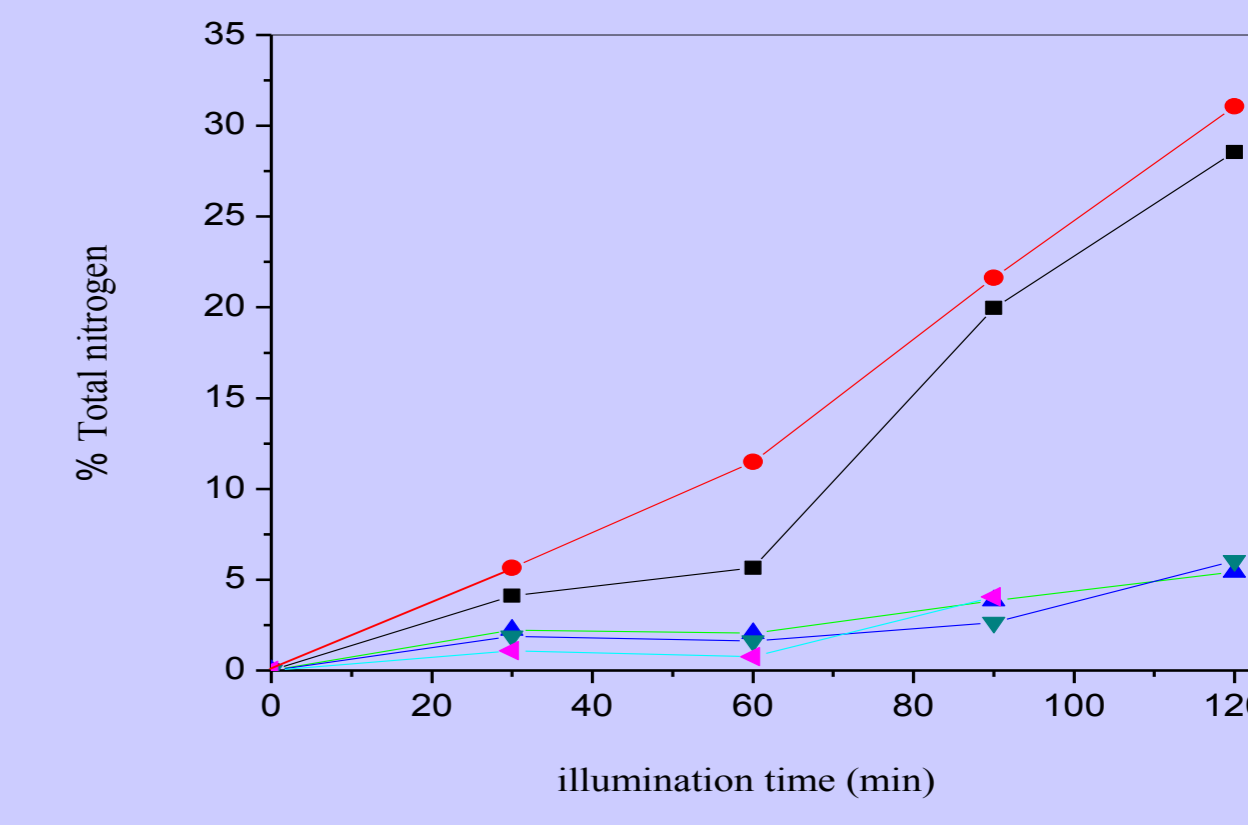


Figure 6: Release of total nitrogen during the photocatalytic mineralization of 20 mg L⁻¹ of bentazone in the presence of 0.5 g L⁻¹ of photocatalyst: [■] TiO₂ P25, (●) TiO₂ P25 and 100 mg L⁻¹ H₂O₂, (▲) Kronos 7000, (▼) Kronos 7000 and 100 mg L⁻¹ H₂O₂, (◄) Kronos 7000 and visible irradiation.

Discussion and Conclusions

Among the various photocatalysts employed in the study, TiO₂ P25 (Degussa) and ZnO (Merck) in the presence of UV-A, resulted in higher initial degradation rates of the herbicide. In contrast, Kronos 7000 or 7500 (Kronos Worldwide, Inc) in the presence of either UV-A or visible irradiation, led to low initial degradation rates. Thus, photocatalytic mineralization of bentazone in the presence of TiO₂ P25 and UV-A irradiation was enhanced by the addition of H₂O₂, resulting in higher initial mineralization rates of the herbicide, while the release of the organic nitrogen in the molecule of BNZ is more effective in the presence of TiO₂ P25 compared to Kronos 7000.

References

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