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Solar photocatalysis of carbaryl rinsate promoted by dye photosensitization

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Abstract

In this study, carbaryl (a carbamate insecticide) rinsate was treated by a novel technology − solar photocatalysis assisted with a dye photosensitizer (methylene blue (MB) or rose Bengal (RB)). The major advantage of this technology is to employ effectively natural solar light instead of artificial lamps as an irradiation source, leading to a considerable decrease in energy consumption and operation cost. Results showed that an increased mineralization and toxicity reduction efficiency for carbaryl rinsate was achieved by adding dyes into the solar photocatalytic system. Among the conditions studied, adding 1×10^{-6} M of MB, which corresponded to 1% of the initial concentration of carbaryl rinsate in the system, renders the most effective microtoxicity reduction of carbaryl rinsate. As a result, a carbaryl removal percentage of 66.2%, a mineralization efficiency of 26.2%, and a toxicity reduction of 44.6% could be achieved. The mineralization of carbaryl was found to follow the pseudo-first order reaction kinetics. The decomposition mechanism of carbaryl was further investigated through identification of the intermediates to elaborate the influence of dye photosensitizer on the solar photocatalysis of carbaryl. On the basis of the intermediates identified, it was believed that hydrolysis, hydroxylation and quinonation may be the major mechanisms for decomposing carbaryl in the process of solar photocatalysis with the aid of dye photosensitizer. On the strength of results obtained in this study, it was revealed that solar photocatalysis along with the aid of a dye photosensitizer, such as MB or RB, was a greatly feasible approach for the pollution control of pesticide rinsate.

Keywords: Solar photocatalysis; Carbaryl; TiO_2 film; Photosensitizer; Methylene blue; Rose Bengal

1. Introduction

The widespread use of pesticide throughout the agricultural industry has resulted in mixed impacts. On one hand, utilization of pesticide produces an enormous increase in agricultural productivity. On the other hand, because of their hazardous nature, the waste and rinsate from spray and storage equipment have been considered as one of the major threats to the environment. Their occurrence has given rise to a challenging natural resources management problem and, at the same time, has provided a source of motivation for many scientific initiatives. Carbaryl (1-naphthyl *N*-methylcarbamate), a carbamate insecticide with a wide range of activity, was one of the most commonly used insecticides. Carbaryl has been found to react with nitrite under certain conditions to give rise to *N*-nitrosocarbaryl, which can be considered to be one of the strongest genetically active agents, a potent mutagen, and a carcinogen [1].

Generally, conventional biological treatment is not very effective for carbaryl rinsate treatment [2]. Instead, activated carbon adsorption is commonly used. However, new environmental laws may consider the spent adsorbents as hazardous waste and require further treatment. Consequently, intensive research for novel technologies with higher efficiency and less amount of waste generated has been stimulated. In the last decade, the photocatalysis using a semiconductor − TiO_2 as a photocatalyst has been considered as one of the emerging wastewater treatment technologies. As TiO_2 is illuminated by UV light with wavelength below 382 nm, the

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UV photons excite the valence band electrons across the band-gap into the conduction band, leaving holes behind in the valence band. The holes in TiO_2 will therefore react with water molecules or hydroxide ions (OH^-) in aqueous solution and produce hydroxyl radicals ($^{\bullet}OH$) [3], which are very strong oxidants capable of oxidizing many organic pollutants.

Some studies [4–6] have reported that highly efficient degradation of xenobiotics could be obtained by a photocatalytic process using TiO_2 powder as catalyst. However, photocatalytic process for slurry system would require additional separation of TiO_2 from the purified water after decomposition reaction, which is an obvious hindrance. In addition, the process was generally equipped with an artificial light source, leading to a considerable increase in operation cost. These drawbacks may be obstacles to the TiO_2 photocatalysis system for practical application. Hence, in recent times, there are many efforts [7–10] on studying the photocatalytic oxidation process using solar light as an irradiation source. In spite of the fact that solar irradiation could be used in photocatalytic process, only approximately 5–7% of the solar spectrum is useful for the TiO_2 band-gap, leading to a low degradation rate and efficiency for refractory organic pollutants [8]. To increase the quantum yield and efficiency of solar photocatalytic process, it may be a feasible approach to use the dye capable of absorbing visible light as a photosensitizer for transferring energy to TiO_2 or O_2 and therefore, promoting the degradation efficiency of pollutants [9]. Nevertheless, many parameters affect the efficiency of dye sensitization on solar photocatalysis and such influences are still not clear nowadays.

Therefore, the objective of this study was to investigate the promoted effect of dye photosensitizer, including methylene blue (MB) and rose Bengal (RB), on the degradation, mineralization and microtoxicity reduction efficiency of solar photocatalytic degradation of carbaryl rinsate. In addition, to intensively understand the effect of dye on the solar photocatalysis of carbaryl rinsate, the decomposition intermediates of carbaryl would be identified to elaborate the possible decomposition mechanism.

2. Materials and methods

2.1. Materials

Carbaryl ($C_{12}H_{11}NO_2$) with a purity of 99.0% was provided by ChemService Co., PA, USA and was used without further purification. Merck HPLC-grade acetonitrile (purity >99.9%) was employed as eluent. Methylene Blue (MB) ($C_{16}H_{18}ClN_3S$, λ_{max}: 668 nm) and rose Bengal (RB) ($C_{20}H_2Cl_4I_4K_2O_5$, λ_{max}: 556 nm) were provided by Koch-Light Lab. Ltd., England. Dyes were used without further purification. The TiO_2 powder P25 (mainly anatase form, mean particle size: 30 nm, BET surface area: $50 \pm 15\ m^2/g$) from Degussa Co. (Frankfurt, Germany) were immobilized on the surface of agitator's blades and the inner surface of the reactor by using PTFE (TEFLON) resin-bonded technique [11].

2.2. Apparatus

Fig. 1 shows the experimental setup for this study. In such a photocatalytic system, separation of photocatalyst from the purified water after decolorization reaction was not necessary, and no other aeration equipment was required for oxygen supply. The effective volume of the photoreactor ($36\ cm\ L \times 27.5\ cm\ W \times 8\ cm\ H$) was approximately 8.0 L. Solar light (light intensity: $0.17–0.23\ mW/cm^2$ at 254 nm, and $1.5–2.0\ mW/cm^2$ at 365 nm as measured using a UVP radiometer (UVP Inc., USA), $100–120\ mW/cm^2$ for visible light as measured using an LI-250 radiometer with LI-200 SA detector (LI-COR Inc., USA)) or artificial UV light (light intensity: approximately $2.3\ mW/cm^2$ at 254 nm measured by a UVP radiometer at a distance of 9 cm from the lamps) supplied by three 15 W low-pressure mercury lamps was used to supply irradiation. The rotating speed of pump was kept at 70 rpm during the experiment. The size of the SS304 blades was $3\ cm\ W \times 15\ cm\ L$ with a thickness of 1 mm. About 0.8 g of TiO_2 powder was applied to the photoreactor. The total area of the resulting TiO_2 films in the photoreactor was approximately $2500\ cm^2$.

2.3. Procedures

Carbaryl rinsate with a concentration of 1×10^{-4} M (20.1 mg/L) was prepared for the experiments. Two types of dyes, including methylene blue (MB) ($C_{16}H_{18}ClN_3S$, λ_{max}: 660 nm) and rose Bengal (RB) ($C_{20}H_2Cl_4I_4K_2O_5$, λ_{max}: 556 nm), were chosen as the photosensitizer for this study due to the fact that their absorbance wavelength of light was located mostly in the range of 500–700 nm, which corresponded to the stronger irradiation range of solar light. Concentrations of photosensitizer added were 1% (1×10^{-6} M) or 2% (2×10^{-6} M) of the initial concentrations of carbaryl rinsate. The prepared pollutant solution was then placed into the photoreactor and irradiated by solar light or artificial UV light for 3 h. Each carbaryl rinsate sample (100 mL) was taken every 0.5 h during each 3 h experiment for further analysis. Experiments without the addition of photosensitizer were also performed in parallel under the same conditions for comparison.

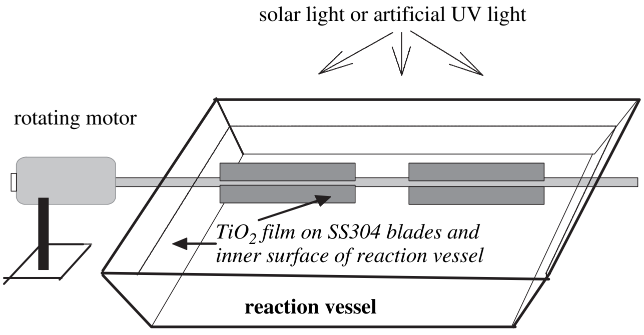

Fig. 1. Schematic diagram of photocatalytic reactor.

2.4. Analysis

2.4.1. Analytical measurement of carbaryl

Prior to analysis, 2 mL of each water sample was filtered through a Gelman 13 mm Nylon membrane (0.22 μm pore size) to remove small particles that could obstruct flow through the column. Residual carbaryl in water was analyzed by HPLC using a Jasco system (Japan). This system was equipped with two PU1580 pumps and a UV1575 detector setting at a wavelength of 280 nm. A Supelco C-18 reversed phase column (*L*: 25 cm, ID: 4.6 mm, particle size: 5 μm) was used. The mobile phase was a mixture of acetonitrile (50%) and deionized water (50%). The flow rate of mobile phase was 1 mL/min. Injection volume of each sample was 25 μL. Under the analytical conditions of HPLC, the retention time of carbaryl was 7.76 min.

2.4.2. Microtoxicity measurement

The microtoxicity of each sample was measured using an SDI M500 (SDI Co., USA) analyzer. Results are expressed as EC$_{50}$ (15 min, 15 °C), which was defined as the effective concentration of pollutant for a 50% reduction of the luminescence of the bacterium *Photobacterium phosphoreum*. A lower EC$_{50}$ value indicates a higher amount of toxic constituent presented in the pollutant solution.

2.4.3. Identification of major intermediates

Identification and confirmation of the major intermediates of carbaryl were accomplished by GC–MS technique. GC–MS measurements were performed on an Agilent 6890N gas chromatograph with Agilent 5973N MSD. The GC column used was an HP-5MS capillary silica column (*L*: 30 m, ID: 0.25 mm, coated with phenylmethylsiloxane (5% phenyl)). Prior to analysis, water sample (20 mL) was concentrated by solid phase extraction with 2 mL of acetonitrile as eluent. The GC–MS operation conditions were described as follows. Injection volume of each sample was 1 μL. Injector temperature was set to 270 °C. Helium was used as the carrier gas with a flow rate of 1 mL/min. The oven was held at 40 °C for 4 min and then ramped up to a temperature of 270 °C at a heating rate of 10 °C/min and held at this temperature for 18 min.

2.4.4. TOC analysis

Total organic carbon (TOC) of each solution was measured in order to understand the amount of carbaryl degraded to CO$_2$ during photocatalytic oxidation. TOC was measured using a Phoenix 8000 analyzer (Dohrman Co., USA).

3. Results and discussion

3.1. Degradation efficiency of carbaryl

The carbaryl rinsate prepared in this study had a TOC value of 14.31 mg/L, an EC$_{50}$ (15 °C, 15 min) of 45.7–47.4%, and a pH of 6.5–7.5. Fig. 2 shows the degradation efficiency of carbaryl rinsate by various photocatalytic processes. It was found that adding dye into the system slightly improved the degradation efficiency of carbaryl for solar photocatalytic system, but was not beneficial for UV–TiO$_2$ photocatalytic system. However, as shown in Fig. 3, a significant increase in mineralization efficiency of carbaryl rinsate, which was defined as the TOC removal percentage, was always achieved by

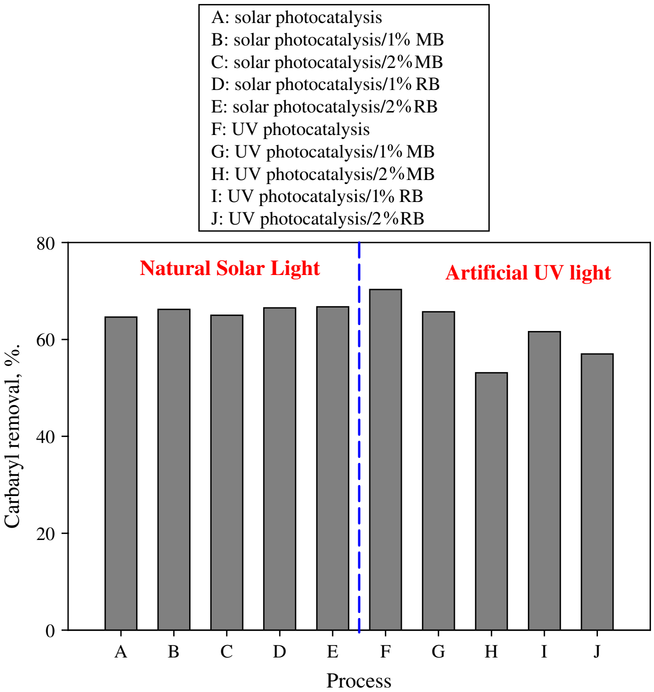

Fig. 2. Degradation efficiency of carbaryl rinsate by various photocatalytic processes.

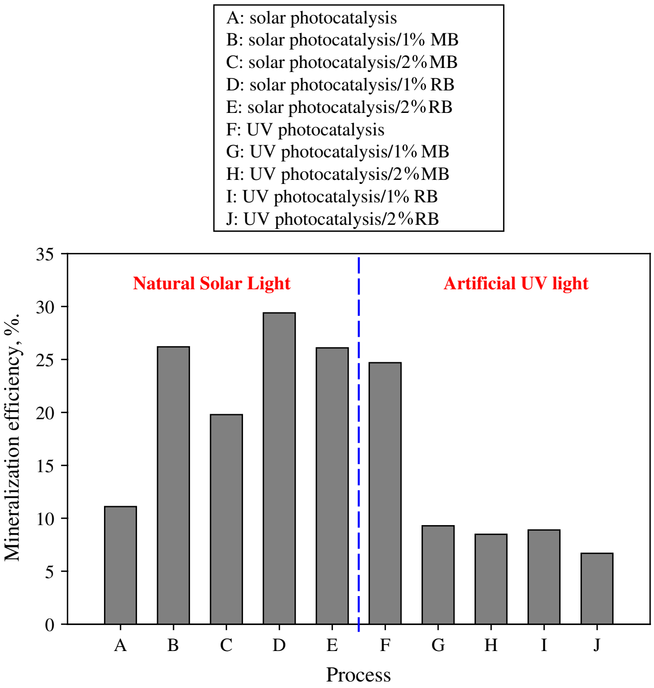

Fig. 3. Mineralization efficiency of carbaryl rinsate by various photocatalytic processes.

adding dye into solar photocatalysis in contrast to the adverse effect in the UV photocatalysis with dye. Such results implied that the color-shielding effect of dye was considerable for UV–TiO_2 photocatalysis, which hampered the mineralization of carbaryl and microtoxicity reduction percentage of carbaryl pesticide rinsate. In other words, dye photo-enhancement effect was not beneficial for UV–TiO_2 photocatalysis. Among the conditions studied, as compared to UV–TiO_2 photocatalytic system, comparable or better mineralization efficiency could be obtained for solar photocatalytic system with the addition of 1% MB or 1–2% RB. The much higher mineralization efficiency of carbaryl for dye photo-enhanced solar photocatalysis meant that higher amount of carbaryl was degraded to CO_2. As shown in Fig. 4, a substantial increase in microtoxicity reduction was also as a result. Specifically, as compared to UV–TiO_2 photocatalysis, solar photocatalysis without photosensitizer could only achieve approximately 70% of the microtoxicity reduction efficiency of UV–TiO_2 photocatalysis. However, with the addition of 1% RB or 1% MB, comparable or approximately 20% increase of the microtoxicity reduction efficiency of UV–TiO_2 photocatalysis could be achieved. It was therefore believed that less toxic intermediates should be produced more in dye promoted solar photocatalysis. The microtoxicity reduction efficiency depends on the type and concentration of photosensitizer applied. Among the conditions studied, by the addition of 1×10^{-6} M of MB, i.e. 1% of the initial carbaryl concentration of rinsate in the solar photocatalytic system, the most effective microtoxicity reduction of carbaryl solution would be obtained, which corresponded to a carbaryl removal percentage of 66.2%, a mineralization efficiency of 26.2%, and a microtoxicity reduction of 44.6%.

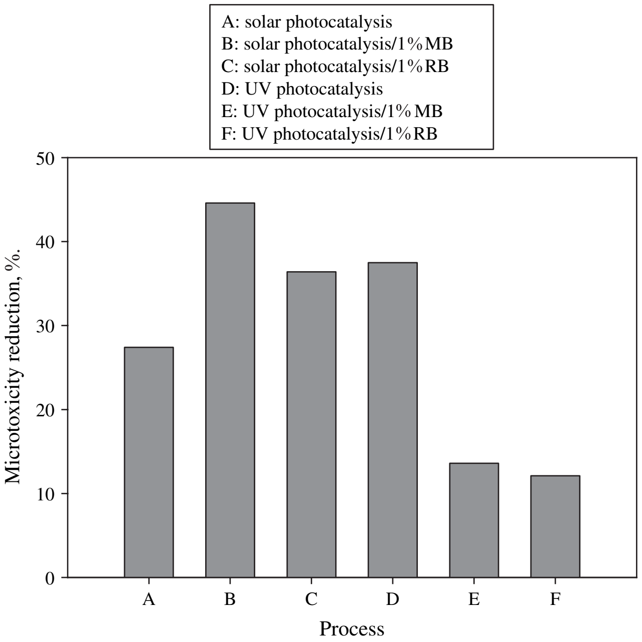

Fig. 4. Microtoxicity reduction of carbaryl rinsate by various photocatalytic processes.

$$TiO_2 \xrightarrow{h\gamma\ (\lambda < 382\ \mathrm{nm})} h^+ + e^- \quad (1)$$

$$e^- + O_2 \rightarrow \bullet O_2^- \quad (2)$$

$$h^+ + OH^- \rightarrow \bullet OH \quad (3)$$

Scheme 1.

$$Dye_{(ads)} \xrightarrow{\text{solar light}} Dye_{(ads)}^* \quad (4)$$

$$Dye_{(ads)}^* + TiO_2 \rightarrow Dye_{(ads)} + h^+ + e^- \quad (5)$$

$$Dye_{(ads)}^* + O_2 \rightarrow Dye_{(ads)} + 2O(^1D) \quad (6)$$

Scheme 2.

We believed that for general solar photocatalytic degradation with TiO_2 as catalyst, the initiation of this process could be described by Scheme 1 (Eqs. (1)–(3)), in which the generated hydroxyl radicals were to oxidize the pollutants. However, for a dye photosensitized solar photocatalysis system, the initiation of this process could also be through the mechanisms of Scheme 2 (Eqs. (4)–(6)) in addition to Scheme 1, in which the adsorbed dye on TiO_2 was excited by solar irradiation and then the excited dye transferred adsorbed energy to TiO_2 or O_2, leading to production of more pairs of electron–hole (Eq. (5)) or singlet oxygen atom ($O(^1D)$) (Eq. (6)) for promoting the degradation efficiency of carbaryl and its degraded intermediates.

The final microtoxicity reduction efficiency depends on the toxicity and relative concentration of the intermediates formed, which are strongly related to the type and concentration of photosensitizer present in the solar photocatalytic system.

3.2. Photocatalytic rate of carbaryl

To quantitatively analyze the effect of dye photosensitization on the efficiency of solar–TiO_2 photocatalysis, a pseudo-first order model expressed by Eq. (7), which was generally used for photocatalytic degradation process for low initial concentration of pollutant [12], was applied to obtain the rate constants of various photocatalytic degradation reactions.

$$-\frac{dC}{dt} = kC \quad (7)$$

where C is the concentration of dye in pollutant solution at time t, and k is the pseudo-first order rate constant. It was found that the mineralization rate of carbaryl followed the pseudo-first order reaction kinetics ($r^2 > 0.95$). The resulting rate constants for mineralization rate of carbaryl are given in Table 1. It was clear that for solar–TiO_2 photocatalysis, an obvious enhancement for mineralization rate of carbaryl was achieved by the addition of dye photosensitizer. In contrast, the presence of dye presents an adverse effect to UV–TiO_2 photocatalysis. By the aid of dye, the mineralization rate of carbaryl in solar–TiO_2 photocatalysis increased from 0.039 h^{-1} to 0.101 h^{-1} and 0.122 h^{-1} for 1% MB and RB addition, respectively, which were 6–28% higher than that of the artificial UV–TiO_2 photocatalysis (0.095 h^{-1}).

3.3. Identification of intermediates and proposed degradation mechanisms of carbaryl

Qualitatively, no matter which light source (UV or solar light) was applied to the photocatalytic process, some aromatic intermediates, including 1-naphthenol and 1,4-naphthalenedione which were also found in the degradation of carbaryl by Fenton process [1], and 2-(5)-hydroxyl-1,4-naphthalenedione were generally identified in the treated carbaryl rinsate. In addition to aromatic intermediates, some substituted phenols, including catechol and 1,2,3-trihydroxybenezene, were also identified. Moreover, it was found that with the aid of dye addition, many byproducts with lower toxicity were identified in the treated carbaryl rinsate, particularly the aromatic ring opened byproducts, such as butanoic acid and propanoic acid, which were less toxic than their parent compound – carbaryl. Accordingly, it was believed that the predominant initiation of the oxidation of carbaryl rinsate should be similar to its base hydrolysis reaction and that of direct UV photodecomposition as mentioned in the study of Bachman and Patterson [13], namely, the carbamate group may be cleaved from the pesticide molecule to form 1-naphthenol. Moreover, the hydroxylation and quinonation may also play a role in the initiation of carbaryl decomposition, leading to the presence of some intermediates such as 1,4-naphthalenedione, 2-(5)-hydroxyl-1,4-naphthalenedione, catechol, and 1,2,3-trihydroxybenzene in the treated carbaryl rinsate. The second step of carbaryl decomposition may possibly be homocyclic ring opening, leading to some substituted alcohols and acids generated. On the basis of the identified intermediates, the possible degradation pathway of carbaryl was proposed in Fig. 5. Basically, hydrolysis, hydroxylation and quinonation are most probably the major mechanisms for decomposing carbaryl in the process of dye assisted solar photocatalysis.

Table 1
Mineralization rate of carbaryl in the presence of dye photosensitizer

Process[a]	Mineralization rate constant (h^{-1})	Relative mineralization efficiency[b] (%)
Solar light/TiO_2 film	0.039	41
Solar light/TiO_2 film/1% MB	0.101	106
Solar light/TiO_2 film/2% MB	0.079	83
Solar light/TiO_2 film/1% RB	0.122	128
Solar light/TiO_2 film/2% RB	0.109	115
UV light/TiO_2 film	0.095	100
UV light/TiO_2 film/1% MB	0.039	41
UV light/TiO_2 film/2% MB	0.029	30
UV light/TiO_2 film/1% RB	0.031	33
UV light/TiO_2 film/2% RB	0.023	24

[a] Reaction time of each process: 3 h.

[b] Relative mineralization efficiency = (rate constant for each process/rate constant for UV TiO_2-photocatalytic process) × 100%.

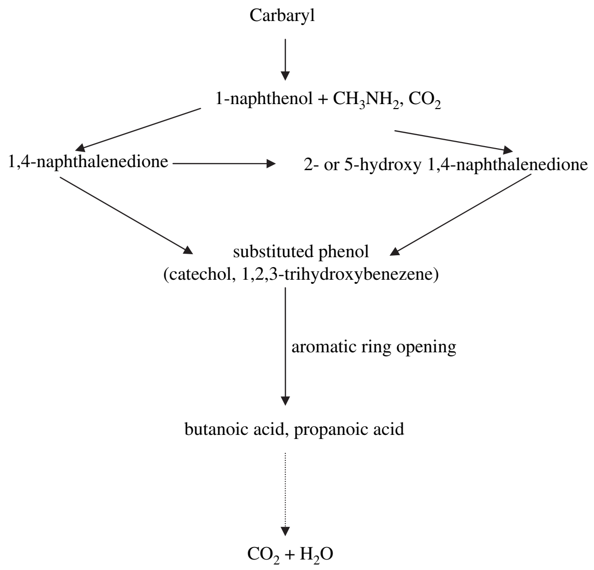

Fig. 5. Proposed degradation pathway of carbaryl in this study.

4. Conclusions

A great increase in mineralization and microtoxicity reduction efficiency could be achieved by adding appropriate ratio of dye (1% of the concentration of pesticide rinsate) into the solar–TiO_2 photocatalytic system. Moreover, on the basis of the intermediates identified, it was believed that hydrolysis, hydroxylation, and quinonation were the major mechanisms for decomposing carbaryl in such a photocatalytic system. Accordingly, the immobilized TiO_2 solar photocatalytic process along with the aid of a photosensitizer, such as methylene blue or rose Bengal, could be a potential alternative for the treatment of pesticide rinsate.

Acknowledgements

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