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PHOTOCATALYTIC DECOMPOSITION OF MALATHION USING METAL OXIDE POWDER

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Abstract

Malathion is an organophosphate insecticide used to control a variety of insects in agricultural productions. The contamination of water by malathion and other organophosphate insecticides has a great hazard to the human and animals due to carcinogenic effect and other toxic effects to nerve system. To remove malathion contamination from water, photocatalysis has been applied as a powerful method. Powder form of some selected metal oxide such as TiO_2, Al_2O_3, Fe_2O_3, and MgO was used. Photocatalytic decomposition of malathion at different conditions (malathion initial concentration, catalyst type and catalyst amount in sample and presence of oxidant) were investigated in a patch reactor. H_2O_2, $K_2S_2O_8$, $(NH_4)_2S_2O_8$, $KMnO_4$, CrO_3 were used as oxidants. Amongst the tested oxides, TiO_2 was found to best decompose malathion and decomposition was increased as the concentration of TiO_2 was elevated up to 14 mg/l. Addition of H_2O_2 to reactor highly enhanced the decomposition process.

Key words: Photocatalysis; TiO_2; Organophosphorous; Malathion; Decomposition.

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Introduction

Malathion is an organophosphate insecticide used to control a variety of insects in agricultural and nonagricultural purposes. Malathion contaminates the environment via spraying on agricultural crops and at agricultural sites, the malathion contamination can be released back to surface water and soil by wet deposition [1]. The contamination by malathion and other organophosphate insecticides has a great hazard to the human and animals due to carcinogenic effect and other toxic effects to nerve system [2-4]. As a result, many effective treatment methods for eliminating insecticides contamination have been studied. Of these, activated-sludge process was used to treat organophosphorous insecticides wastewaters but with low efficiently due to the resistance of the pesticides to biodegradation [5].

In recent years, TiO_2 has been used as an effective photocatalyst for decomposition of a wide range of insecticides, including organophosphorous type [6,7]. Heterogeneous photocatalysis was proved to be a successful method to decompose a large variety of insecticides in water [8,9].

Photocatalytic decomposition using TiO_2 as catalyst is especially suitable for decrease or removes the insecticides contamination due to a remarkable activity of TiO_2 compared to conventional physical, biological and chemical methods [10,11]. Photocatalysis is the photo-excitation of a solid semiconductor (TiO_2) via absorption of electromagnetic radiation in the visible and ultraviolet range [12]. Advanced oxidation processes including photodegradation reactions is one of the most promising methods for malathion removal. The photocatalytic decomposition of insecticides defined as a cyclic photo process in which the insecticides decomposed with spontaneous regeneration of catalyst allow the sequence to continue until all the contaminants destroyed [13,14].

In this work, the following parameters were investigated to study the photocatalytic decomposition of malathion: the initial concentration of malathion, the type and amount of applied catalysts, time of exposure, and presence of oxidants (type and amount).

Experimental

Chemicals

The following are the chemicals used in this work: Malathion (purity >95%, Nasr Company for Intermediate chemicals), absolute ethanol (C_2H_5OH, Aldrich), Titanium oxide (TiO_2, commercial, average size = 200 µm), Aluminium oxide, (Al_2O_3, Sigma) Ferric oxide (Fe_2O_3, Sigma), Magnesium oxide (MgO, Sigma), Hydrogen peroxide (H_2O_2, Aldrich) Potassium peroxydisulfate ($K_2S_2O_8$, Fluka), Ammonium peroxydisulfate $(NH_4)_2S_2O_8$, Fluka), Potassium permanganate ($KMnO_4$, Algomhoria Co.), and Chromium oxide (CrO_3, Aldrich).

Instrumentation and Operating Conditions

An Agilent 7890A GC coupled with flame photometric detector was employed for analyzing the contaminated samples before and after decomposition, the operating conditions for analysis of malathion are listed below;

GC	Agilent 7890 A
Sampler	Agilent 7683B, 5.0-µL syringe
Carrier	Nitrogen 2 ml/min.
Column	Agilent J&W HP-5 MS Ultra Inert 30 m × 0.25 mm × 0.25 µm
Oven	45 °C hold 1 min, to 110 °C (20 °C/min), hold 1 min °C/min, to 280 °C, (20 °C/min), hold 1 min.
Inlet	splitless; injector temperature 250 °C, 40 psi until 0.75 min, purge flow 50 mL/min at 1.0 min Injection
Detection	FPD Phosphorous mode, , Detector temperature 250 °C, (H_2 75 ml/min) , (Air 100 ml/min), (N_2 60 ml/min).

Determining the reference calibration curve of malathion

Stock solution of malathion was prepared by dissolving 200 mg of malathion in 1000 ml absolute ethanol. A series of standard concentrations were prepared by diluting the stock solution (20, 40, 60, 80,100 ppm).These standards were analyzed by GC/FPD and a calibration curve of malathion concentration Vs. peak height was recorded.

Photocatalytic decomposition experiment

The photocatalytic decomposition of malathion was conducted in a 250 ml UV reactor showen in figure (1). The reactor houses a UV-source (10W high-pressure mercury lamp, 12 cm, emission wavelength = 254 nm).

Fig.1. The photochemical cell used in the photocatalytic process

Study the effect of catalyst type

In order to study the effect of the catalysts on the photo catalysis of malathion, experiments were conducted employing different catalysts (TiO_2, Al_2O_3, Fe_2O_3, MgO) using same catalyst concentration 10 mg/l against same initial concentration of malathion (200 ppm).

Study the effect of the initial concentration of malathion

As will be shown shortly, TiO_2 gave best results. Accordingly effect of initial concentration of malathion was carried out with TiO_2 only. 10 mg of TiO_2 powder (Anatas) was added to 100 ml of malathion solution with different concentrations (100, 200, 300, 400, 500 ppm), malathion solution was Irradiated in the UV reactor. At specific time intervals samples where withdrawn from the reactor and filtered through a 0.7 µm filter then centrifuged to remove the TiO_2 particles from the solution, and then residual malathion concentrations were determined by GC/FPD.

Study the effect of catalyst concentration

In order to study the effect of the catalyst's initial concentration on the photocatalysis of malathion, experiments were conducted employing different concentrations of TiO_2 varying from 4 to 16 mg/l while using the same initial concentration of malathion (200 ppm).

Study the effect of oxidant type

In this study five oxidants was evaluated [(H_2O_2 (1 mM), $K_2S_2O_8$ (1 mM), $(NH_4)_2S_2O_8$ (1 mM), $KMnO_4$ (1 mM), CrO_3 (1 mM)] to enhance the photodecomposition efficiency.

RESULTS AND DISCUSSION

Study the effect of catalyst type

The variation in degradation efficiencies of malathion for different catalysts are shown in Figure 2. It is obvious that TiO_2 has the higher decomposition efficiency amongest the others. It is clear that after 10 minutes of radiation, the decomposition efficiencies of malathion are (79, 56.5, 53.5, 31.8) for (TiO_2, Al_2O_3, Fe_2O_3, MgO) respectively. This difference is related to the characteristics of catalysts, thier surface area, band gap and particle size. Titanium dioxide used have surface area 50 m^2 /g, diameter 200 µm, and band gap 3.2 eV, Distigushable of using commercial TiO_2-photocatalyst is interesting as cost effective approach.

TiO_2 exhibits larger surface area and a smaller particle size which are basicly responsible from one hand, for higher reaction rates at small concentrations, and from the other, for provoking more easily light scattering while on the contrary, the other oxides requires higher amounts in order to achieve similar reaction rates before light scattering takes place [16,17].

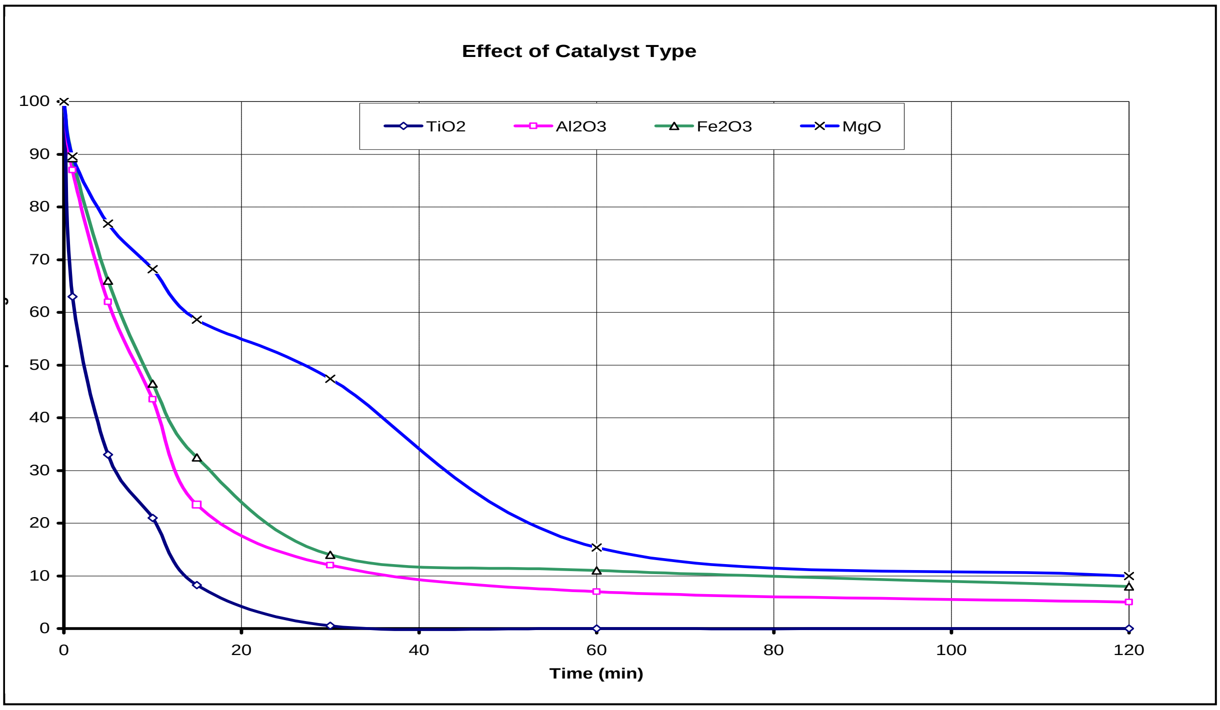

Fig.2. the effect of catalyst type on the photodecomposition process

Study the effect of the initial concentration of Malathion

The variation in degradation efficiencies of malathion at different initial concentrations of malathion are shown in Figure 3. Obviously, the degradation efficiencies decrease significantly with an increase in the initial concentration of malathion, it was clear that, when the initial concentration of malathion was 100 ppm, the degradation efficiency in 20 min was 93% , while at the initial concentration 500 ppm, the degradation efficiency was 55%, the same time.

It is reported that the recombination of photogenerated electrons and holes at the surface of TiO2 can completes within 10^{-9} s, which implies that the contaminants could not be degraded unless they are adsorbed on the surface of TiO2.[6,15], thus surface adsorption process is of paramount importance in controlling the degradation of malathion. At a fixed dosage of TiO2 and consequently constant total sites available for absorption, the degradation efficiency is expected to decrease with an increase in the initial concentration of malathion.

Fig.3, shows that as the initial concentration of malathion increased, the rate of decomposition decreased and the time of decomposition increased

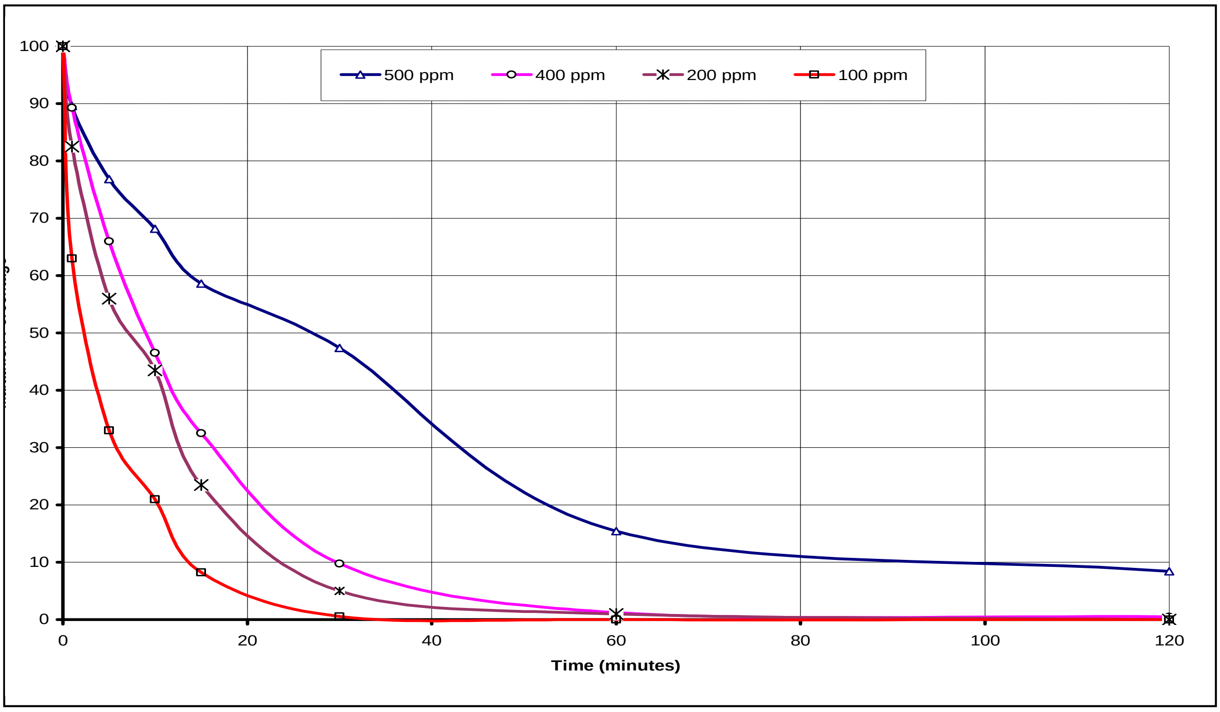

Fig.3. The effect of the initial concentration of malathion on the photodecomposition process

Study the effect of catalyst concentration

The effect of catalyst concentration on the photocalytic decomposition of malathion was showed in figure 4, It is obvious that the decomposition rate is directly proportional to the concentration of catalystuntill the concentration reached to 100 ppm, however, above this value, the decomposition rate becomes independent of the concentration the catalyst, this is due to, the suspended particles of the catalysts block the UV-light passage and increase the light scattering [18].

Effect of the addition of an oxidant

The addition of an oxidant into a semiconductor suspension has been proven to enhance the photodegradation rate of a variety of organic pollutants.[17,18,19]
the addition of five oxidants [H_2O_2, $K_2S_2O_8$, $(NH_4)_2S_2O_8$, $KMnO_4$, andCrO_3] was evaluated at the same conditions and ploted in figure 5, Obviously, the presence of low concentration of oxidant (1.0 mmol/L) pronouncedly elevated the degradation effeciency of malathion.

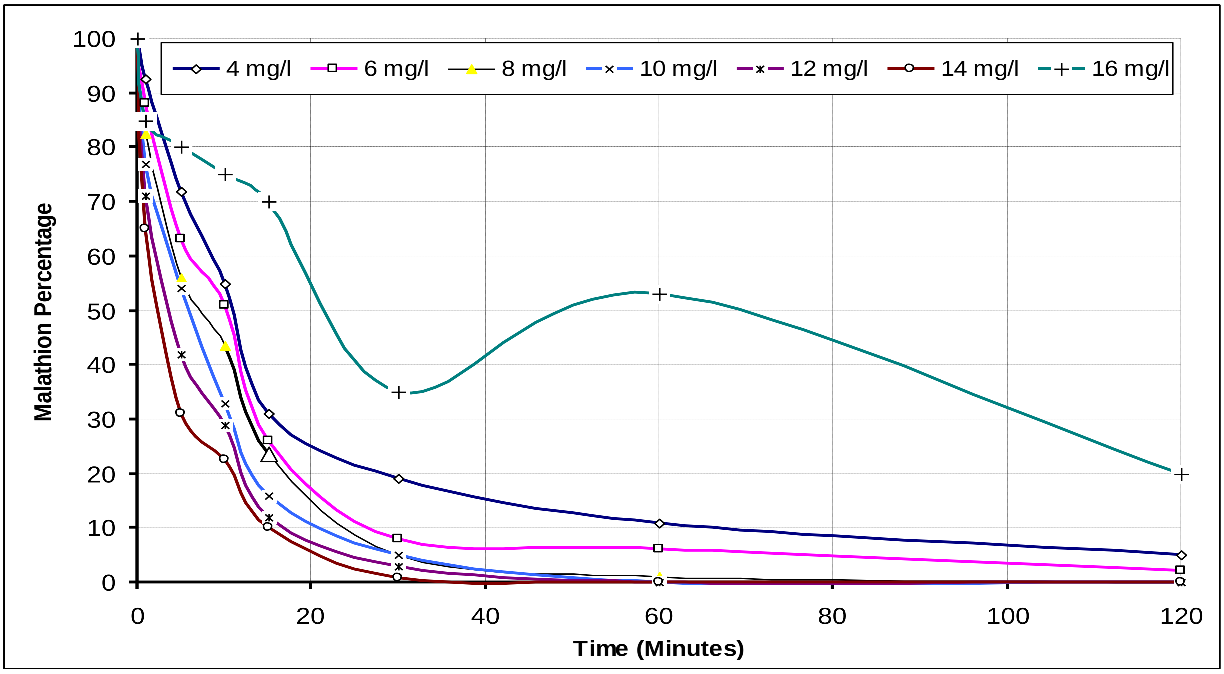

Fig.4. the effect of catalyst concentration on the photodecomposition process

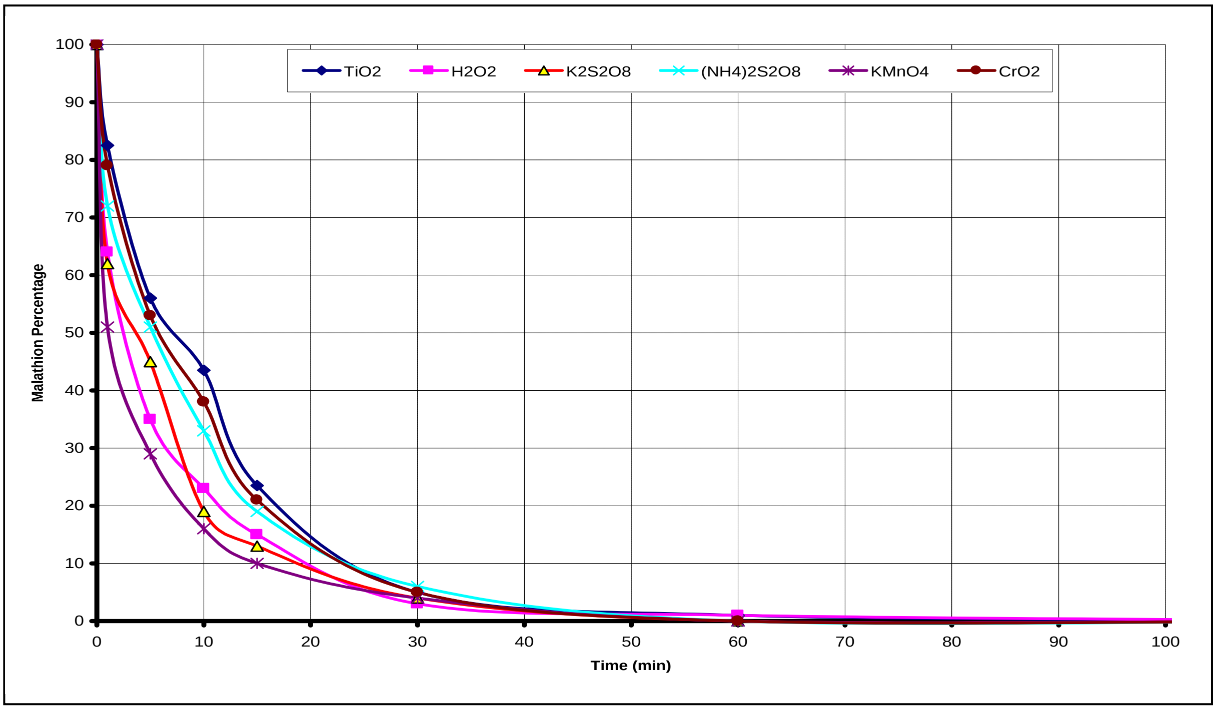

Fig.5. the effect of oxidant type on the photodecomposition process

A further increase in degradation efficiency was not observed with an increase in concentration of oxidant, Instead, a slight decrease occurred when the concentrations of oxidant were above 6.0 mmol/L, As strong oxidants,can serve as efficient scavengers of electrons to prevent electron-hole recombination at the surface of catalyst through the following reactions [17,20]:

$$H_2O_2 + e \longrightarrow OH + OH^-$$
$$S_2O_8^{-2} + e \longrightarrow SO_4^- + SO_4^{-2}$$

Furthermore, hydroxyl radicals and sulfate radicals , two highly oxidizing species produced in the above reactions, would also contributeto the decomposition of malathion. But, at a concentration high enough, excessive adsorption of $H_2O_2/K_2S_2O_8$ on TiO_2 surface probably prevents malathion from approaching the surface of TiO2, resulting in a slight decrease in malathion degradation as shown in Fig. 6. In addition, hydroxyl radicals may be scavenged by excessive H_2O_2.

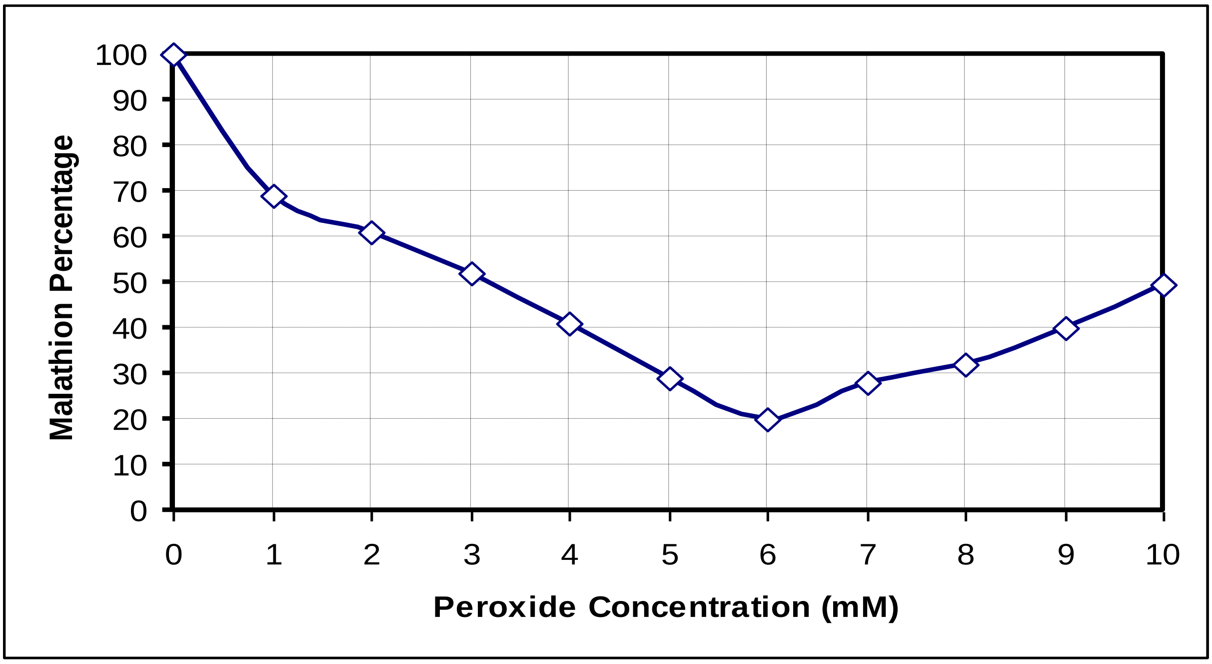

Fig.6. the effect of oxidant concentration on the photodecomposition process

Conclusion

The photocatalytic decomposition of malathion has been studied using TiO_2, Al_2O_3, Fe_2O_3, and MgO as catalysts., Titanium dioxide proved to be more efficient photocatalyst since the oxidation and decomposition of malathion at higher reaction rates. at optimal operating parameters, the degradation efficiency could reach 100% in 30 min when the concentration of malathion is below 100 ppm. Titanium dioxide loading has significant effect on the degradation of malathion. The degradation efficiency increases with elevated concentration of TiO2 suspension up to 14 mg/L, then the efficiency reduced slightly when the concentration is above 14 mg/L due to a lightshielding effect. The presence of oxidants enhance photodegradation efficiency of malathion. However, the increment in degradation efficiency may be suppressed to some extent due to being scavenged of OH radicals species by excessive $H_2O_2/K_2S_2O_8$ at a high concentration level.

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