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Photocatalytic Decomposition Of Dimethoate Using Some Selected Metal Oxides Powder

M. I. Awaad[*], M. S. Fayed[*], M. K. Abd El Magid[*], A. Baraka[*]

Abstract

Dimethoate is an organophosphorous insecticide used to control a variety of insects in agricultural productions. The contamination of water by dimethoate and other organophosphate insecticides represents a great hazard to the humans and animals due to carcinogenic effect and other toxic effects on nerve system. To remove dimethoate contamination from water, photocatalysis has been applied as a powerful method. Powder form of some selected metal oxides such as TiO_2, Al_2O_3, Fe_2O_3, and MgO were used. Photocatalytic decomposition of dimethoate at different conditions (dimethoate initial concentration, catalyst type and catalyst concentration, temperature, and presence of oxidant) was investigated in a batch reactor. Oxidants such as H_2O_2, $K_2S_2O_8$, and $(NH_4)_2S_2O_8$ were used. Amongst the tested oxides, TiO_2 achieved the best decomposition efficiency of dimethoate and the decomposition increased as the concentration of TiO_2 increased up to 100 mg/l. Addition of H_2O_2 to reaction system highly enhanced the decomposition process.

Key words: Photocatalytic decomposition; TiO_2; Organophosphorous; Dimethoate.

[*] Egyptian Armed Forces

Introduction

Dimethoate is an organophosphate insecticide used to control a variety of insects in agricultural and nonagricultural purposes. Dimethoate contaminates the environment via spraying on agricultural crops and at agricultural sites. The dimethoate contamination can be released back to surface water and soil by wet deposition [1]. The contamination by dimethoate and other organophosphate insecticides has a great hazard to the humans and animals due to carcinogenic effect and other toxic effects on 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 efficiency due to the resistance of the insecticides to biodecomposition [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 decreasing or removal of 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 process including photodecomposition reactions is one of the most promising methods for dimethoate removal. The photocatalytic decomposition of insecticides defined as a cyclic photo process in which the insecticides decompose with spontaneous regeneration of catalyst allows the sequence to continue until all the contaminants are destroyed [13,14].

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

Experimental

Chemicals

The following chemicals are used in this work: Dimethoate (purity >95%, Nasr Company for Intermediate chemicals), deionised water (H_2O, Aldrich), 1,2 dichloroethane ($C_2H_4Cl_2$, Sigma), Titanium oxide (TiO_2, commercial, average particle size = 200 µm), Aluminium oxide, (Al_2O_3,BDH), Ferric oxide (Fe_2O_3, Sigma), Magnesium oxide (MgO, Sigma), Hydrogen peroxide (H_2O_2, Aldrich), Potassium peroxydisulfate ($K_2S_2O_8$, Fluka), and Ammonium peroxydisulfate ($(NH_4)_2S_2O_8$, Fluka).

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 dimethoate 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 dimethoate

Stock solution of dimethoate was prepared by dissolving 200 mg of dimethoate in one liter deionized water. A series of standard concentrations were prepared by diluting the stock solution (20, 40, 60, 80,100 mg/l).These standards were extracted by using 1,2 dichloroethane before analysis by GC/FPD and a calibration curve of dimethoate concentration Vs. peak height was recorded.

Photocatalytic decomposition experiment

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

The photodecomposition efficiency of the dimethoate (η) is expressed by:

$$\eta = \left(\frac{C_o - C}{C_o} \right) * 100$$

where, C_o is the initial concentration of the contaminant (mg/l), and C is the concentration at time (t).

Effect of catalyst type

In order to study the effect of the catalysts type on the photocatalytic decomposition of dimethoate, experiments were conducted employing different catalysts (TiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$, MgO) using same catalyst concentration of 100 mg/l with the same initial concentration of dimethoate (200 mg/l).

Effect of the initial concentration of dimethoate

In this part of the study, the effect of initial concentration of dimethoate was carried out with TiO$_2$ as a catalyst. TiO$_2$ (Anatas, 10 mg) was added to dimethoate solution (100 ml) with different concentrations (100, 200, 300, 400, 500 mg/l). Dimethoate solutions were 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. The residual dimethoate concentration was determined by GC/FPD.

Effect of catalyst concentration

In order to study the effect of the catalyst's concentration on the photocatalytic decomposition of dimethoate, experiments were conducted employing different concentrations of TiO_2 varying from 10 to 200 mg/l while using the same initial concentration of dimethoate (200 mg/l).

Effect of oxidant type

In this study three oxidants were applied [(H_2O_2 (1 mM), $K_2S_2O_8$ (1 mM), and $(NH_4)_2S_2O_8$] to enhance the photodecomposition efficiency.

Effect of reaction temperature

In order to study the effect of temperature on the photocatalytic decomposition of dimethoate, the photocatalytic decomposition experiments were carried out at different temperatures varying from 20 to 50 ^{o}C.

RESULTS AND DISCUSSION

Effect of catalyst type

The variation of the photocatalytic decomposition efficiencies of dimethoate (η) for different catalysts is shown in figure (1). It is obvious that TiO_2 has the highest decomposition efficiency amongest the other catalysts. It is clear that after 30 minutes of UV radiation, the decomposition efficiencies of dimethoate are (98, 79, 73, 60) for TiO_2, Al_2O_3, Fe_2O_3, MgO respectively. This difference could be related to the characteristics of catalysts, their surface area, band gap and particle size. The used titanium dioxide have surface area of 4 m^2/g, diameter 200 µm, and band gap 3.2 eV. Using of commercial TiO_2-photocatalyst is interesting as cost effective approach, in addition to the photoinduced reactivity and the wide-band gap of titanium dioxide. 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 other hand, the other oxides require higher amounts in order to achieve similar reaction rates before light scattering takes place [16,17].

Effect of the initial concentration of Dimethoate

The variation in photocatalytic decomposition efficiencies of dimethoate at different initial concentrations of dimethoate is shown in figure (2). Obviously, the decomposition efficiencies decrease with an increase in the initial concentration of dimethoate, it was clear that, when the initial concentration of dimethoate was 100 mg/l, the decomposition efficiency after 20 min was 77 %, while at the initial concentration 500 mg/l, the decomposition efficiency was 58.6 %, for the same irradiation time.

It is reported that the recombination of photogenerated electrons and holes at the surface of TiO_2 can complete within 10^{-9} s, which implies that the contaminants could not be degraded unless they are adsorbed on the surface of TiO_2.[6,15]. Thus surface adsorption process is of great importance in controlling the decomposition of dimethoate. At a fixed dosage of TiO_2 and consequently constant total sites available for adsorption, the decomposition efficiency is expected to decrease with an increase in the initial concentration of dimethoate.

Effect of catalyst concentration

The effect of catalyst concentration on the photocalytic decomposition of dimethoate is shown in figure (3). It is obvious that the decomposition rate is directly proportional to the concentration of catalyst untill the concentration reachs 100 mg/l. However, above this value, the decomposition rate becomes independent of the catalyst concentration. This is due to, the suspended particles of the catalyst which block the UV-light passage and increase the light scattering [18].
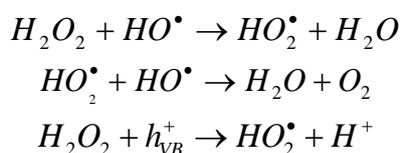
Effect of the addition of an oxidant on the photocatalytic decomposition process

The addition of an oxidant into a catalyst suspension has been shown to enhance the photodecomposition rate of a variety of organic pollutants.[17,18,19]. The effect of addition of three oxidants [H_2O_2, $K_2S_2O_8$, and $(NH_4)_2S_2O_8$] on the photocatalytic decomposition of dimethoate was evaluated at the same experimental conditions , the result of these experiments are shown in figure (4). Obviously, the presence of low concentration of oxidant (1.0 mmol/L) pronouncedly elevated the decomposition effeciency of dimethoate.

In order to study the effect of concentration of the oxidant on the photocatalytic process, experiments of the photocatalytic decomposition of dimethoate employing different initial concentrations of the oxidant varying from 1 to 10 mM solution were conducted. In figure (5), it is obvious that, the photocatalytic decomposition rate increased with increases the concentration of peroxide until the concentration reached 6 mM, after this concentration, no significant change in the reaction rate was observed, on the contrary the rate decreased slightly. At low concentration of peroxide, it acts as an electron acceptor and consequently it can promote the charge separation, moreover it can also produce OH$^\bullet$ radicals according to the following equations [6]:

$$H_2O_2 + e^-_{CB} \rightarrow HO^- + HO^\bullet$$

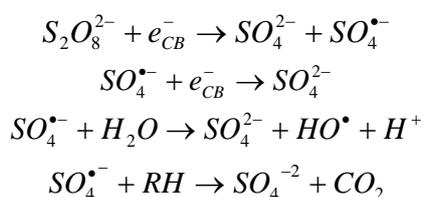$$H_2O_2 + O_2^- \rightarrow HO^- + HO^\bullet + O_2$$
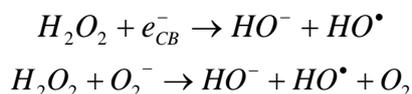
At high concentrations of peroxide, it may act as a powerful OH$^\bullet$ scavenger and also react with the photogenerated hole, such as follows [6]:

$$H_2O_2 + HO^\bullet \rightarrow HO_2^\bullet + H_2O$$

$$HO_2^\bullet + HO^\bullet \rightarrow H_2O + O_2$$

$$H_2O_2 + h^+_{VB} \rightarrow HO_2^\bullet + H^+$$

Consequently, the optimum concentration of hydrogen peroxide which gives the best results was found to be 6 mM.

The effect of adding another oxidant (peroxydisulfate) was studied. It gave approximately the same results of peroxide. The mechanism of action of $K_2S_2O_8$ is suggested as follows [16, 18]:

$$S_2O_8^{2-} + e^-_{CB} \rightarrow SO_4^{2-} + SO_4^{\bullet-}$$

$$SO_4^{\bullet-} + e^-_{CB} \rightarrow SO_4^{2-}$$

$$SO_4^{\bullet-} + H_2O \rightarrow SO_4^{2-} + HO^\bullet + H^+$$

$$SO_4^{\bullet-} + RH \rightarrow SO_4^{-2} + CO_2$$

Where h_{VB}^{+} is the hole at valance band, e_{CB}^{-} is the electrons at conduction band, *RH* refers to the contaminant. $K_2S_2O_8$ traps the photogenerated electrons, preventing the recombination with the positive hole and at the same time produces the sulfate radical, which is a very strong oxidizing agent (reduction potential of SO^{4-} (E^{o} = 2.6 V) [18].

The use of $K_2S_2O_8$ as oxidant is similar to peroxide at low concentrations, in which, the photocatalytic decomposition rate increased with increasing the concentration of $K_2S_2O_8$. While in case of using high concentration, the photocatalytic decomposition rate still increased even at very high concentrations of $K_2S_2O_8$. When comparing the two oxidants, it was clear that, the $K_2S_2O_8$ was more effective than hydrogen peroxide, due to its ability to achieve a higher photocatalytic rates, and doesn't act as radical scavenger at high concentrations while there is no dependence on the oxidant/contaminant molar ratio.

Effect of temperature

From figure (6), it is clear that at fixed illumination time, increasing temperature from 20 to 50 ^{o}C, the photocatalytic decomposition efficiency of the contaminant slightly increase. The enhancement of the photodecomposition is probably due to the increasing collision frequency of molecules. Irradiation is believed to be the primary source of electron/hole pairs at ambient temperature because the band gap is too high to overcome by thermal excitation [18,19].

To explain the effect of temperature on the photocatalytic decomposition process, the apparent activation energy (E_a) has been calculated from the Arrhenius equation

$$k_{ap} = k_{ap}^{0} e^{-\frac{E_a}{RT}}$$

where k_{ap} (min^{-1}) is the apparent rate constant for pseudo-first order kinetic model, k_{ap}^{0} the temperature absolute independent factor (min^{-1}), *R* the gas constant (8.31 J/K mol), *T* is the solution temperature, and E_a the apparent activation energy of the photocatalytic decomposition (J/mol), which represents the total activation energy of both adsorption and photocatalytic decomposition of dimethoate.
The linear transform of Equation is;

$$\ln k_{ap} = \ln k_{ap}^{0} - \frac{E_a}{RT}$$

The slope of linear plots of ln k_{ap} versus 1/*T* is equal to ($-E_a/R$), the higher slope means that, the system is more dependent on temperature, and the lower slope means that, the system is less dependent on temperature [18, 19]. The value of the activation energy was calculated for dimethoate from figure (7), calculated E_a was 2.125 kJ/mol for TiO_2 system. According to the small E_a value, it is clear that, the photocatalytic decomposition of dimethoate by TiO_2 is slightly temperature dependant [18,19].

Conclusion

The photocatalytic decomposition of dimethoate has been studied using TiO_2, Al_2O_3, Fe_2O_3, and MgO as catalysts., Titanium dioxide proved to be more efficient photocatalyst. For the oxidation and decomposition of dimethoate were of at higher reaction rates. At optimal operating conditions, the decomposition efficiency could reach 100% in 30 min when the

concentration of dimethoate is below 100 mg/l. Titanium dioxide loading has significant effect on the decomposition of dimethoate. The decomposition efficiency increases with increased concentration of TiO_2 suspension up to 100 mg/l, then the efficiency decreases slightly of concentrations above 100 mg/l due to a lightshielding effect. Low concentrations of oxidants enhance photodecomposition efficiency of dimethoate. However, the increment in decomposition efficiency may be suppressed to some extent since OH radical species are scavenged by excessive H_2O_2 at a high concentration level. The photocatalysis process is mild temperature dependent.

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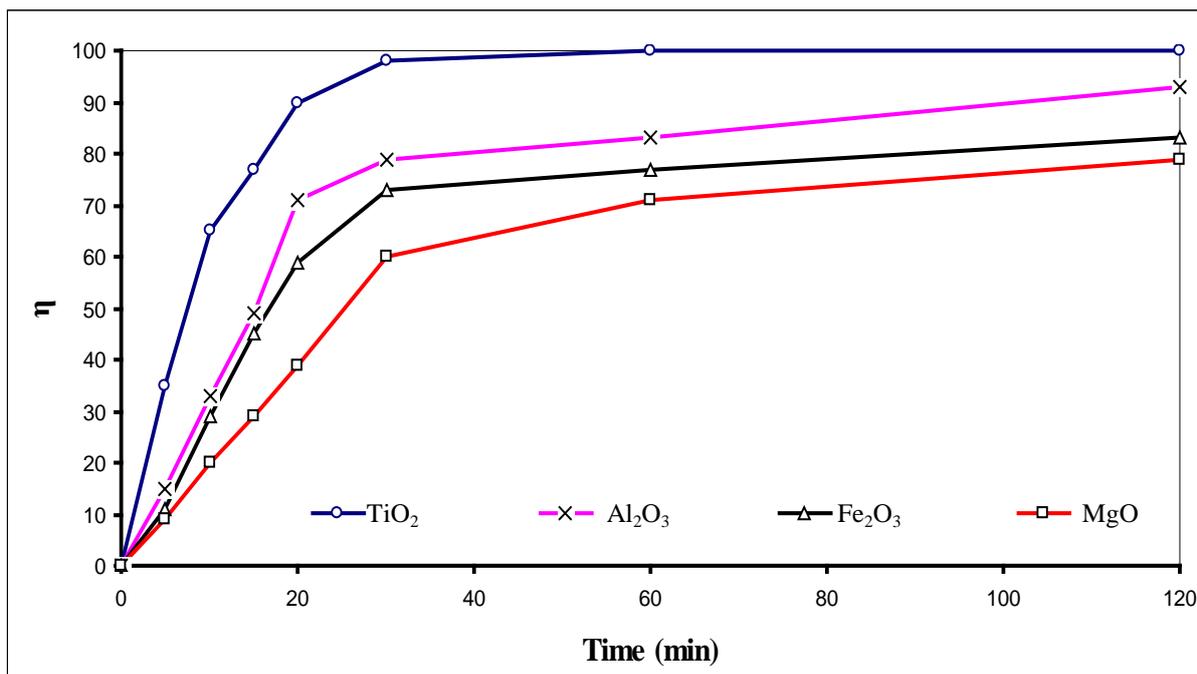
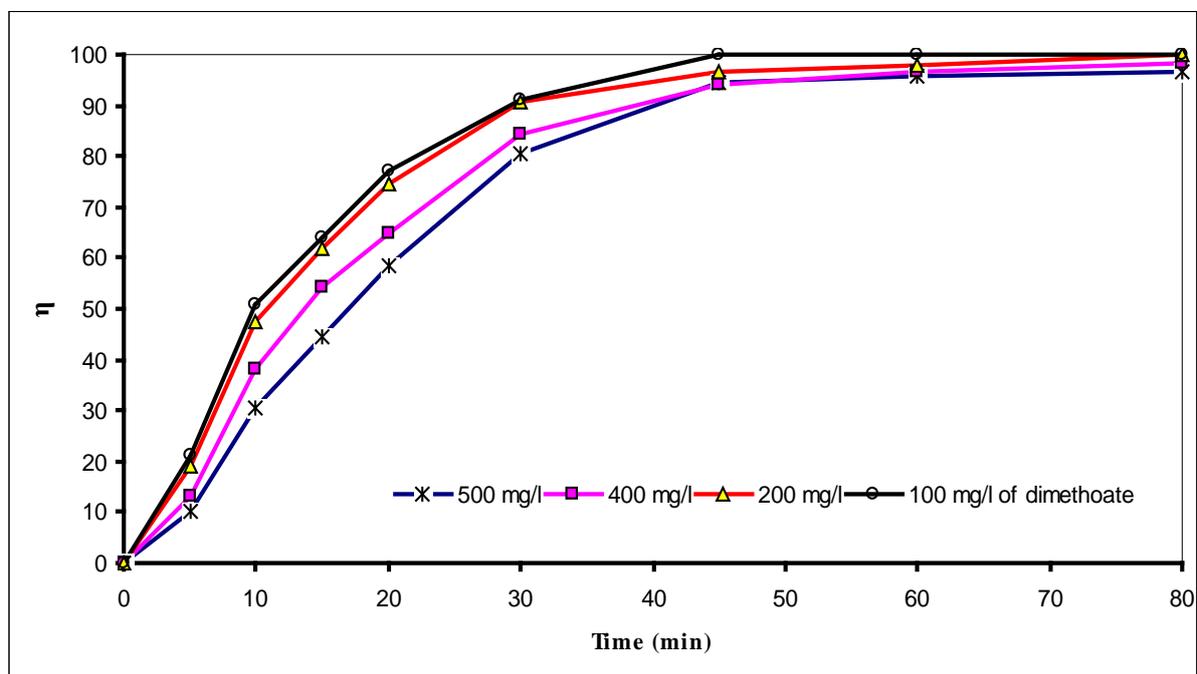**Fig.1. Effect of catalyst type on dimethoate photodecomposition at 30 ^{o}C**

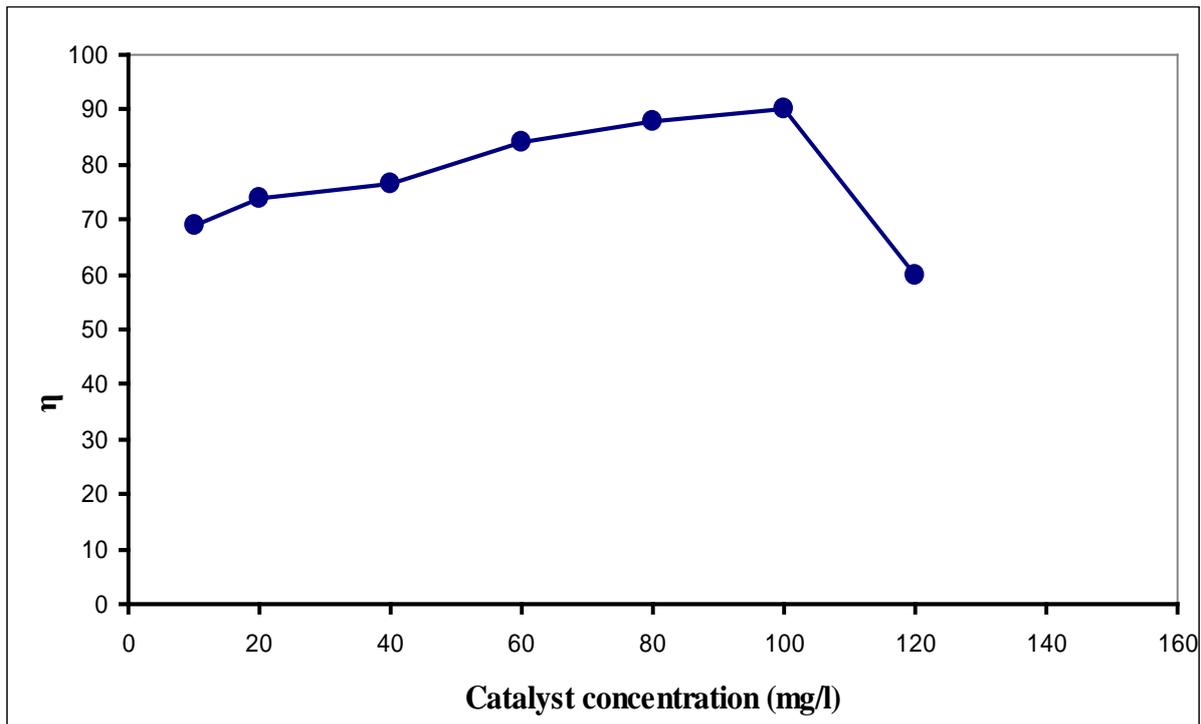**Fig.2. Effect of the initial concentration of dimethoate on its photodecomposition at 30 ^{o}C**

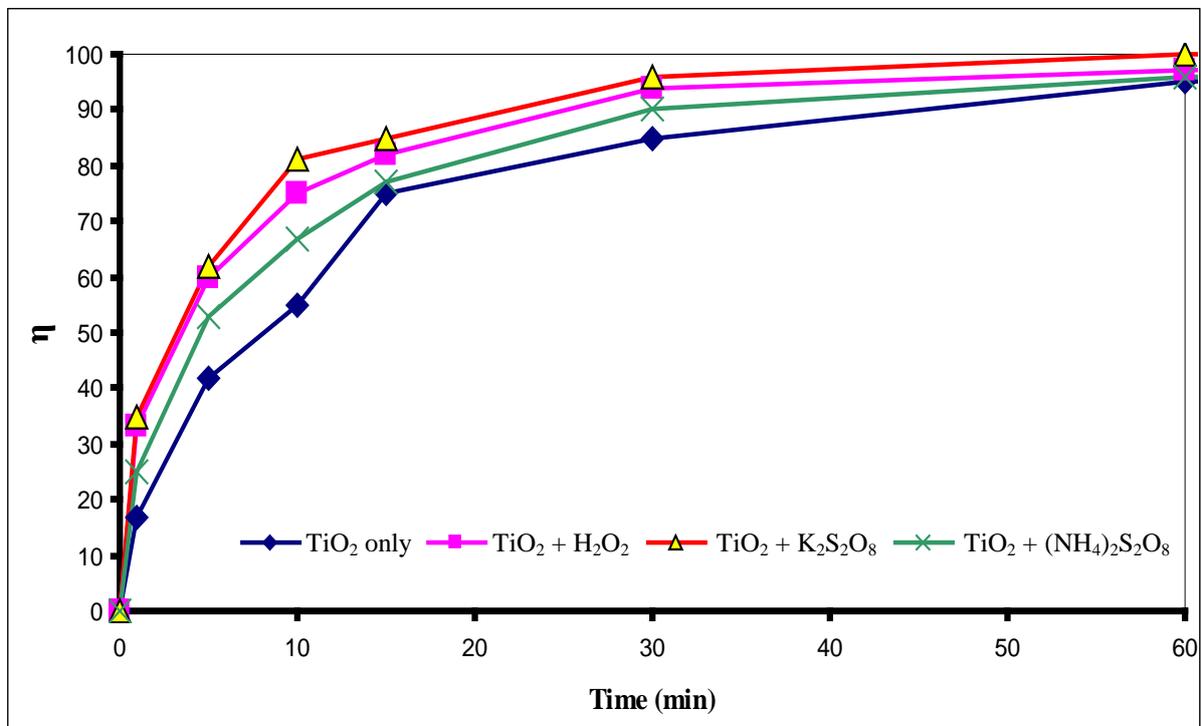**Fig.3. Effect of TiO₂ concentration on dimethoate photodecomposition at 30 °C**

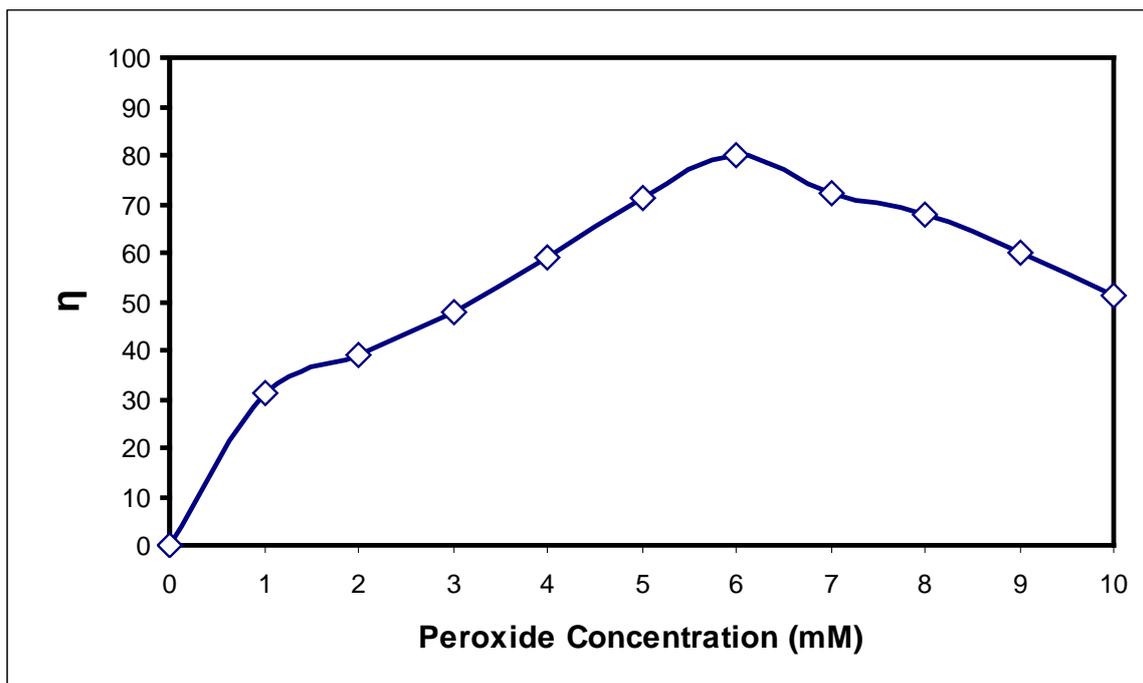**Fig.4. Effect of oxidant type on dimethoate photodecomposition at 30 °C**

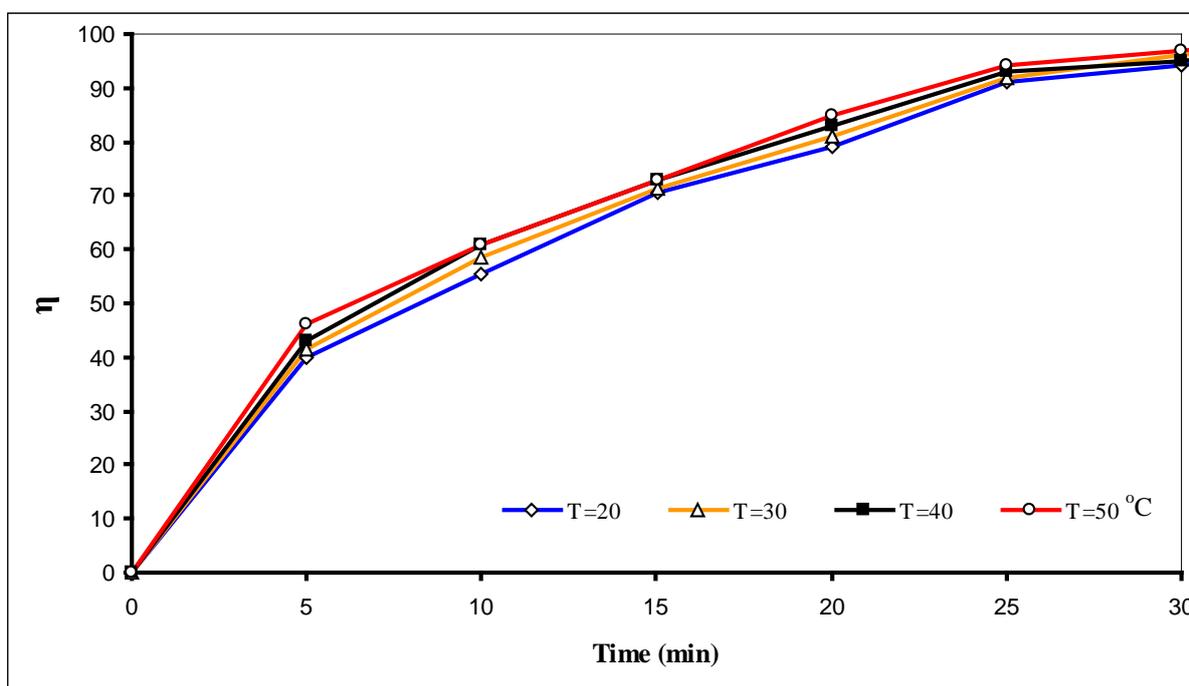**Fig.5. Effect of oxidant concentration on dimethoate photodecomposition at 30 ^{o}C**

Fig. 6. Effect of temperature on the photocatalytic decomposition of dimethoate by TiO$_2$ at different illumination times
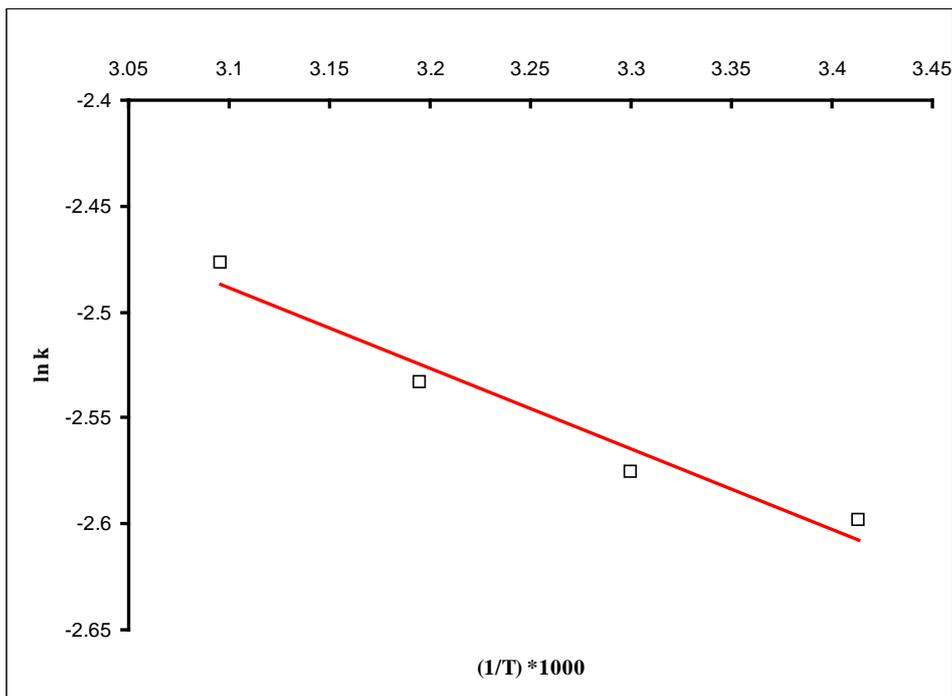
Fig.7. ln k Vs (1/T) relation for the photocatalytic decomposition of dimethoate of by TiO₂