ADVANCED OXIDATION PROCESSES FOR THE REMOVAL OF ORGANO-PHOSPHORUS PESTICIDES FROM WASTEWATER"

M.I.Badawy*, E.R. Souaya**, Montaser Y. Ghaly* & Tarek A. Shafy*

*   National Research Centre (NRC), Egypt.

**   Faculty of Science, Ein Shams University

ABSTRACT

The combinations of Fenton reaction, UV/H_2O_2 and photo-Fenton process in the degradation of organo-phosphorus containing substrates such as fenitrothion, diazinon and profenofos have been investigated. A laboratory set-up was designed to evaluate and select the optimal oxidation process. Several parameters were also studied as: initial pH, COD/H_2O_2 ratios, $Fe(II)/ H_2O_2$ ratios and the type of photo-catalyst to define the optimum operating conditions. The kinetic study indicated that the degradation rate of the used model substances was first order and the calculated reaction constants were affected by the parameters studied. The oxidation processes were repeated at the optimum operating conditions for the degradation of the mixture of the used model substances to represent the real wastewater effluent from pesticides producing company. A rough comparison of specific energy consumption was also evaluated to compare between the photochemical processes. The experimental results shows that the light-enhanced Fenton reaction (photo-Fenton) has proven to be a most effective and economic treatment process under acidic conditions and might be an alternative to the other traditional processes.

I. INTRODUCTION

Pesticides used in Egypt are of different types such as organochlorine, organophosphours, carbamates, urea, anilides and pyrethoid. The four general categories of these pesticides are insecticides, fungicides, herbicides and bactericides. Organophsphours insecticides are of great significance in pest control and increasingly used instead of organochlorine insecticides. Organophosphours insecticides represent more than 80% of total insecticides used in Egypt [1].

Pesticides and chemical industry are considered that of the most industrial activities generate wastewaters containing toxic and non-biodegradable compounds that remain in the environment even after the wastewater have been subjected to conventional processing system [1,2]. Therefore, human population is exposed to pesticides and other organic micro-pollutants either through drinking water or via the food supply. In addition to the formation of mutagenic compounds during the conventional oxidation processes [3,4]. Therefore, it was very important to develop water and wastewater treatment technologies for the removal of toxic and refractory organic compounds (ROCs) from water and wastewater. Advanced oxidation processes are considered one of the most attractive methods for the treatment of the water and wastewater that contain toxic and non-biodegradable pollutants. ·

Advanced Oxidation processes (AOPs) use combinations of oxidants, ultraviolet irradiation and catalysts to generate hydroxyl radicals (OH·) in solutions and have attracted interest for the degradation of biorefractory or hazardous organic compounds in wastewater. The organic pollutants are oxidized by free radicals and mineralized to water, carbon dioxide and mineral salts. A number of studies have indicated the potential for using Advanced Oxidation Processes (AOPs) to completely destroy micro-pollutants such as pesticides.

The Fenton reaction (Fe^{2+}/ H$_2$O$_2$), and Fenton-like reactions (Fe^{3+}/ H$_2$O$_2$), have been widely applied in the treatment of non-biodegradable wastewater in the field of Advanced Oxidation Processes (AOPs) [5,6]. However, Fenton systems (Fenton reaction + Fenton-like reaction) have two limitations ((1) large production of iron sludge, (2) slow reduction of ferric ions by H$_2$O$_2$) in their application [7,8]. Illumination of the system by UV was suggested to overcome the limitations of the Fenton system. The photoreduction of various ferric species contributes to the production of ferrous ions and radical species [9]. For the development of

effective wastewater treatment methods, complete degradation of the contaminants to harmless end products (CO_2) and mineral salts is important.

The present work investigates the degradation of three model compounds of organo-phosphorus pesticides by Advanced Oxidation processes using UV, UV/H_2O_2, Fenton and photo-Fenton treatment.

2. EXPERIMENTAL METHODS

2.1. Model Substrates and Materials

Fenitrothion, diazinon and profenofos (from Supelico) were used as model substances of organo-phosphorus pesticides. All reagents employed were not subjected to any further purification. They were chosen because their toxicity and they are widely used as insecticides in Egypt. The physical and chemical properties of the selected model substances are listed in Table (1). Ferrous sulfate heptahydrate ($FeSO_4.7H_2O$) and ferric chloride ($FeCl_3$) (from Merck) were used as sources of Fe(II) and Fe(III) catalyst to compare between the influence of the type and valance of the catalyst. Sulfuric acid and sodium hydroxide (from Merck). Hydrogen peroxide solution (35% w/w) in stable form was provided by Merck. Water used throughout was distilled water.

2.2. Experimental Set-up

A laboratory unit was used for the batch experiments. The schematic diagram of the experimental set-up used in this study is shown in Figure (1). The reactor was cylindrical with 0.85L volume and was made from quartz glass, which was available for the transfer of the radiation. Heraeus TNN 15/32; 150W medium-pressure mercury lamp (from Germany). Heraeus TQ 150, was used as UV emitter and light source. The medium-pressure lamp emitted a power of 62W in the UV-C ($100<\lambda<280nm$) range (indication Heraeus), corresponding to $1.32*10^{-5}$ Einstein s^{-1}.

The UV lamp was immersed centrally in the glass tube and equipped with a cooling water jacket system to maintain the reaction solution at a room temperature, which was placed in the reactor vessel. The reaction chamber was filled with the reaction mixture, which was placed between the reactor walls and UV lamp system. Mixing was accomplished by means of a closed external circulating loop through the illuminated part of the photoreactor by the

use of a peristaltic pump. The flow system was assembled with polytetrafluorethylene (PTFE) or glass tubing and connectors.

2.3. Experimental Procedures

Synthetic solutions from the studied compounds at constant initial concentrations (50 ppm, to simulate high-loaded organo-phosphorus pesticides containing industrial wastewater), were prepared in distilled water. The laboratory unit was filled separately with 0.85L of each model substance solution. The desired pH value was adjusted with sulfuric acid before startup, and then a given weight of iron salt was added. The iron salt was mixed very well with the tested model substance solution before the addition of a given volume of hydrogen peroxide. For the dark processes (Fenton reaction), the reaction time starts when the solution is injected by hydrogen peroxide. For light photo-processes, the time at which the ultraviolet lamp was turned on was considered time zero or the beginning of the experiment which was taking place simultaneously with the addition of hydrogen peroxide. The hydrogen peroxide dosage was based on the stoichiometric ratio with respect to COD. The solution was circulated at a flow rate of 180 lh^{-1} for one hour.

2.4. Analytical Methods

Samples were taken at regular time intervals from the reaction vessel and were analyzed immediately to avoid further reaction. As literature reported [10], Fenton and photo-Fenton reaction cannot proceed at pH>10. Therefore, the reaction was stopped instantly by adding NaOH to the reaction samples before H_2O_2 analysis. One drop of $Na_2S_2O_3$ (0.1N) was also added to each sample to decompose any residual hydrogen peroxide and prevent hydrogen peroxide from reacting with organic substrates during the analysis. Hydrogen peroxide was detected by a modified iodometric titration method [11].

Total organic carbon measurements (TOC) were carried out by using a Shimadzu TOC-Analyzer 5000 equipped with an auto-sampler ASI-5000. The pH was measured by means of a WTW pH-Meter 537 equipped with a pH combination electrode E56. Chemical oxygen demand (COD) was carried out via a Hach-2000 spectrophotometer using dichromate solution as the oxidant in strong acid media [12].

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3. RESULTS & DISCUSSION

In the Fenton and photo-Fenton processes, the H_2O_2 was oxidized and $OH^•$ was produced. The formation of $OH^•$ depends on several factors such as pH, dose of Fe^{3+}, initial concentration of H_2O_2 and the ratios between organic loads and H_2O_2. Therefore, the effects of the previous factors were investigated.

3.1. Effect of pH

The pH value has a decisive effect on the oxidation potential of $OH^•$ radicals because of the reciprocal relation of the oxidation potential to the pH value ($E^0 = 2.8$ V and E^{14} =1.95V). Furthermore, the concentration of inorganic carbon and the hydrolytic speciation of Fe(III) species are strongly affected by the pH value. Therefore, it is required to determine the role of pH in the photo-assisted Fenton reaction.

The TOC degradation of model substances by Fenton and photo-Fenton treatment as a function of pH are shown in Figure (2) (a & b). The experiments have been carried out a pH range from 2 to 5. The results clearly indicate that the extent of degradation decreases with the increase in pH value for pH>3. This demonstrates the most effective pH value for degradation of the selected model substrates by both Fenton and photo-Fenton treatment is 3. This is consistent according to Kuo [13], more $Fe(OH)^+$ is formed at pH 2-4 and the activity of $Fe(OH)^+$ is higher than Fe^{2+} in Fenton and photo-Fenton reaction. This may be a reason for the optimal degradation of model substances in this range. At acidic pH values, it has been shown that hydrogen peroxide decomposes to produce $OH^•$ radicals. For pH values above 4 the degradation strongly decreases because at higher pH values iron precipitates as its hydroxide which reduces the transmission of the radiation into the water in case of photo-Fenton treatment [14]. Another reason for the inefficient degradation at pH>3 is due to the dissociation and auto-decomposition of H_2O_2 [15]. A maximum TOC degradation of 86.9, 56.7, 89.7% for fenitrothion, diazinon and profenofos respectively, were obtained with the photo-Fenton treatment within 30 minutes at a pH=3. While 54.2, 12.9, and 46.2% TOC degradation for fenitrothion, diazinon and profenofos respectively were obtained with Fenton reaction within 90 minutes at the same pH value.

3.2. Effect of UV irradiation -

Free radicals can be obtained from catalytic reaction of iron salt with hydrogen peroxide either in absence or presence of UV-light. Figure (3) (a & b) provides the time-percentage TOC degradation data for the model substances by both of Fenton and photo-Fenton treatment, respectively. It was found that in Fenton treatment, the TOC degradation of fenitrothion, diazinon and profenofos after 90 min obtained was 54.1, 12.9, and 50.3% respectively. In this case, due to the limited ferrous ion concentration, the concentration of OH^- radicals produced may be limited, i.e., one molecule of Fe^{2+} produces only one OH^- radical as shown by Reaction (1).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^\bullet \qquad\qquad \text{Reaction (1)}$$

In contrast to the Fenton reaction, the TOC degradation was increased in the photo-Fenton reaction. In the irradiated reaction, the UV irradiation contributes by photolysis of Fe^{3+} complex ions and H_2O_2 to the formation of OH^- radicals as shown by Reaction (2).

$$Fe^{3+} + H_2O_2 + hv \rightarrow Fe^{2+} + OH^\bullet + H^+ \qquad\qquad \text{Reaction (2)}$$

In the presence of H_2O_2, the regenerated Fe^{2+} from the photolysis of Fe^{3+} species is subsequently reoxidized by H_2O_2 and produces new OH^- radicals, so that the oxidation of organic compounds is accelerated. About 86.9, 56.7, 89.7% of TOC degradation of fenitrothion, diazinon and profenofos, after 30 min was only obtained by photo-Fenton treatment. As be noticed that the degradation of diazinon with either Fenton or photo-Fenton treatment has lower values of % TOC removal. These results can be explained on the basis of different activation of benzene ring. Diazinon has heterocyclic ring, which is less activated, so that hydroxylation and ring cleavage are very difficult. On the other hand, profenofos and fenitrothion have a rather activated ring, so that the oxidation and ring cleavage are much easier. Profenofos has two electron attracting groups in p- and o-positions, meanwhile fenitrothion has electron donating group in p-position (NO_2 group). Therefore, the degradation of profenofos is faster than fenitrothion.

3.3. Effect of COD:H_2O_2 ratio

The H_2O_2 dosage was based on the stoichiometric ratio with respect to COD. This was calculated assuming complete oxidation of COD as follows:

$$1g\ COD = 1g\ O_2 = 0.03125\ mol\ O_2 = 0.0625\ mol\ H_2O_2 = 2.125\ g\ H_2O_2.$$

To determine the optimum COD: H_2O_2 ratio, experiments were carried out by varying the H_2O_2 dosage at constant concentrations of the selected models and COD. Figure (4) (a & b) illustrates the % TOC degradation as a function of COD: input H_2O_2 ratios. The investigation has been carried out ratios of 1:1.1, 1:2.2, 1:3.3 and 1: 4.4. The experimental results of Figure (4) shows that the % TOC degradation increases either by Fenton or photo-Fenton treatment over the stoichiometric ratio; this can be explained by the effect of the additionally produced OH$^•$ radicals. Addition of H_2O_2 exceeding the stoichiometric ratio of COD: H_2O_2 1: 2.1 did not improve the respective maximum degradation. This may be due to auto-decomposition of H_2O_2 to oxygen and water and the recombination of OH radicals as follows:

$$2H_2O_2 \rightarrow 2H_2O + O_2,\quad\quad\quad\quad\quad\quad\quad\quad\quad Reaction\ (3)$$

$$OH^• + H_2O_2 \rightarrow H_2O + HO_2^•\quad\quad\quad\quad\quad\quad\quad Reaction\ (4)$$

Since the OH free radical reacts with H_2O_2, the H_2O_2 itself contributes to the OH scavenging [16]. Therefore, H_2O_2 should be added at the optimal concentration to achieve the best degradation. As can be seen also from Figure (4), the optimum COD: H_2O_2 ratio for the oxidation of organic model substances by photo-Fenton treatment was 1:2.2, while it was 1:4.4 in case of treatment by Fenton process. That means, the treatment with photo-Fenton process reduces the consumption of H_2O_2 to avoid the auto-decomposition step (Reaction (3)) and consequently the total costs. About 86.9, 56.7, 89.7% of TOC reduction of fenitrothion, diazinon and profenofos respectively was obtained by photo-Fenton process after 30 min reaction time and COD: H_2O_2 ratio of 1:2.1. In contrast 54.2, 12.9, and 46.2% of TOC reduction of fenitrothion, diazinon and profenofos respectively was obtained by Fenton process after 90 min reaction time.

3.4. Effect of H_2O_2:Fe(II) ratio

To observe the optimal initial concentration of H_2O_2:Fe(II) on degradation of the model substances, experiments were conducted by varying the initial [Fe(II)] at fixed [H_2O_2]$_0$. pH and COD: [H_2O_2]$_0$ ratio. Figure (5) (a & b) shows the degradation of the model substances by Fenton and photo-Fenton treatment with variation of [H_2O_2]$_0$:[Fe(II)]$_0$ for a reaction of 90

& 30 min for both Fenton and photo-Fenton processes respectively. The results indicates that the extent of degradation remains almost the same value with the increase in $[H_2O_2]_0:[Fe(II)]_0$ ratio in the range of 10 to 100 with Fenton treatment and 10 to 50 with photo-Fenton treatment, further increase of $[H_2O_2]_0:[Fe(II)]_0$ ratio actually decrease the extent of degradation of model substances. Thus, the optimal ratios of $[H_2O_2]_0:[Fe(II)]_0$ are 100 & 50 for the treatment of model substances by Fenton & photo-Fenton treatment respectively. As can be seen from Figure (5), the treatment of the model substances by photo-Fenton reduced the $[H_2O_2]_0:[Fe(II)]_0$ to the half comparing with the treatment with Fenton process. That means, the consumption of iron (II) amount was reduced to the half by the photo-Fenton process. A higher addition of iron salt by using photo-Fenton treatment resulted in brown turbidity that hinders the absorption of the UV light required for photolysis and caused the recombination of OH radicals. In this case, Fe^{2+} reacted with OH radicals as a scavenger according to Reaction (5) [17].

$$OH^{\bullet} + Fe^{2+} \longrightarrow OH^- + Fe^{3+} \qquad\qquad \text{Reaction (5)}$$

It is desirable that the ratio of H_2O_2 to Fe^{2+} should be as small as possible, so that the recombination can be avoided and the sludge production from iron complex is also reduced.

3.5. Degradation kinetics

The degradation kinetics of the model substances by the Advanced Oxidation processes used in this study may be expressed by a pseudo-first order kinetics according to the following relationship Equation (1):

$$\ln[TOC]/[TOC]_0 = -k_0 t \qquad\qquad \text{Equation (1)}$$

in which $[TOC]_0$ and $[TOC]$ are the total organic carbon of the organic substances at 0 and t times, and k_0 the expected pseudo-first order rate constant.

Changes in the TOC degradation rates obtained with profenofos as model substance during UV, hydrogen peroxide photolysis, Fenton and Photo-Fenton reactions are shown in Figure (6). Pseudo-first order rate constants (k_0) and the % TOC conversion after 30 min of reaction time φ_{30} for the degradation of profenofos by different Advanced Oxidation Processes calculated from the degradation curves are presented in Table (2).

Profenofos was degraded at a slow rate by the dark oxidation with Fenton reaction. The results of this study demonstrated that UV radiation improves the performance of the Fenton reagent system quite significantly, and at the same concentrations of hydrogen peroxide, photo-Fenton reaction led to a more rapid decomposition of profenofos than that observed during the Fenton reaction. As listed in Table (2), the addition of UV radiation to the dark Fenton reaction led to 10-fold increase in the reaction rate constant for profenofos degradation (from 0.0085 to 0.0973 min^{-1}). Still, the application of the more complicated and therefore costly method is not reasonable, because more than 70% degradation in the Fenton treatment was reached in several minutes (90min). The degradation of profenofos with hydrogen peroxide photolysis involved a long reaction time if compared with the photo-Fenton reactions, so that 70% TOC destruction of profenofos required 60 min of treatment. The experimental data in Figures (6) shows that adding Fe^{3+} (the higher valance of iron metal) to the degradation of profenofos by UV/H_2O_2 system enhanced the rate of profenofos oxidation with a rate equal nearly to photo-Fenton treatment with adding Fe^{2+}.

3.6. Specific energy consumption

After the photo-catalytic oxidation has proven to be effective method for the destruction of organo-phosphorus compounds in water, the efficiency and the crucial parameters for an up-scaling of this process have to be evaluated. In most cases the goal of current technical application of advanced oxidation processes id the destruction of water pollutants and not the energy consuming complete degradation of the substrates content. Therefore the economical most important parameter is the efficiency of substrate consumption. Figure (7) provides a rough comparison of the energy required to remove 70% of the initial TOC of 50 ppm aqueous solution of profenofos by different photo-chemical oxidation processes used in this study. The energy consumption of each photochemical process is estimated, as kWh/kg based on the time needed to remove 70% of the initial TOC of profenofos aqueous solution. It may be noted that the consumed specific energy was calculated only from the transformed UV radiation, which represented only a part of the total electrical energy. The output energy amount to be 62W. The specific energy consumption E, (kWh/Kg TOC) needed to remove 70% TOC of profenofos aqueous solution can be estimated from the following Equation (2) [18].

$$E_s = \frac{P_{ur} * t}{[\Delta TOC] * V} \qquad \text{Equation (2)}$$

where, P_{ur} (kW) is the electrical power consumed by the UV-lamp = 62 W, $[\Delta TOC]$ (kg) is the change in TOC concentration of the profenofos = 63.35 mg/L and represent 70% TOC removal of profenofos, t (h) is the time at which 70% TOC of profenofos was removed and equal 15,30 and 105 min for photo-Fenton by using Fe(II), photo-Fenton by using Fe(III) and UV/ H_2O_2 processes respectively and V is the irradiated reaction volume (L) and equals 1L. The photo-Fenton process is more economical than UV/H_2O_2 process with an energy reduction 9-fold for the UV/ H_2O_2/Fe(II) system 5-fold for the UV/ H_2O_2/Fe(III) system, respectively, over UV/ H_2O_2 process. In this study the photo-Fenton process consider the optimal and economical method for the degradation of such organo-phosphorus compounds.

3.7. Degradation of synthetic mixture

A synthetic mixture of profenofos; diazinon; fenitrothion (50 ppm of each) was prepared to simulate a real wastewater effluent from pesticides producing company. Figure 8 shows Time-percentage total TOC degradation data for the oxidation of the mixture by different AOPs including UV, H_2O_2/Fe(II), UV/ H_2O_2, UV/ H_2O_2/Fe(II),), UV/ H_2O_2/Fe(III). As shown from the figure, the photo-Fenton process either by using Fe (II) or Fe(III) recorded the best % total TOC removal comparing with the other AOPs.

4. CONCLUSION

The results from this study showed that the % TOC degradation rate of model substances was strongly accelerated by the photo-assisted chemical oxidation processes. The photo-assisted Fenton process, the combination of homogeneous system of UV/ H_2O_2/ Fe^{2+}, produced the highest photochemical elimination rate of both compounds in order of profenofos > fenitrothion > diazinon. The oxidation rate was influenced by many factors, such as the pH value, reaction time COD: H_2O_2, Fe^{2+}: H_2O_2 ratio, the amount of iron salt and its valence. The optimum operating conditions obtained for the best degradation were pH=3; COD: H_2O_2 = 4.4:1, H_2O_2: Fe^{2+} ratio=100:1 by the oxidation of model substances by Fenton treatment and pH=3; COD: H_2O_2 = 2.2:1, H_2O_2: Fe^{2+} ratio=50:1 by the oxidation of model substances by photo-Fenton treatment.
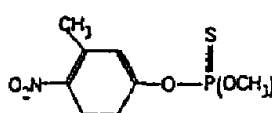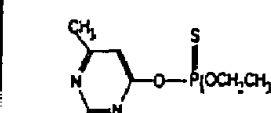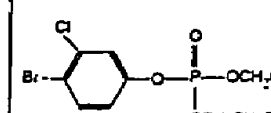
The advantages of the photo-assisted Fenton process as an oxidative pre-treatment step over the dark Fenton process are economic, less energy demand, efficient, low investment and harmless process products.

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Table (1) Physical & Chemical Properties of Organo-Phosphorus Model Substances used in This Study.

	Fenitrothion	Diazinon	Profenofos
Chemical Formula	C₉H₁₂NO₅PS	C₁₂H₂₁N₂O₃PS	C₁₁H₁₅BrClO₃PS
Molecular Weight	277.2	304.3	373.6
Density	1.328 gm/ml (at20°C)	1.117 gm/ml (at20°C)	1.455gm/ml (at20°C)
Chemical Structure			

Table (2) Degradation of Profenofos by Different AOPs.

Type of process	k_{exp}	φ_{30}
UV	0.0052	13.7
Fenton (H_2O_2/Fe^{2+})	0.0085	23.2
UV/ H_2O_2	0.0214	48.5
UV/ H_2O_2/Fe^{3+}	0.0589	81.1
UV/ $H_2O_2/$ Fe^{2+}.	0.0973	94

FIGURES
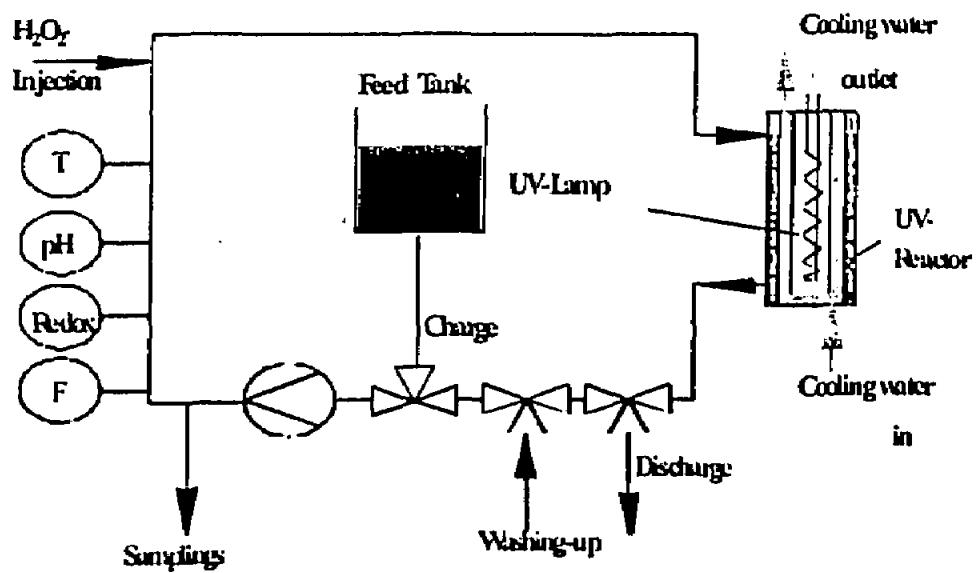
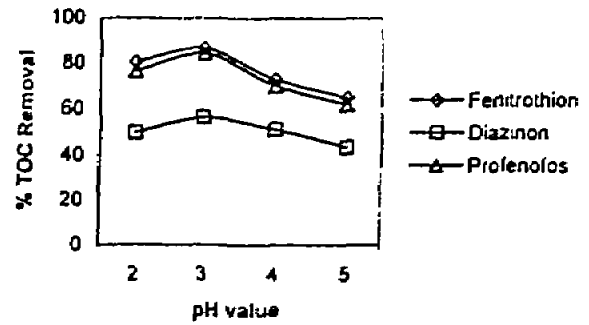

Fig, 1. Schematic diagram of AOPs system
experimental set-up.
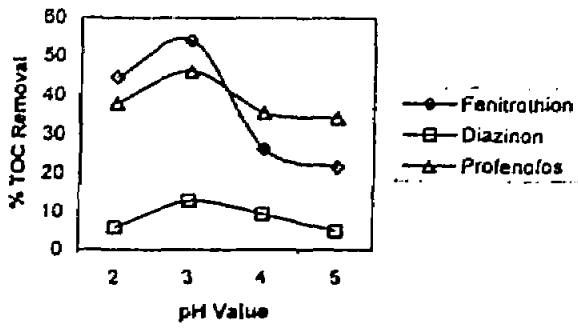
Fig. 2.a. Effect of pH Values on Fenton Oxidation Processes for Model substances Degradation. *[Reaction time=90min; COD:H$_2$O$_2$=1:2.2, Fe(II): H$_2$O$_2$=1:100].*

Fig. 2.b. Effect of pH Values on photo-Fenton Oxidation Processes for Model substances Degradation. *[Reaction time=30min; COD:H$_2$O$_2$=1:2.2, Fe(II): H$_2$O$_2$=1:100].*
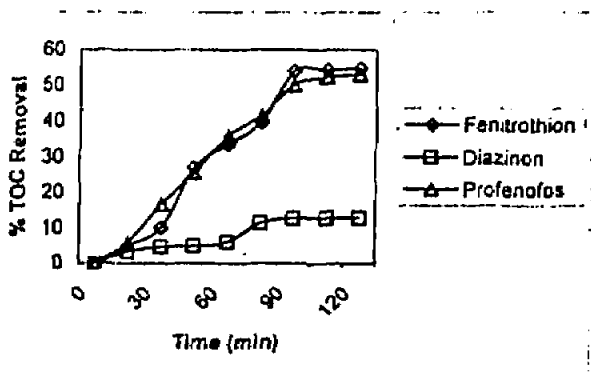
Fig. 3.a. Time-percentage TOC degradation data for model substances treatment by Fenton treatment. *[pH=3; COD:H$_2$O$_2$=1:2.2, Fe(II): H$_2$O$_2$=1:100].*
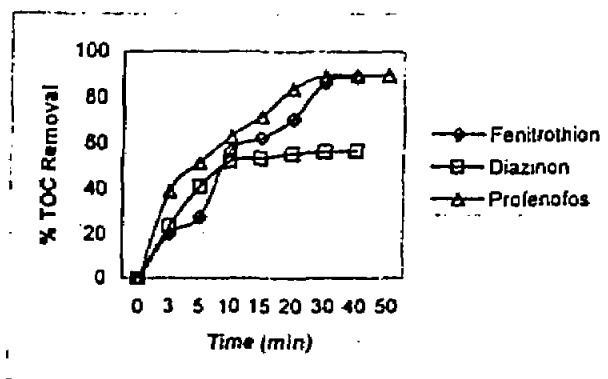
Fig. 3.b. Time-percentage TOC degradation data for model substances treatment by photo-Fenton treatment. *[pH=3; COD:H$_2$O$_2$=1:2.2, Fe(II): H$_2$O$_2$=1:100].*
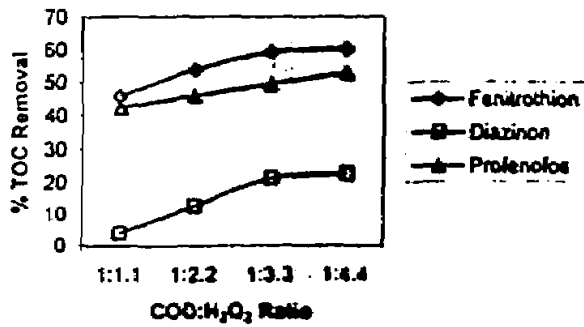
Fig. 4.a. Effect of COD:H₂O₂ on Fenton Oxidation Processes for Model substances Degradation. *[Reaction time=90min; pH=3. Fe(II): H₂O₂=1:100].*
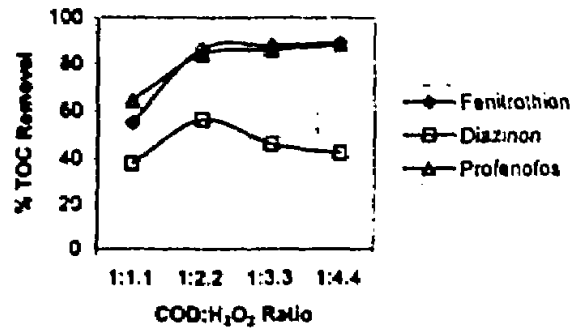
Fig. 4.b. Effect of COD:H₂O₂ on photo-Fenton Oxidation Processes for Model substances Degradation. *[Reaction time=30min; pH=3, Fe(II): H₂O₂=1:100].*
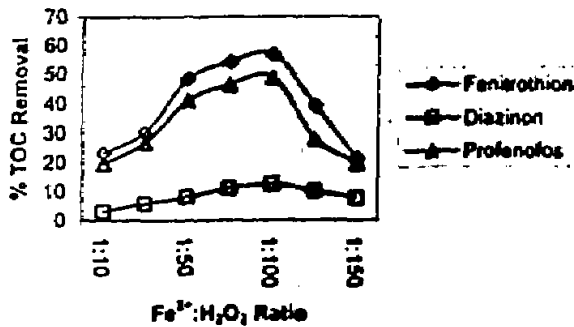
Fig. 5.a. Effect of Fe⁺²:H₂O₂ on Fenton Oxidation Processes for Model substances Degradation. *[Reaction time=90min; COD:H₂O₂=1:2.2, pH=3].*
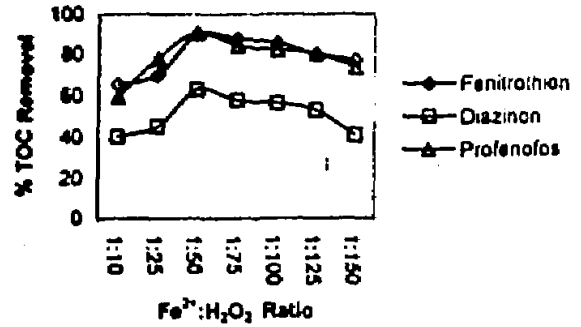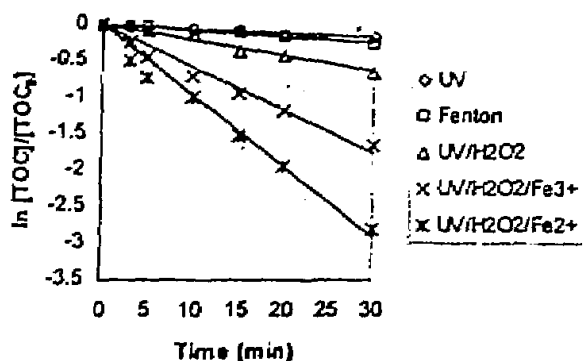

Fig. 5.b. Effect of Fe⁺²:H₂O₂ on photo-Fenton Oxidation Processes for Model substances Degradation. *[Reaction time=90min: COD:H₂O₂=1:2.2, pH=3].*

Fig. 6. Pseudo-First-Order Plot for Degradation of Profenofos by Different AOPs. [Profenofos (50ppm), UV, UV/H₂O₂ (pH=5, H₂O₂=8.99mM), H₂O₂/ Fe²⁺ ,UV/ H₂O₂/ Fe²⁺, UV/ H₂O₂/ Fe³⁺, (pH=3, Fe²⁺ & Fe³⁺ =0.089mM, H₂O₂=8.99mM)].
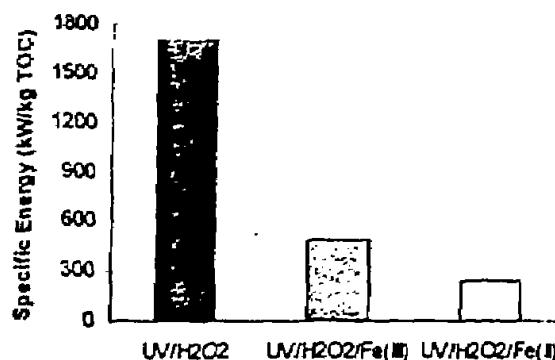
Fig. 7. Estimation of Specific Energy Required for Removal of Profenofos during Photo-Chemical Oxidation Processes
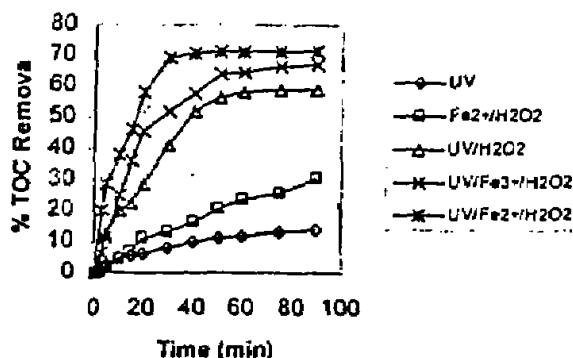
Fig. 8. Degradation of mixture of Profenofos, Diazinon and Fenitrothion by Different AOPs. [Profenofos,; Diazinon; Fenitrothion (50ppm for each); UV, UV/H₂O₂ (pH=5, H₂O₂=27.9mM). H₂O₂/ Fe²⁺ ,UV/ H₂O₂/ Fe²⁺, UV/ H₂O₂/ Fe³⁺, (pH=3, Fe²⁺ & Fe³⁺ =1.12mM).