

## **FENTON AND SOLAR PHOTO-FENTON OXIDATION OF INDUSTRIAL WASTEWATER CONTAINING PESTICIDES**

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### **ABSTRACT**

Assessment the efficiency of Fenton process ( $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ ), versus photo-Fenton reaction ( $\text{TiO}_2/\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{UV}$ ) for removal of Chloropyrifos, and COD from pesticide wastewater were investigated. Solar compound parabolic collectors (CPC) pilot scale with borosilicate tubes was used for photo-Fenton process. The effect of reaction time, initial pH and dosage of  $\text{H}_2\text{O}_2$ ,  $\text{FeSO}_4$ ,  $\text{TiO}_2$  were studied for both processes. The results obtained indicated that the optimum pH and reaction time were 3.6, and 120 min respectively. Both Fenton and photo-Fenton reaction were very effective for removal of COD and Chloropyrifos at dosage of 2 gm/L for  $\text{TiO}_2$ , 4 gm/L for  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , and 1 gm/L for  $\text{H}_2\text{O}_2$ . However, photo catalytic oxidation process improved the removal efficiency of Chloropyrifos by a value of 27 % as compared to Fenton process. The effluent quality of COD resulting from Fenton reaction was 3070 mg/L and significantly decreased up to 2190 mg/L after the post-precipitation using lime. Photo-Fenton reaction achieved an effluent quality of 2230 mg/l for COD of which greatly decreased up to 1650 mg/L with lime precipitation. Based on these results, it is recommended to apply photo-catalytic oxidation process for treatment of wastewater rich pesticide.

Keywords: Fenton, Photo-Fenton, Pesticides, Wastewater

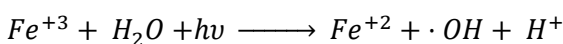
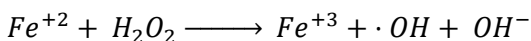
### **1. INTRODUCTION**

Pesticides have been a ubiquitous solution for pest control in intensive agriculture since the 1950s. As conventional biological wastewater treatments cannot effectively dispose of many of pesticides and other toxic pollutants (Ballesteros Martín et al. 2009).

The response has been the drive to make efficient removal of recalcitrant organic pollutants from industrial wastewater effluent to detract the risk of pollution problems from such toxic chemicals to enable its reuse. Consequently, many researches were executed for evaluation of an effective treatment technology that can easily destroy these bio-persistent organic contaminants. Due to their incomplete degradation during conventional wastewater treatment, they are prevalent in wastewater effluents at low concentration. Despite their low concentration, these contaminants have raised substantial health concern due to their extremely high endocrine disrupting potency and toxicity (Ahmed et al. 2011; Daneshvar et al. 2007)

Advanced oxidation processes (AOPs) have been recognized as an especially efficient approach for pesticide degradation (Moreira et al. 2012; Zapata et al. 2010). They are chemical oxidation processes distinguished by the generation of powerful reactive and unselective species such as hydroxyl radicals ( $\text{HO}\bullet$ ), which are able to degrade even the most recalcitrant organic molecules into relatively innocuous and less persistent end products such as  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and inorganic ions (Navarro et al. 2011; Vilar et al. 2011)

Fenton reaction is an advanced oxidation technology that works through the generation of highly reactive hydroxyl radical ( $\cdot\text{OH}$ ) by the combination of  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$  (Li et al. 2009; Vilar et al. 2012). The basis of the chemistry is the Fenton reaction ( $\text{Fe}^{2+} + \text{H}_2\text{O}_2$ ) which produces  $\text{HO}\cdot$  and results in oxidation of the  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  (Sarria 2003). The photo-Fenton reaction typically gives enhanced rates and a faster mineralization of recalcitrant organics than the dark reaction and can take the advantage of UV irradiation from the solar light (Navarro et al. 2011). In the reaction of the photo-Fenton process  $\text{Fe}^{2+}$  ions are oxidized by  $\text{H}_2\text{O}_2$  to  $\text{Fe}^{3+}$  and one equivalent  $\text{HO}\cdot$  is produced (Elmolla and Chaudhuri 2010; Lapertot et al. 2006). In aqueous solutions the resulted  $\text{Fe}^{3+}$  act as the light absorbing species that produce another radical while the initial  $\text{Fe}^{2+}$  is reproduced as illustrated in the following equations (Silva et al. 2012):



The photo-Fenton reaction could be enhanced by adding semiconductor material like  $\text{TiO}_2$  or  $\text{ZnO}$  (Chen et al. 2013; Selvam et al. 2007). Titanium dioxide is a solid semiconductor Nano particles that upon light excitation generates electrons in the conduction band and holes in the valence band (Arques et al. 2007; Fang, Yang, and Liao 2012). The holes could initiate oxidation of the recalcitrant organics. The radiation with wavelengths shorter than 380 nm is absorbed by titanium dioxide, and produce hydroxyl radicals. The UV fraction of sunlight can be employed in the process (Malato et al. 2002; Maldonado et al. 2007).

The aim of this work is to evaluate Fenton reaction ( $\text{Fe}^{+2}/\text{H}_2\text{O}_2$ ) versus photo-Fenton ( $\text{UV}/\text{Fe}^{+2}/\text{H}_2\text{O}_2$ ) and  $\text{TiO}_2$  assisted photo-Fenton ( $\text{UV}/\text{TiO}_2/\text{Fe}^{+2}/\text{H}_2\text{O}_2$ ) reactions for treatment of real industrial wastewater rich with Chloropyrifos collected from pesticides company utilizing the natural sunlight as a source of UV irradiation. For this purpose, pilot scale was designed and fabricated according to compound parabolic collectors technology (CPC).

## 2. MATERIALS AND METHOD

### 2.1 Pesticide wastewater

The industrial wastewater was collected from agrochemical and pesticides company situated in Nubaria, Egypt. The facility produced 10 m<sup>3</sup>/d wastewater and it is mainly discharged into sewerage network without any treatment. The main pesticide in this wastewater is Chloropyrifos (200 mg/l). Chemical structures of Chloropyrifos is shown in Fig 1. The color of wastewater was dark brown with strong odor. The organic content in terms of COD was between 23000-26000 mg/l.

### 2.2 Chemicals

The Titanium dioxide ( $\text{TiO}_2$ ) was used as a catalyst for oxidation process. The  $\text{TiO}_2$  was obtained in Nano scale powdered form (p25) from Acros. Ferrous sulphate hydrate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ), Hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), Sulfuric acid, acetic acid glacial, and Acetonitrile was purchased from Sigma Aldrich.

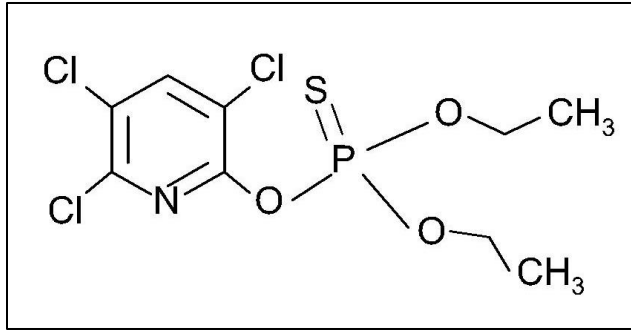


Figure 1 Chlorpyrifos chemical structure

### 2.3 Pilot plant and experiments

Photo-Fenton experiments were carried out using compound parabolic collectors pilot scale placed in Burg Alarab City, Egypt (Latitude 30°52', Longitude 29°35') on the roof of environmental engineering department in EJUST. The energy source of the reaction was the natural irradiation from sun light during the period of April and May 2013. The pilot photo-reactor module is (0.36 m<sup>2</sup>) and consists of six borosilicate tubes with diameter 1 inch and length 75 cm mounted on a curved polished aluminum reflector sheet with radius of curvature 9.2 cm. The reactor is connected from both the inlet and outlet with a tank provided with stirrer for mixing of wastewater and avoiding any precipitation of wastewater. A recirculation pump is connected between the tank and the reactor inlet. A schematic sketch for the pilot plant is shown in Fig 2.

The reactor was fed with 4 L of the wastewater. The pH was adjusted by H<sub>2</sub>SO<sub>4</sub> or NaOH, and then the H<sub>2</sub>O<sub>2</sub>, FeSO<sub>4</sub>.7H<sub>2</sub>O, and TiO<sub>2</sub> were added. The wastewater was pumped to flow through the tubes and return to the tank several times until the desired contact time was achieved.

The solar irradiation was measured by Met one Portable Weather Station (Model Number 466A) installed in the same location. The normalized illumination time ( $t_{30w}$ ) was used to compare between photo-catalytic experiments instead of exposition time ( $t$ ). The normalized illumination time was calculated by the following equation:

$$t_{30w,n} = t_{30w,n-1} + \Delta t_n \left( \frac{UV}{30} \right) \left( \frac{V_i}{V_t} \right)$$

$$\Delta t_n = t_n - t_{n-1}$$

where  $t_n$  is the experimental time for each sample, UV is the average solar ultraviolet radiation (W/m<sup>2</sup>) measured during  $\Delta t_n$ ,  $t_{30w}$  is the normalized illumination time, which refers to a constant solar UV power of 30W/m<sup>2</sup> (typical solar UV power on a perfectly sunny day around noon),  $V_t$  is the total reactor volume and  $V_i$  is the total irradiated volume.

Fenton experiments were carried out in 500 ml beakers set on a magnetic stirrer. pH was adjusted by using H<sub>2</sub>SO<sub>4</sub> or NaOH, then H<sub>2</sub>O<sub>2</sub>, and FeSO<sub>4</sub>.7H<sub>2</sub>O were added with certain amounts during the stirring. The stirring was kept on until the desired reaction time completed, the samples

were settled for 30 minutes. The calcium hydroxide was used to enhance the sedimentation of the suspended matter.

In order to investigate the effect of pH on Fenton reaction and the optimum pH, seven Fenton reaction experiments of different pH ranged between 2.5 to 11.4 were executed using 1 g/l of  $\text{H}_2\text{O}_2$ , and 4 g/l of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ . The stirring time was 45 minute for all samples. To study the effect of  $\text{H}_2\text{O}_2$  on Fenton and Photo-Fenton processes, experiments were carried out with different doses of  $\text{H}_2\text{O}_2$  ranged between zero and 2 g/l. In both processes the amount of added  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  was 4 g/l. The stirring time for Fenton experiments was 45 minutes, while the normalized illumination time in photo-Fenton experiments was 120 minutes. To evaluate the effect of  $\text{TiO}_2$  on photo-Fenton reaction, Different doses of  $\text{TiO}_2$  were used in experiments with normalized illumination time 120 minutes and using 4 g/l of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and 1 g/l of  $\text{H}_2\text{O}_2$ .

For Fenton process, samples were taken after stirring time 15,20,30,45, and 60 minutes to study the effect of reaction time on the removal efficiency of Chloropyrifos and COD, while for photo-Fenton process the samples were taken at  $t_{30,w}$  equal 30,60,90,120,150, and 180 minutes.

## 2.4 Analytical methods

The concentration of Chloropyrifos is monitored by Shimadzu HPLC by C-18 phenomenex reverse phase column, degasser (Model 20A5), pump (Model LC-20AT), and prominences Diode Array Detector (modelSPD-M20A). The mobile phase was acetonitrile, water, and acetic acid glacial with volume percent ratio 82:17.5:0.5 at wavelength 300 nm and flow rate 1.5 ml/min. All samples were filtered by micro syringe filters (0.2  $\mu\text{m}$ ). Analysis of COD was performed according to the APHA Standard Methods.

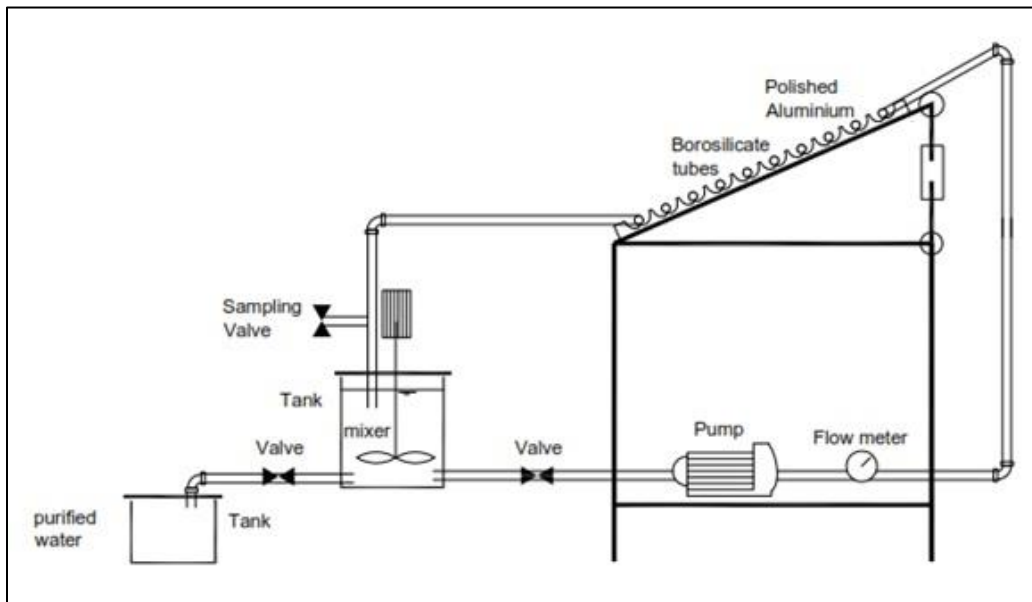


Figure 2 Solar photo oxidation system

### 3. Results and discussions

#### 3.1 Effect of pH

The pH value has a considerable effect on Fenton reaction, because of the big influence to the oxidation potential of  $\text{OH}\cdot$  according to the reciprocal relation of the oxidation potential to the pH value ( $E_0 = 2.8 \text{ V}$  and  $E_{14} = 1.95 \text{ V}$ ) (Badawy, Ghaly, and Gad-Allah 2006).

Fig 3 shows the effect of pH value on the removal efficiency of COD and Chloropyrifos from wastewater. The results revealed that the removal efficiency of COD and Chloropyrifos was improved at the acidic conditions, raising the pH from 2.5 to 3.6 improved the removal efficiency of Chloropyrifos and COD from 57% and 83% to 61.8 and 86.6 % respectively. Further raising of pH value above 3.6 decreases the removal efficiency of Chloropyrifos and COD. The COD was further improved resulting a removal efficiency of 90.5% by adding CaOH. Similar findings was reported by (Li et al. 2009) who found that the decomposition rate of  $\text{H}_2\text{O}_2$  is low at pH exceeding 4.0 resulting a drop in hydroxyl radicals production.

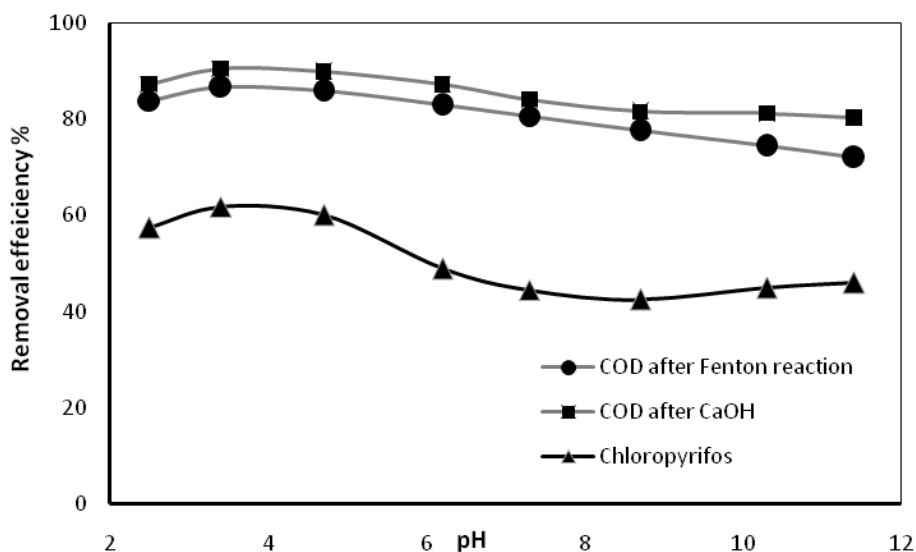
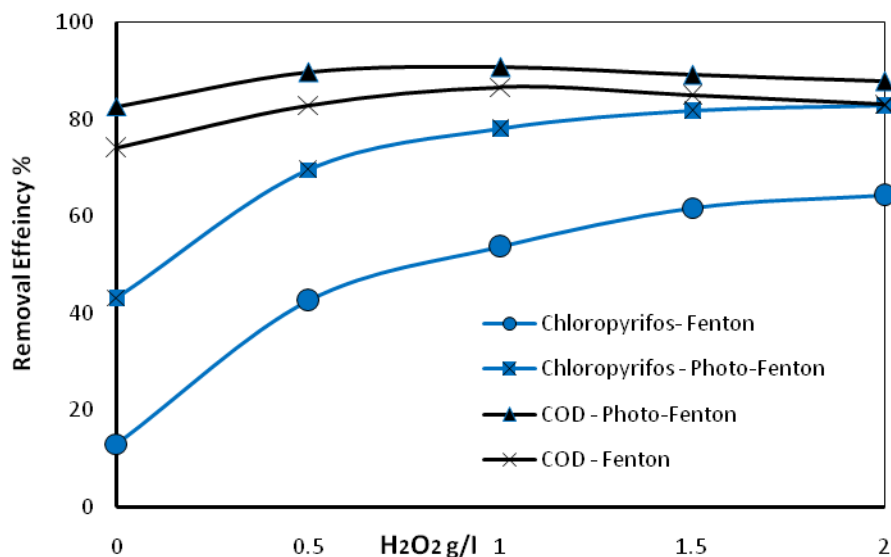


Figure 3 Effect of pH on Fenton reaction

#### 3.1.2 Effect of $\text{H}_2\text{O}_2$

The results in Fig 4 show the efficiency of Fenton versus photo-Fenton process for COD and Chloropyrifos removal at different doses of  $\text{H}_2\text{O}_2$ . The results reveal that increasing the dosage of  $\text{H}_2\text{O}_2$  improved the degradation efficiency of pesticides in Fenton and photo-Fenton processes. Increasing the dosage of  $\text{H}_2\text{O}_2$  from 0.5 to 1.5 g/l increased the removal efficiencies of COD and Chloropyrifos from 82% to 86% and from 42% to 61.8% respectively for Fenton process. However, further increasing of the  $\text{H}_2\text{O}_2$  dose up to 2 g/l slightly improved the removal efficiency of COD and Chloropyrifos as shown in Fig. 4.



**Figure 4** Effect of H<sub>2</sub>O<sub>2</sub> on oxidation processes

On the other hand, the optimum dose in photo-Fenton process was 1g/l with removal efficiency of 78% for Chloropyrifos, and 91% for COD. However at H<sub>2</sub>O<sub>2</sub> dosage exceeding 1 g/l Chloropyrifos degradation efficiency slightly increased to 81%, and the COD removal decreases to 89%, because the residuals of H<sub>2</sub>O<sub>2</sub> after Fenton or photo-Fenton reaction are contributed to COD value. Moreover, the photo-Fenton process improved the degradation of Chloropyrifos more than Fenton process with about 20%.

### 3.3 Effect of Fe<sup>+2</sup>

Fenton and photo-Fenton experiments were executed with different doses of FeSO<sub>4</sub>·7H<sub>2</sub>O ranged from 1 to 5 g/l. The results of these experiments are shown in Fig 5. Increasing the dose of FeSO<sub>4</sub>·7H<sub>2</sub>O obviously improved the removal efficiency of COD and Chloropyrifos. In Fenton reaction, adding 3g/l of FeSO<sub>4</sub>·7H<sub>2</sub>O increased the removal efficiency of Chloropyrifos and COD from 19% to 58% and from 41% to 85%, while in photo-Fenton process 3 g/l of FeSO<sub>4</sub>·7H<sub>2</sub>O raised the removal efficiency of Chloropyrifos and COD from 73.3% to 58% and from 51% to 89.3%, however increasing the dosage more than 3 g/l resulted no significant improvement in pesticides degradation, and this is attributed to the consuming of some Fe<sup>+2</sup> ions in coagulation of suspended particulates existing in the wastewater.

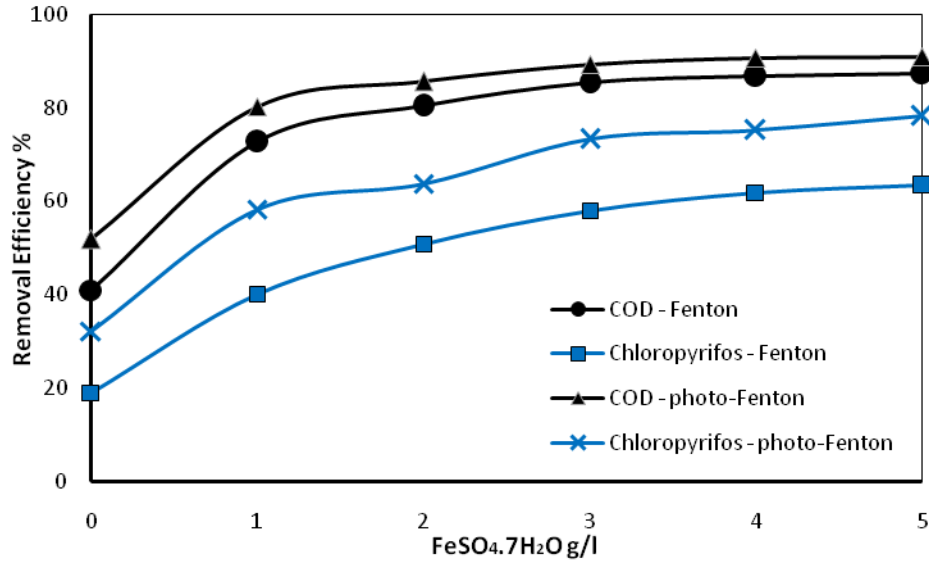


Figure 5 Effect of FeSO<sub>4</sub>.7H<sub>2</sub>O on oxidation processes

### 3.4 Effect of adding TiO<sub>2</sub> in photo-Fenton process

The effect of using TiO<sub>2</sub> as a catalyst in photo-Fenton process was investigated by adding different amount of TiO<sub>2</sub>. The results of different photo experiments are shown in Fig 6. The results showed that the photo-oxidation activity of the pesticides is improved with increasing the dose of TiO<sub>2</sub> until reaching 1.5 g/l. Increasing the catalyst more than 1.5 g/l gives no significant improvement in degradation of Chloropyrifos.

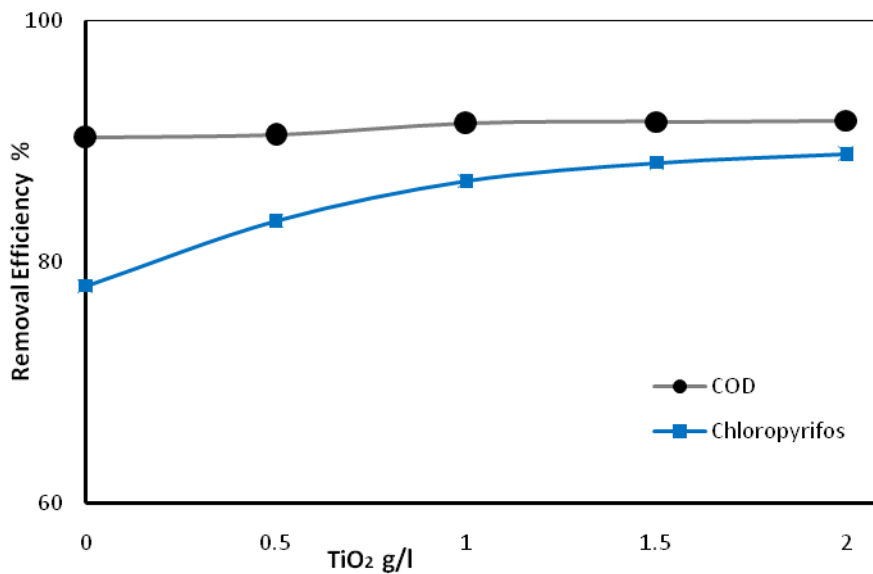


Figure 6 Effect of TiO<sub>2</sub> on photo-catalytic oxidation

The experiments showed considerable differences in treatment efficiency between the catalysis photo-oxidation and the non-catalysis photo-oxidation. Using titanium dioxide improved the Chloropyrifos degradation more than Fenton process by 27% and 10% more than photo-Fenton process. These results could be attributed to the increasing of active surfaces with heightening the dosing of TiO<sub>2</sub>,

which is the semiconductor in the reaction. Accordingly, the formation of electron hole pairs on the surface of catalyst and the high reactive hydroxyl radicals increased, which cause the oxidation of pesticides and other organic matter into another intermediates. However, increasing the dosing of TiO<sub>2</sub> more than considerable limits may cause agglomeration of particulates, which decrease the active sites on the semi-conductor surface. Furthermore, the increasing of catalyst loading increases the turbidity of the solution, and detract the amount of sunlight reaching to the active surfaces.

### 3.6 Effect of reaction time.

The effect of reaction time on the removal of Chloropyrifos and COD was investigated as shown in Fig 7. The removal efficiency was 61.8% for Chloropyrifos, and 86% for COD at reaction time of 45 minutes. Prolonging the reaction time to 60 minutes improved the degradation efficiency of Chloropyrifos by a value of only 2% and improved the COD removal with 1%, accordingly, the optimum stirring time considered to be 45 minutes.

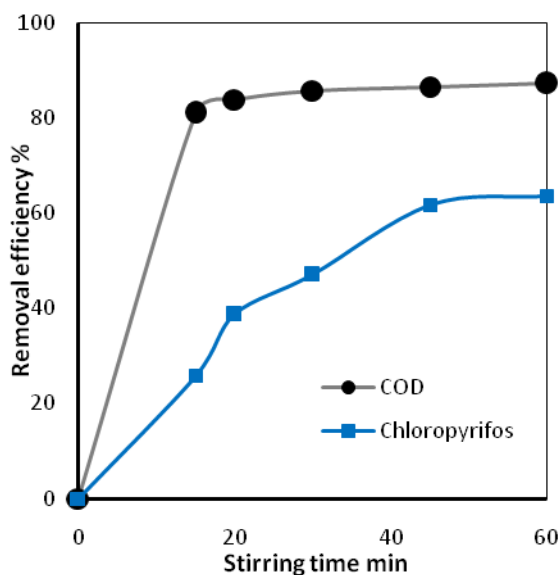


Figure 7 Effect of Stirring time on Fenton reaction

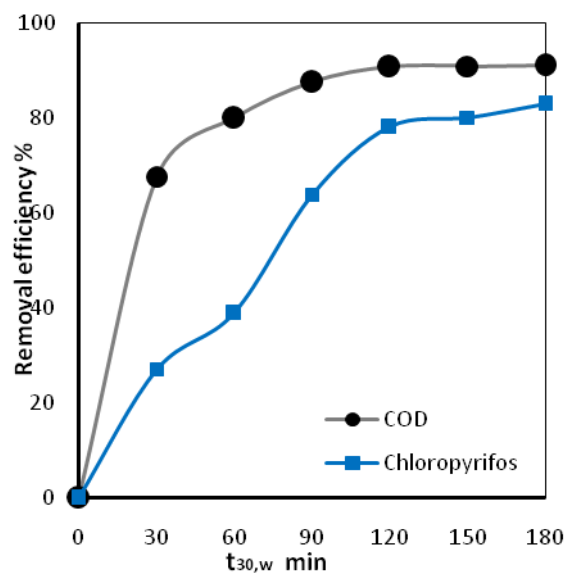


Figure 8 Effect of reaction time on photo-Fenton reaction

For photo-Fenton experiments, the normalized illumination time  $t_{30,w}$  is representing the reaction time. The results of Chloropyrifos and COD removal efficiency at different  $t_{30,w}$  values are shown in Fig 8. The optimum normalized illumination time is 120 minutes, which achieved 91% removal of COD and 78% degradation of Chloropyrifos. Increasing the illumination time more than 120 min gave slight improvement on the removal efficiency of pesticides and COD because most of H<sub>2</sub>O<sub>2</sub> and Fe<sup>+2</sup> were consumed, which detract the rate of organic matter degradation.

### 3.7 Chloropyrifos degradation kinetics

The degradation rate of Chloropyrifos can be expressed by a pseudo-first-order pattern, with the following differential equation demonstrating the relationship of C and t.

$$-\frac{dC}{dt} = k_{obs} C$$

Integrating this differential equation leads to:



$$\ln \frac{C_0}{C} = k_{obs}t$$

Where  $k_{obs}$  is the constant reaction rate,  $C_0$  is the initial concentration of target pollutant in aqueous solution, and  $C$  is the residual concentration of pollutant at time  $t$ .

The model was applied to the Chloropyrifos removal in Fenton and photo-Fenton experiments under the optimal conditions and dosing. The values of  $\ln(C_0/C)$  versus normalized illumination time are shown in Fig 9, and 10. The least square regression was used to calculate the  $k_{obs}$ , and  $R^2$ . For Fenton process the value of  $k_{obs}$  was 0.0208, while for photo-Fenton reaction the value of  $k_{obs}$  was 0.0118. Despite the final degradation performance of photo-Fenton reaction is higher than the final performance of Fenton reaction, but the reaction rate was smaller, and this attributed to the high mixing achieved by magnetic stirrer in Fenton reaction experiments. The correlation coefficient ( $R^2$ ) for the model of Fenton reaction was 0.941, and for photo-Fenton reaction was 0.964. The values of  $R^2$  indicate that the pseudo-first-order equation is more suitable for the photo-Fenton reaction more than Fenton reaction.

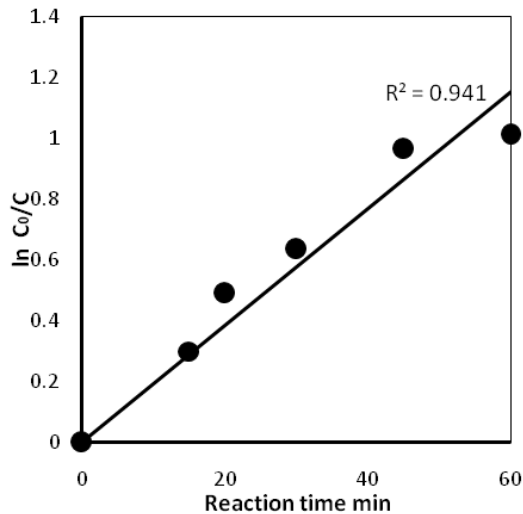


Figure 9 Kinetics of Fenton reaction

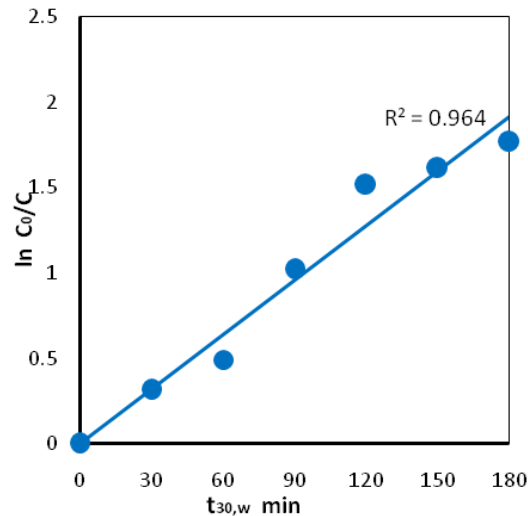


Figure 10 Kinetics of photo-Fenton reaction

#### 4. CONCLUSION

In this work, the Treatment of industrial wastewater containing Chloropyrifos by Fenton and photo-Fenton processes was evaluated, and the following remarks are concluded: (i) Degradation of Chloropyrifos by Fenton reaction is highly influenced by the pH of wastewater, and the optimum pH was 3.6. (ii) The optimum doses of  $H_2O_2$  and  $FeSO_4 \cdot 7H_2O$  are 1.5 g/l and 3 g/l respectively in Fenton reaction, while in photo-Fenton process they were 1g/l and 3 g/l in same order. (iii) The removal efficiency of COD was 86% and 91% in Fenton and photo-Fenton processes respectively, and the degradation efficiency of Chloropyrifos was 61.8% and 78% in Fenton and photo-Fenton processes respectively. (iv) Using  $TiO_2$  as a catalyst in photo oxidation improved the Chloropyrifos degradation more than Fenton process by 27% and 10% more than photo-Fenton process, and the optimal dose of  $TiO_2$  was 1.5 g/l (v) The optimum reaction time in Fenton reaction is 45 minutes, while the most proper normalized illuminated time for photo-Fenton reaction is 120 minutes. (vi) The degradation of pesticides in both process were expressed by a pseudo-first-order pattern and gave good correlation.

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