



Combined Solar advanced oxidation and PAC adsorption for removal of pesticides from industrial wastewater

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Abstract

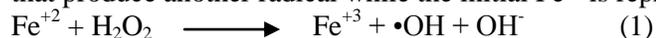
The efficiency of solar heterogeneous TiO₂ photocatalysis and homogeneous photo-Fenton reaction for removal of Lambda Cyhalothrin, Chlorpyrifos and Diazinon from pesticide wastewater industry was investigated. The effluent quality was not complying for discharge into sewerage network. Therefore, adsorption of the remaining portions of pesticides using powdered activated carbon (PAC) was assessed. The combined processes provided almost complete removal of pesticide fractions i.e. 97% for Lambda Cyhalothrin, 91% for Chlorpyrifos, and 100% for Diazinon. The experimental data were further analyzed by the Freundlich and the Langmuir isotherm. Pseudo first order and pseudo-second order kinetics models were tested for the experimental results.

Keywords: Pesticides wastewater; Advanced oxidation; Heterogeneous; Chlorpyrifos; Lambda Cyhalothrin; Powdered activated carbon

1. Introduction

The use of pesticides is widely increased in the last decades in intensive agriculture activities [1]. Contamination of water streams with pesticides rich wastewater became critical and prevalent [2]. Because of their high toxicity even at relatively low concentrations, the conventional biological treatment based on microorganism activity is not a proper technology for treatment of pesticide wastewater industry [3].

Advanced oxidation processes (AOPs) have been realized as particularly efficient technologies for pesticides degradation [4, 5]. In AOPs, powerful chemical reactions with the aid of energy source are able to destroy even the most recalcitrant organic molecules and convert them into relatively benign and less persistent end products such as CO₂, H₂O and inorganic ions [6–9]. Among AOPs diverse processes, heterogeneous photocatalysis and photo-Fenton processes using artificial or solar irradiation have been recognized to be effective for the degradation of several types of pesticides existing in industrial wastewater [8–10]. In the heterogeneous photocatalysis, the ultraviolet light ($\lambda < 400\text{nm}$) are utilized as an energy source and a semiconductor photo-catalyst like ZnO or TiO₂ [11]. TiO₂ is distinctive with high surface area, good particle size distribution, excellent chemical stability, and the possibility of using sunlight as a source of irradiation [3, 12]. For photo-Fenton process, Fe²⁺ or Fe³⁺ and H₂O₂ are a source of hydroxyl radicals (HO•). The basis of the chemistry is the Fenton reaction (Fe²⁺ + H₂O₂) which produces HO• and results in oxidation of the Fe²⁺ to Fe³⁺ [13, 14]. The photo-Fenton reaction typically provides 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 [9, 15]. In the reaction of the photo-Fenton process Fe²⁺ ions are oxidized by H₂O₂ to Fe³⁺ and one equivalent HO• is produced. In aqueous solutions the resulted Fe³⁺ act as the light absorbing species that produce another radical while the initial Fe²⁺ is reproduced as illustrated in the following equations [16, 17]:



Even though AOPs have been recognized to be very effective in degradation of recalcitrant organics, degradation of pesticides needs longer treatment time and complete degradation is rarely achieved [18]. In addition, their operation cost is considered to be very high [20,21].

Adsorption of hazardous matter from contaminated water by activated carbon has been recognized to be economic and efficient technology, especially in disposing of low concentrations of organic contaminants [20]. The systems based on activated carbon were reported to have high efficiency for removal of a wide variety of toxic pollutants [21–23]. Adsorption is a physical phenomenon, depending largely on the surface area, pore size, pH, solution temperature, and the nature of adsorbent and its substituent groups [24]. Removal of the pesticides by activated carbon was recently reported to be effective. For instance, Gupta et al. [28] reported that Methoxychlor, atrazine, and methyl parathion were eliminated by powdered activated carbon made from waste rubber tire with efficiency of 91%, 82.1% and 71.78% respectively. Moreover, Moussavi et al. [29] showed that Diazinon is removed with efficiency of 98% by adsorption onto NH₄Cl induced activated carbon. Also, Jusoh et al. [27] found that Malathion could be adsorbed on the granular activated with adsorption capacity of 909.1 mg/g. Accordingly, the results concluded from the literature demonstrate the good potential of applications of activated carbon adsorption for the removal of pesticides.

The present study aims to investigate the treatment of wastewater containing Lambda Cyhalothrin, Chlorpyrifos, and Diazinon by two stages of treatment. The 1st stage is advanced oxidation using TiO₂ solar photocatalysis, versus solar photo-Fenton reaction. The 2nd stage is adsorption by commercial powdered activated carbon (PAC). The effect of contact time, pH, and PAC adsorbent dose were evaluated. Moreover, the experimental data were analyzed by the Freundlich and the Langmuir isotherms. Also, Pseudo 1st order and pseudo-second order kinetics models were tested for describing the adsorption kinetics.

2. Materials and Methods

2.1. Pesticide wastewater

The wastewater was collected from an agrochemical and pesticides company situated in Nubaria, Egypt. Components of pesticides in the wastewater are Lambda Cyhalothrin, Chlorpyrifos, and Diazinon. Chemical structures of pesticides fraction namely Lambda Cyhalothrin, Chlorpyrifos and Diazinon are shown in (Fig. 1).

2.2. Chemicals and adsorbent

The TiO₂ in Nano powdered scale (p25) was obtained from Acros. Ferrous sulphate hydrate (FeSO₄·7H₂O), Hydrogen peroxide (H₂O₂), Sulfuric acid, acetic acid glacial, and Acetonitrile were purchased from Sigma Aldrich. Powdered activated carbon (PAC) purchased from Adwic with bulk density of 0.37 gm/cm³, and the specific surface area of 1050 m²/gm.

2.3. Photo-oxidation experiments

Photo-Fenton and photocatalysis experiments were carried out using compound parabolic collector placed in Borg Alarab City, Egypt (Latitude 30°52', Longitude 29°35') on the roof of environmental engineering department. The energy source of the reaction was the natural irradiation from sunlight. The photo-reactor module is (0.36 m²) 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 containing the pesticide wastewater and provided with stirrer to avoid precipitation of solids and to ensure the homogeneity of feedstock. The wastewater was continuously circulated in closed cycle. A schematic diagram of the experimental set-up is shown in (Fig. 2).

The reactor was fed with 4 L of the pesticide wastewater, and the pH was adjusted to ≈4.0 by few drops of H₂SO₄, then the TiO₂ was added in case of photocatalysis experiments, or H₂O₂, and FeSO₄·7H₂O in case of photo-Fenton experiments.

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 equations [1, 12, 28]:

$$t_{30w,n} = t_{30w,n-1} + \Delta t_n (UV/30) (V_i/V_t) \quad (3)$$

$$\Delta t_n = t_n - t_{n-1} \quad (4)$$

Where t_n : the experimental time for each sample, UV : the average solar ultraviolet radiation (W/m²) measured during Δt_n, t_{30w} : the normalized illumination time, which refers to a constant solar UV power of 30W/m² (typical solar UV power on a perfectly sunny day around noon), V_t : the total reactor volume and V_i : the total irradiated volume. To investigate the kinetics of pesticides degradation, was carried out at different t_{30w}.

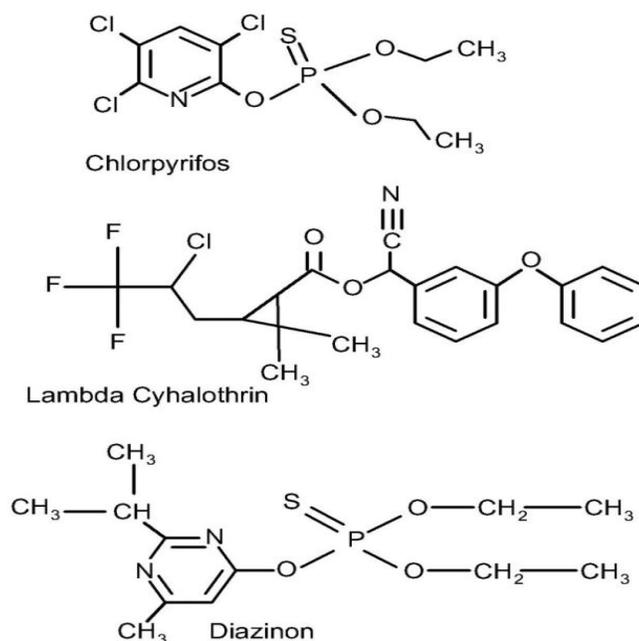


Figure 1: Chemical structure of pesticides.

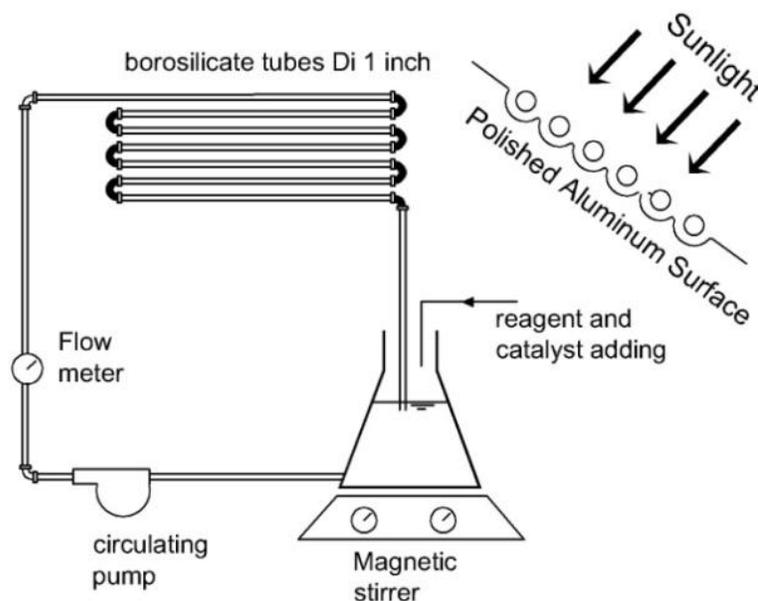


Figure 2: Schematic sketch of the solar reactor.

2.4.(PAC) Adsorption experiments

The photocatalysis and photo-Fenton treated effluent was used as a sole of substrate for adsorption experiments. A series of 250 mL flasks were filled with 100 ml of pretreated wastewater, and placed on magnetic stirrer. To investigate the effect of pH, it was adjusted before adding the PAC and varied from 3.0 to 11.0 by adding H₂SO₄ or NaOH. The stirring began with adding the PAC with dosages ranged from 0.03 to 0.2 gm/L. Samples were taken at different time intervals to study the effect of contact time. The adsorption of pesticides kinetic studies, at time t, q_t (mg/g), was determined according to the following equation [29–31]:

$$q_t = (C_0 - C_t) V / m \quad (5)$$

Where C₀ and C_t (mg/L) are the initial liquid-phase concentration of pesticides and the concentration at time t, respectively. V (L) is the volume of the solution and W (g) is the mass of dry adsorbent used.

Langmuir and Freundlich isotherms were applied. Samples were taken at different irradiation time from photocatalysis and photo-Fenton experiments and used in adsorption experiments to obtain data with different initial concentrations. The adsorption of pesticide fractions at equilibrium q_e was calculated according to the equation [32]:

$$q_t = (C_0 - C_e) V / m \quad (6)$$

Where c_e is the liquid-phase concentrations of pesticides at equilibrium.

2.5. Analytical methods

The degradation of pesticides was monitored by Shimadzu HPLC by C-18 phenomenex reverse phase column, degasser (20A5), pump (LC-20AT), and prominences Diode Array Detector (SPD-M20A). The influent and treated effluents were filtered by micro syringe filters (0.2 μ m). Chlorpyrifos was determined by mobile phase acetonitrile, water, and glacial acetic acid with ratio of 82:17.5:0.5 (v/v) at wavelength of 300 nm and flow rate of 1.5 ml/min. Diazinon and Lambda Cyhalothrin was measured by mobile phase acetonitrile, and water with ratio of 75:25 and 80:20 (v/v) , wavelength of 254 and 230nm respectively and constant flow rate 1.5 ml/min.

3. Results and discussion

3.1 Advanced oxidation as a pretreatment processes

Pesticides degradation by solar photo-Fenton versus solar photocatalysis is shown in (Fig. 3). In photocatalysis process, the rate of pesticides degradation was higher during the first 120 minutes of irradiation time. After 120 minutes, the low concentrations of pesticides beside consuming most of hydroxyl radicals detracted the rate of pesticides degradation. The samples taken after the first 120 minutes showed removal efficiency of Lambda-Cyhalothrin, Chlorpyrifos, and Diazinon of 63.7%, 60.75%, and 38.2%, respectively. The proportional modesty of the removal of Diazinon is attributed to the low concentration in raw wastewater compared to other pesticides. [10, 12].

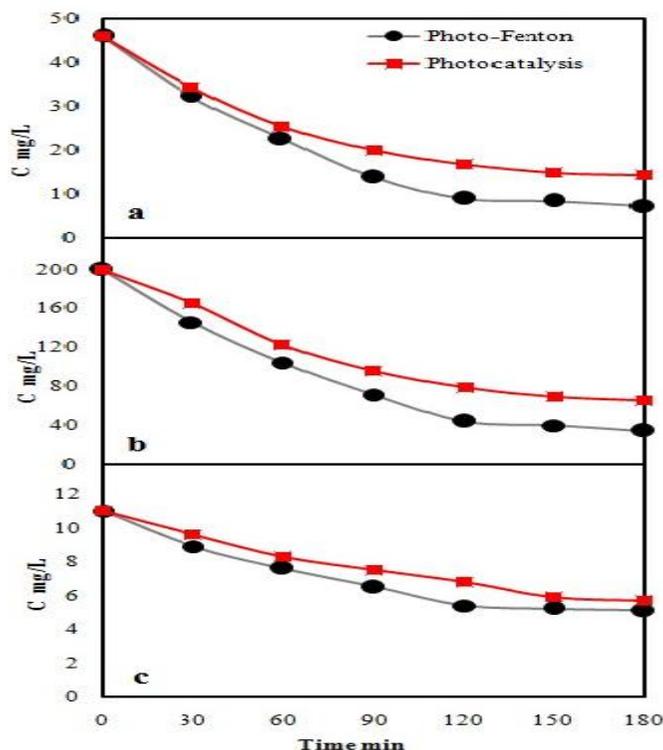


Figure 3: Pesticides degradation by photocatalysis and photo-Fenton adsorption **a** Lambda Cyhalothrin. **b** Chlorpyrifos. **c** Diazinon.

At early stages of the photo-Fenton reaction, molecules of pesticide are degraded with high rate by hydroxyl radicals, leading to organic intermediates with a drop in pesticides concentration. After 90 minutes of irradiation time the rate of degradation of pesticides was decreased due to the consumption of hydroxyl radicals and the low

concentrations of pesticides compared to the beginning of the reaction process. After 120 minutes the removal efficiency of Lambda-Cyhalothrin, Chlorpyrifos, and Diazinon, was 80.65%, 78.05%, and 50.9% respectively. Increasing the irradiation time more than 120 min resulting a slight improvement in the removal efficiency of pesticides because most of H_2O_2 and Fe^{+2} were consumed, which detract the rate of organic matter degradation. The photo-Fenton reaction was more efficient in degradation of pesticide fractions as compared to photocatalysis process (UV/TiO_2) as shown in Fig. 3. This observation could be explained in terms of the sources of hydroxyl radicals in each process. In photocatalysis, the hydroxyl radicals are formed only when positive holes react with water. On the other hand, in photo-Fenton reaction the hydroxyl radicals are formed from many sources, summarized in the photolysis of $Fe(OH)^{+2}$ which is predominant species of $Fe(III)$, reaction of Fe^{+2} with H_2O_2 as expresses in equation 1, photolysis of H_2O_2 molecules in presence of UV irradiation into two hydroxyl radicals, and photo decomposition of Fe^{+3} with carboxylates in presences of visible light to compose new Fe^{+2} which reproduce more radicals in presence of H_2O_2 [33, 34].

3.2. Post-treatment by powdered activated carbon (PAC)

PAC was used for removal of the remaining portions of pesticide fractions from catalytically pretreated effluent. Several experiments including contact time, pH, and adsorbent dosage were carried out.

3.2.1. Effect of contact time and initial pesticides concentration

The rate of uptake of pesticides on the activated carbon is shown in (Fig. 4) for two different initial concentrations from photocatalysis and photo-Fenton processes.

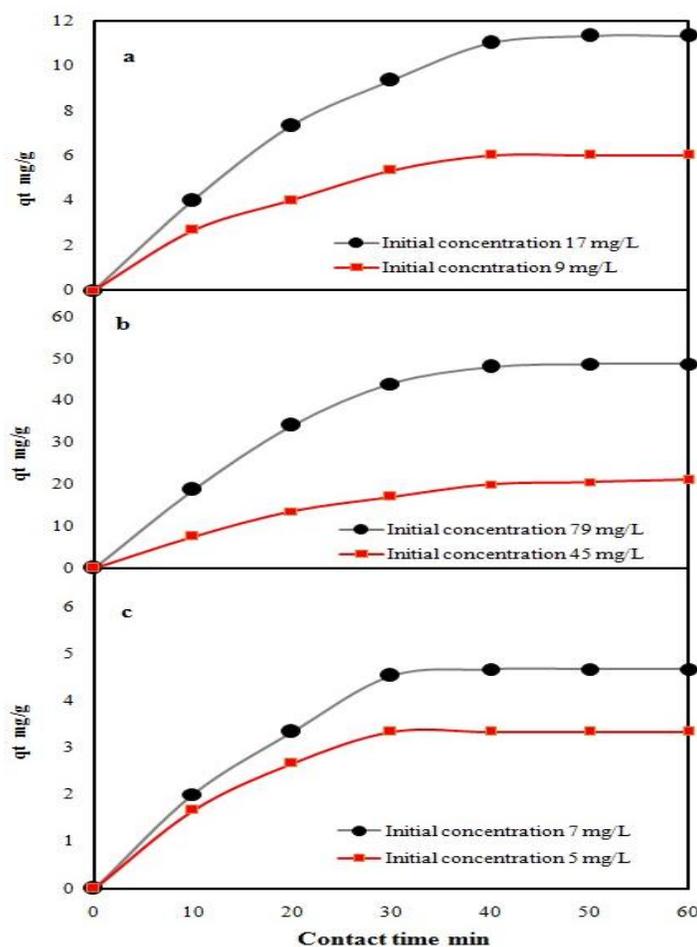


Figure 4: Effect of contact time and initial concentration of pesticides on adsorption **a** Lambda Cyhalothrin. **b** Chlorpyrifos. **c** Diazinon.

For all pesticide fractions the sorption began quiet rapid and then gradually slowed down until reached the equilibrium. Equilibrium was attained after 40 minutes for Lambda Cyhalothrin and Chlorpyrifos, and 30 minutes for Diazinon. Increasing the initial concentration of pesticides did not affect the time of adsorption equilibrium, but it increased the amount of pesticides adsorbed. An increase in adsorption of Lambda Cyhalothrin was observed from 6 mg/g at initial concentration of 9 mg/L to 11.3 mg/g at initial concentration of 17 mg/L. For Chlorpyrifos the adsorption increased from 21 mg/g at initial concentration of 45 mg/L to 50 mg/g at initial concentration of 79 mg/L. For Diazinon similarly, the adsorption of Diazinon increased from 3.3 mg/g at initial concentration of 5 mg/L to 4.7 mg/g at initial concentration of 7 mg/L. This increase in the adsorption amount at higher initial concentrations of pesticides fractions is due to the higher opportunity for active sites on the PAC surface to adsorb more substances.

3.2.2. Effect of pH

The effect of pH on the adsorption of pesticide fractions is shown in (Fig. 5). The results showed that the adsorption capacity of PAC is reduced by increasing the pH value from 3.0 to 11.0. The q_e decreased from 11.3 to 2.3 mg/g, from 48 to 29.2 mg/g, and from 4.7 to 2.4 mg/g for Lambda Cyhalothrin, Chlorpyrifos, and Diazinon at increasing the pH values from 3 to 11 respectively. This mainly can be attributed to the increasing of deprotonation of functional groups with the increase of pH [25]. This deprotonation leads to more negative charges on the surface of activated carbon. The negative charges cause electrostatic repulsion forces between the activated carbon surface and the pesticides which detract the opportunities of adsorption on the active sites [35, 36]. Similar trends were observed by Hameed group [37, 38].

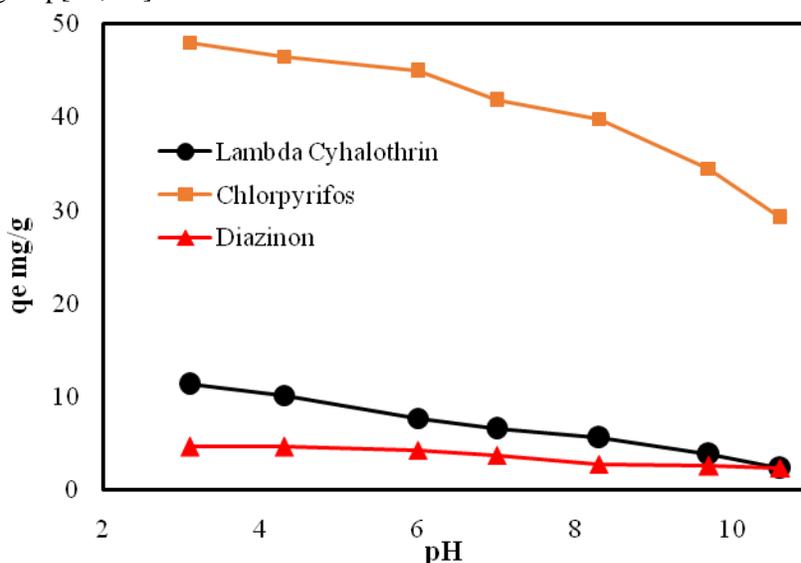


Figure 5: Effect of pH on adsorption.

3.2.3. Effect of adsorbent dose

The effect of adsorbent dose at different initial concentration of pesticide fractions is shown in (Fig. 6). It could be seen that increasing the dose of adsorbent significantly influences the removal of Lambda Cyhalothrin, Chlorpyrifos, and Diazinon. Initially the removal of pesticides was rapidly increasing with increasing the dose of adsorbent. Raising the dose of adsorbent from 0.03 to 0.15 g/L the removal of Diazinon was improved from 52% and 46% at initial concentration of 5 and 7 mg/L respectively to 100%. Likewise, the removal efficiency of Lambda Cyhalothrin was increased from 26 to 97% and from 58 to 100% for initial concentrations of 17 and 9 mg/L respectively. The removal of Chlorpyrifos was also improved from 43 to 91% and from 49 to 92% at initial concentrations of 79 and 45 mg/L respectively. This is probably attributed to the increase of adsorbent dosage leads to the increase of active surface area resulting a more dispersion intensity of adsorbent [25]. However, there is no significant improvement in the removal of pesticides at increasing the dose of adsorbent up to 0.2 gm/L. Thus, PAC dosage not exceeding 0.15 g/L is recommended.

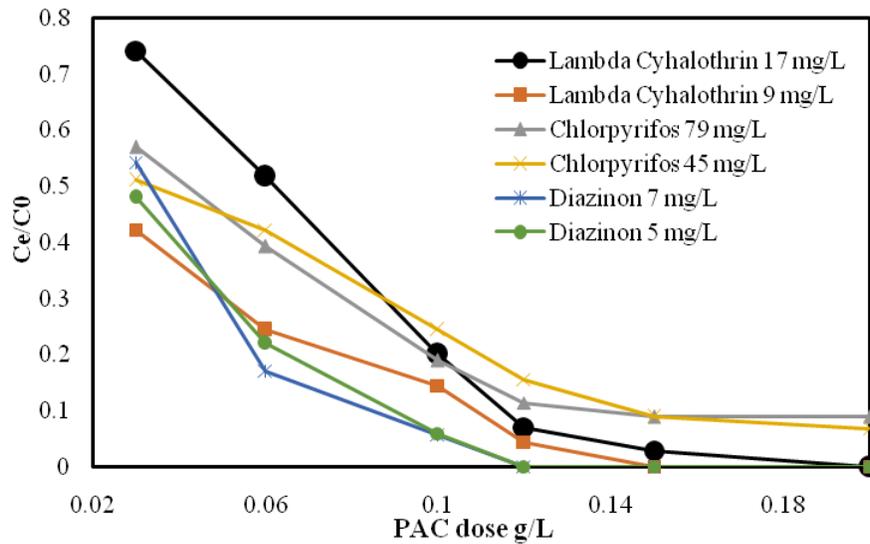


Figure 6: Effect of adsorbent dose on adsorption.

3.2.4. Adsorption kinetics

The modeling of adsorption kinetics of Lambda Cyhalothrin, Chlorpyrifos, and Diazinon were investigated by Lagergren pseudo first order model and pseudo second order model. The pseudo first order is described by the following equation [39, 40]:

$$dq/dt = k_1 (q_e - q_t) \quad (7)$$

Where k_1 : the rate constant of pseudo-first-order model (min^{-1}), q_t : the amount of pesticide adsorbed at time t (mg/g), and q_e : the amount of pesticide adsorbed on adsorbent at equilibrium (mg/g). After integrating this equation with the initial conditions, the equation becomes [38]:

$$\text{Log} (q_e - q_t) = \text{log} q_e - (k_1 t / 2.303) \quad (8)$$

The values of $\text{log} (q_e - q_t)$ are plotted against time in (Fig. 7.a). Linear regression was performed to obtain theoretical q_e , k_1 , and correlation coefficient R^2 and the results are presented in Table 1. The pseudo first order model showed high R^2 values and relevant values of theoretical q_e compared to experimental q_e values, and these are indication of a good representation of the model to the adsorption of Lambda Cyhalothrin, Chlorpyrifos, and Diazinon.

The pseudo second order model is expressed by the following equation [41]:

$$dq/dt = k_2 (q_e - q_t)^2 \quad (9)$$

Where k_2 is the rate constant of pseudo-second-order model (g/mg/min). After integrating with the initial conditions, the form can be obtained as [29, 36]:

$$t / q_t = (1/k_2 q_e^2) + (t/q_e) \quad (10)$$

The values of t/q_t were plotted against time as shown in (Fig.7.b), and theoretical q_e , k_2 , and R^2 were calculated by linear regression as illustrated in Table 1. The values of R^2 obtained from pseudo second order model were less than the R^2 values of pseudo first order model. Moreover, the difference between theoretical and experimental values of q_e was much higher. Accordingly, the adsorption of Lambda Cyhalothrin, Chlorpyrifos, and Diazinon by PAC is considered suitable to be described by pseudo first order model. Similar results were reported by Moussavi et al.(2013) for adsorption of pesticides by activated carbon.

3.2.5. Equilibrium modeling

Adsorption isotherms are used to describe the relationship between the amount of adsorbed matter at equilibrium (q_e) and the effluent concentration C_e by a mathematical model. Both of Langmuir and Freundlich isotherms were studied to describe the experimental results of Lambda Cyhalothrin, Chlorpyrifos, and Diazinon. Linear regression was used to find out the constants of each model.

Langmuir isotherm is described in the following linear form [21, 23]:

$$(1/q_e) = (1/Q_0) + (1/K_L Q_0) (1/C_e) \quad (11)$$

where K_L is a constant related to the affinity of the binding sites. Q_0 is the amount of adsorption per unit mass of adsorbent to form a complete monolayer on the surface bound at high C_e . The relation of $1/C_e$ and $1/q_e$ is plotted in (Fig. 8.a).

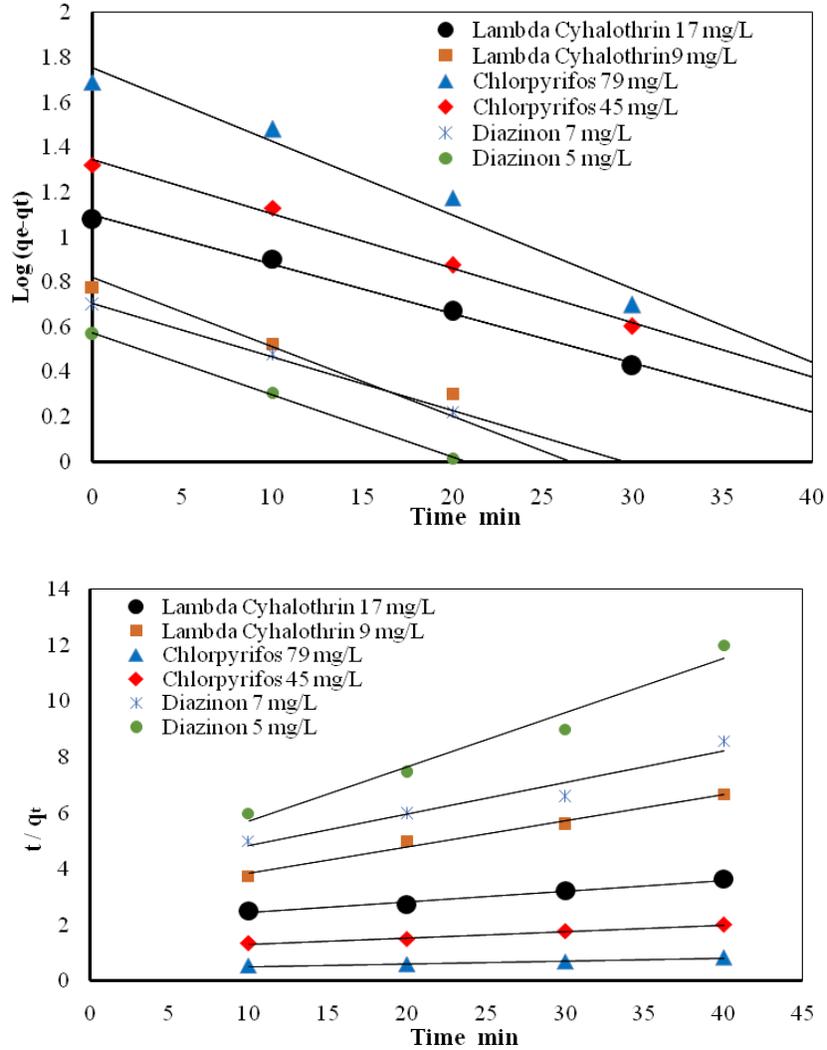


Figure 7: a) Pseudo first order kinetics for adsorption of pesticides. b) Pseudo second order kinetics for adsorption of pesticides

Table 1 Comparison between pseudo first order and pseudo second order adsorption kinetics

Pesticide	C_0 mg/L	q_e experimental mg/g	Pseudo 1 st order			Pseudo 2 nd order		
			q_e theoretical mg/g	K_1 min ⁻¹	R^2	q_e theoretical mg/g	K_2 g.mg ⁻¹ .min ⁻¹	R^2
Lambda Cyhalothrin	17	11.3	12.5	0.0484	0.994	25.6	0.00074	0.980
	9	6.0	6.6	0.0691	0.966	10.8	0.00297	0.985
Chlorpyrifos	79	48.7	56.6	0.0737	0.967	111.1	0.00019	0.951
	45	20.5	22.1	0.0553	0.994	45.5	0.00045	0.986
Diazinon	7	4.7	5.1	0.0530	0.998	8.8	0.00344	0.944
	5	3.3	3.7	0.0621	0.998	5.1	0.01014	0.965

Freundlich isotherm is expressed in the following linear form [32, 42]:

$$\ln q_e = \ln K_F + (1/n) \ln C_e \quad (12)$$

Where K_F is a constant describe the adsorption capacity of the sorbent, and n is a constant describe the favorability of adsorption. The relation of $\ln C_e$ and $\ln q_e$ is plotted in (Fig 8.b)

The values of Langmuir and Freundlich isotherms constants and R^2 are listed in Table 2. It could be seen that the application of Langmuir isotherm showed a higher correlation than Freundlich isotherm in terms of R^2 . The high correlation fitting of Langmuir isotherm to the experimental data may be due to homogeneous distribution of active sites onto PAC surface when using the high mechanical mixing, because in Langmuir equation, it is assumed that the surface is homogenous [38]. Similar results were reported in the adsorption of different pesticides with powdered activated carbon [27].

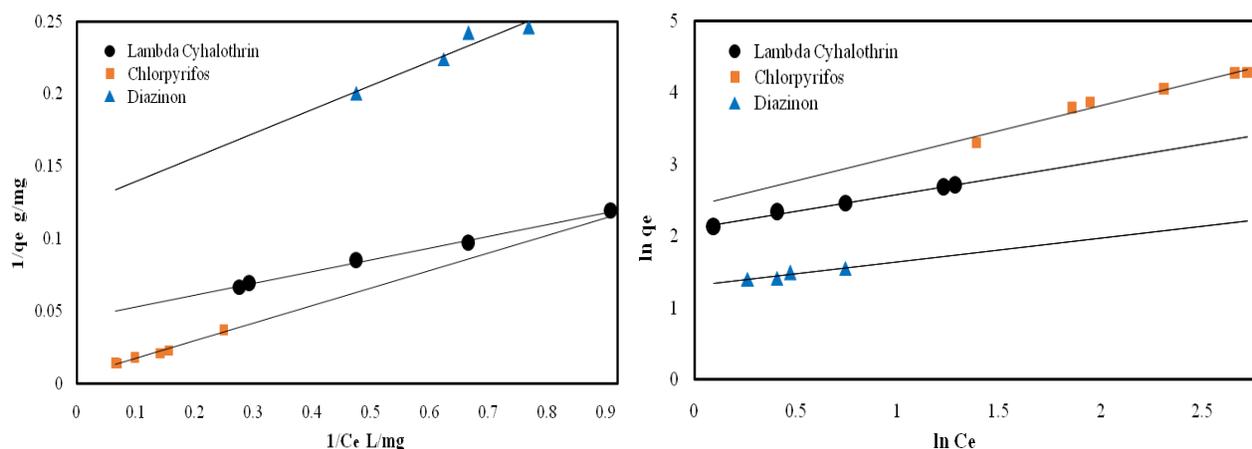


Figure 8: a) Langmuir adsorption isotherm. b) Freundlich adsorption isotherm.

Table 2 Model parameters of Langmuir and Freundlich isotherms

Pesticide	Langmuir isotherm			Freundlich isotherm		
	Q_0 mg/L	K_L	R^2	K_F	n	R^2
Lambda Cyhalothrin	22.7	0.543	0.996	8.25	2.13	0.991
Chlorpyrifos	199.6	0.041	0.982	11.3	1.43	0.969
Diazinon	8.13	0.745	0.921	3.63	3.01	0.892

Conclusions

The removal of pesticide fractions (Lambda Cyhalothrin, Chlorpyrifos, and Diazinon) from industrial waste water by TiO_2 solar photocatalysis, and solar photo-Fenton followed by adsorption using powdered activated carbon was investigated. Primary treatment by TiO_2 photocatalysis after 120 minutes of irradiation time achieved removal efficiency of 63.7%, 60.75%, and 38.2% for Lambda-Cyhalothrin, Chlorpyrifos, and Diazinon respectively. Photo-Fenton process was better than photocatalysis process in degradation of pesticides in terms of removal performance, and achieved removal efficiency of Lambda Cyhalothrin, Chlorpyrifos, and Diazinon after 120 minutes of irradiation time 80.65%, 78.05%, and 50.9%, respectively.

At optimum pH value of 3 and dosage of 0.15 g/L, the removal efficiency of Lambda-Cyhalothrin, Chlorpyrifos, and Diazinon was 97%, 91%, and 100% respectively. The Pseudo first order kinetics was more suitable to describe the adsorption of Lambda Cyhalothrin, Chlorpyrifos, and Diazinon. The equilibrium data was fitted to Langmuir and Freundlich isotherms. Langmuir isotherm was better to describe the equilibrium data in terms of higher correlation coefficient.

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