PHOTOCATALYTIC DEGRADATION OF CHLORPYRIFOS BY USING SYNTHESIZED NANO TITANIUM

إزالة الكلوربيريفوس باستخدام تكنولوجيا التحفيز الضوئي عن طريق النانو تيتانيوم المصنع

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KEYWORDS:
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Photodegradation,
Titanium dioxide

الملخص العربي - كلوربيريفوس هو واحد من اكثر المبيدات استخداما في العملية الزراعية نظرا لقلة تكلفته وكفائته العالية في السيطرة علي الحشرات. صرف المياه الصناعية لمصانع المبيدات بدون معالجتها يسبب العديد من المشاكل الخطيرة للكائنات الحية والبيئة. التحفيز الضوئي يعتبر طريقة فعالة لإزالة المواد العضوية الخطيرة من المياه. في هذه الدراسة يتم دراسة ازالة الكلوربيريفوس باستخدام التحفيز الضوئي عن طريق استخدام اكسيد التيتانيوم الذي تم تحضيره باستخدام طريقة السول- جيل تحت تاثير ظروف تشغيل مختلفة مثل جرعة المحفز والأس الهيدروجيني للمحلول والتركيز الابتدائي للكلوربيريفوس وزمن الاضاءة. تم استخدام مطيافية تشتت الطاقة بالاشعة السينية والتحليل الوزني الحراري لتوصيف اكسيد التيتانيوم. النتائج تشير الي ان كفاءة الازالة بالتحفيز الضوئي تتاثر بظروف التشغيل المختلفة. كفاءة التحفيز الضوئي تقل مع زيادة تركيز الكلوربيريفوس الابتدائي. الوسط المتعادل هو الأنسب لإزالة الكلوربيريفوس. تفاعلات التحفيز الضوئي تتبع معادلة التفاعلات من الدرجة الأولى ومعدل التفاعل يتناسب عكسيا مع تركيز الكلوربيريفوس الابتدائي. تم عمل نموذج رياضي لتوضيح العلاقة بين كفاءة الإزاله وعوامل التشغيل المختلفة

Abstract—**Chlorpyrifos is one of the most popular used organophosphorus pesticides because of its low cost and high efficiency in controlling pests in agriculture. Presence of pesticides in aquatic environments causes serious problems to living organisms. Photocatalysis considers an effective route for the removal of resistant hazardous organic wastes from aqueous solutions. In this study, the photocatalytic degradation of chlorpyrifos in aqueous solution by using synthesized prepared nano titanium dioxide (TiO₂) by sol-gel method was investigated under various operational conditions such as catalyst dose, pH of the solution, initial concentration of chlorpyrifos and illumination time. Energy dispersive X-ray Spectroscopy (EDX) and Thermo gravimetric analysis (TGA) were used for the nano TiO₂ characterization. The results depicted that the photocatalytic degradation of chlorpyrifos was strongly influenced by the operational parameters. The photocatalytic degradation decreased with increasing the initial concentration of chlorpyrifos. Neutral pH of the solution is the optimum for the photocatalytic degradation of chlorpyrifos. The photocatalytic reactions approximately followedPseudo-first order kinetics and the reaction rate was inversely related to the feed concentrations. A model was performed with regression coefficient of 88.45 % to express the relation between removal efficiency and operational conditions.**

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I. INTRODUCTION

Industrial effluents and agricultural runoff are the major sources of pesticides [1]. Industrial wastewater contains pesticides has several impacts on the environment [2]. The exposure to pesticides is very dangerous because it has been related to a number of health problems such as birth defects; cancer, neurologic and endocrine (hormone) system disorder [3-4]. Available traditional water treatment

methods such as air stripping, coagulation, flocculation, sedimentation, filtration and adsorption only transfer the pollutants from one phase to another phase and the pollutants are not completely degraded [5]. Advanced oxidation processes (AOPs) are one of the best alternatives for pesticides and other bio-resistant organic removal from industrial wastewater. Semiconductor photocatalysis is one of the remarkable advanced oxidation processes which accelerates photoreaction by using a catalyst [6]. There are different types of semiconductor such as (TiO_2, ZnO, WO_3, CdS, $GaAS$, PbS). Among various oxide semiconductors photocatalysts, TiO_2 has been proven to be the most convenient for widespread environmental applications due to its biological and chemical inertness, strong oxidizing power, commercially available, nontoxicity and long-termstability against photocorrosion [7-8]. Reaction mechanisms of photocatalytic processes have been discussed indetail in the literature [9-14]. Briefly in photocatalysis process, TiO_2 is activated by photons having an energy level higher than its band gap. Then, electrons are excited from the valence band to the conduction band forming an electron/hole pair (e−/h+). The conduction band (e−) react with oxygen to form super-oxide oxygen and the valence band (h+) react with wateror hydroxide ion (OH⁻) adsorbed on the catalyst surface to form hydroxyl radicals (•OH) which are strong oxidant. Organic pollutants on or near the surface of TiO_2 will be attacked and oxidized by hydroxyl radical. It causes decomposition of toxic and bio-resistant compounds into harmless species such as CO_2, H_2O. Chlorpyrifos is one of the most widely organophosphate pesticides, it is used for the control of pests, flies and mosquitoes [6]. This paper aims to study the photocatalytic degradation of chlorpyrifos in the presence of the synthesized nano titanium by sol-gel method, in addition to investigate the effect of operational conditions such as illumination time, catalyst dose, initial chlorpyrifos concentration and pH on the degradation efficiency of chlorpyrifos. Characterization of the prepared catalyst was carried out using energy dispersive X-ray Spectroscopy (EDX) and thermo gravimetric analysis (TGA). Kinetic photochemical behavior of chlorpyrifos using the prepared nano titanium as a photocatalyst was also studied.

II. MATERIAL AND METHODOLOGY

A. Materials

Titanium isopropoxide (95%) was obtained from (Alfa Easer) and palmitic acid was purchased from (Lobachemie). Chlorpyrifos was obtained from commercial source and was used as received. Ammonium hydroxide and isopropanol were purchased from (Adwic). Distilled water had been used through the study. PH was adjusted by using HCL and NaOH solutions with concentration of 1 M.

B. Preparation of nano TiO_2

In this study, Sol-gel method was used for the preparation of nano titanium which described by Baker et al. [8]. Distilled water (200 ml) and palmitic acid (82.7 mmol) were stirred in a beaker. Ammonium hydroxide had been added to the solution to make it homogenous. Then,

isopropanol (50 ml) and titanium isopropoxide (16.7 mmol) were mixed and added drop wise to the palmitic acid solution for 2 hours and stirred for 12 hours. The color of the final mixture became milky white and finally white colloidal gel was formed. Then, the white colloidal gel was dried at 115ºC for 48 hours to yield the white powder. Finally, the powder was calcined at 500ºC for 3 hours.

C. Experimental apparatus and procedure for chlorpyrifos

Experimental work was carried out on a photoreactor apparatus. The schematic of the used system is shown in Fig. 1. The photoreactor consisted of a 250 ml beaker, magnetic stirrer and a 400-watt metal halide lamp. The height of the lamp was fixed to be 10 cm above the beaker. A 100 ml of desired concentration of chlorpyrifos was prepared and placed in the reactor and the required catalyst dose was added. Firstly, the solution was stirred for 30 min in dark to achieve adsorption, and then the lamp was switched on to begin the photocatalytic reaction. During irradiation, a sample was taken every 30 min. The degradation of the chlorpyrifos was monitored by HPLC (Agilent, 1200 series). The optimum HPLC condition was achieved with acetonitrile: water (80:20) as mobile phase, flow rate of 1.5 ml/min, on Zorbax Eclipse XDB-C18 column, temperature 40ºC, detector 230 nm and injection volume 30 μl. The following equation describes the degradation efficiency(x) as a percentage at any time (t)

$$X(\%) = \frac{C_o - C}{C_o} * 100 \qquad (1)$$

Where the initial concentration of chlorpyrifos is C_o and the concentration of chlorpyrifos at time t is C.
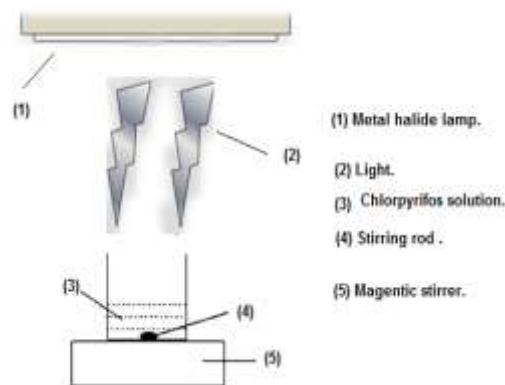

Fig. 1. Schematic of photoreaction experiment setup.

(1) Metal halide lamp.

(2) Light.

(3) Chlorpyrifos solution.

(4) Stirring rod.

(5) Magentic stirrer.

D. Nano titanium characterization

Energy dispersive X-ray Spectroscopy (EDX) was managed by a Jeol JEM 2100 to confirm the chemical composition of the prepared nano titanium. Thermo gravimetric analysis (TGA) was performed by simultaneous TGA-DSC model SDT Q600 to confirm the removal of organic carbon after calcination.

III. RESULTS AND DISCUSSION

A. Characterization of nano titanium

1) Energy dispersive X-ray Spectroscopy (EDX)

The elemental composition of the prepared nanoparticles is confirmed using (EDX), which detected Ti, O elements as shown in Fig. 2. The grid used in this technology is the reason for the other signals appeared.
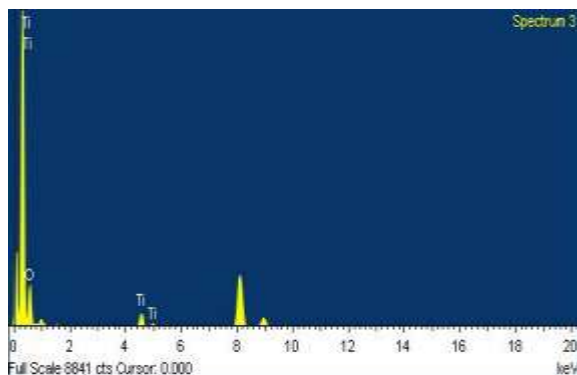

Fig. 2. EDAX pattern of prepared TiO2 nanoparticles.

2) Thermo gravimetric analysis (TGA)

Most of the organic carbon coming from the precursors was removed after calcination, which was confirmed by thermo gravimetric analysis (TGA) as shown in Fig. 3. A total mass loss of only 2.637 % for prepared TiO_2 indicated that most of the organic precursors were decomposed by high temperature sintering. The negligible mass loss could be attributed to residual organic and the loss of water adsorbed from environment.
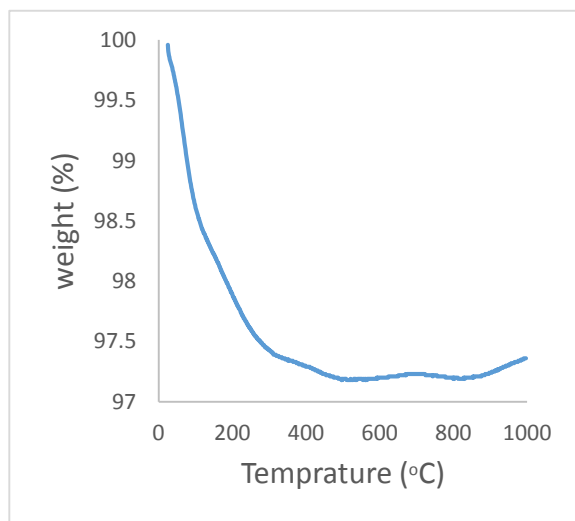

Fig. 3. TGA curve for TiO2.

B. Effect of TiO_2 dose on removal efficiency

Fig. 4 shows the change of chlorpyrifos concentration with irradiation time using various dosage of TiO_2 for the same chlorpyrifos concentration 100 mg/L and pH=7 ± 0.5. The results revealed that increasing the catalyst dose increases the number of adsorbed organic molecules and the available active sites available for photon absorbance [6]. Therefore, the photocatalytic degradation efficiency of chlorpyrifos increases by increasing the TiO_2 dosage. Full degradation achieved at catalyst doses 0.25,0.5, 1 g/L, but for catalyst dose 0.1 g/L the removal efficiency was 97.5% at the same illumination time 150 min. Increasing the catalyst does not improve the removal efficiency in all cases, since above certain catalyst dose clustering of catalyst particles takes place and thus causes a decrease in the number of active sites on its free surface. The decrease in photodegradation in this case can be explained by the decrease in surface area of catalyst due to aggregation of TiO_2 [15-16]. Another reason, at higher catalyst dose the solution becomes more turbid resulting in the reduction of light penetration by the scattering effect [17].
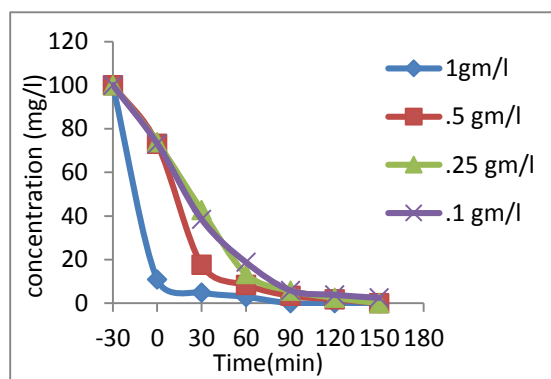

Fig. 4. Effect of catalyst dose on the photocatalytic degradation efficiency using chlorpyrifos concentration =100 mg/L and pH=7 ± 0.5.

C. Effect of initial concentration of chorpyrifos

Fig. 5 shows the effect of initial chlorpyrifos concentration varies from 100 to 400 mg/L on the removal efficiency using a catalyst dosage of 0.25 g/L at pH value of 7 ± 0.5. At low concentration of chlorpyrifos the light goes easily through the solution to irradiate the TiO_2, therefore the photonic efficiency increases resulting in higher photocatalytic degradation. While the chlorpyrifos initial concentration increased from 100 to 400 mg/L, the photocatalytic degradation efficiency decreased from 100% to 65%, respectively. The reason for this result may be explained by the number of adsorbed molecules of chlorpyrifos increased on the surface of TiO_2, which reduced the active sitesavailable for hydroxyl ions adsorption and consequently, the generation of hydroxyl radicals reduced [18-19]. Another reason, as the chlorpyrifos concentration increased, the photon get intercepted before they can reach the catalyst surface hence, the adsorption of photons by the catalyst decreases, and consequently the catalyst surface will not be excited and chlorpyrifos degradation will be reduced [20-22].
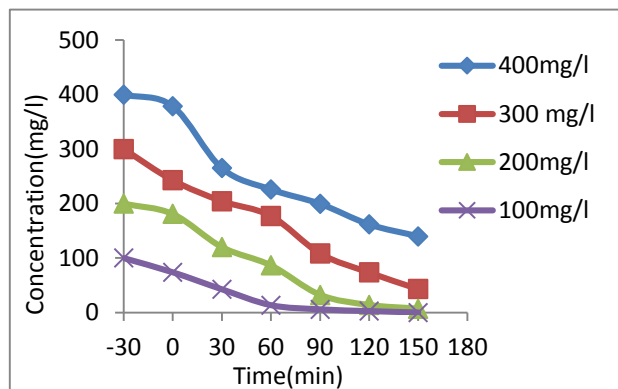
Fig. 5.   Effect of chlorpyrifos concentrationsonphotocatalytic degradation efficiency using catalyst dose = 0.25 g/L and pH=7 ± 0.5.

Fig. 6. Effect of pH on photodegradationefficiency using catalyst dose = 0.25 gm/L and initial chlorpyrifos concentration =100 mg/L.

D.Effect of pH on the removal efficiency

The effect of initial pH on photodegradation efficiency of chlorpyrifos is shown in Fig. 6. The solution pH has a great effect on the photocatalytic degradation as it states the surface charge of photocatalyst and the size of aggregation [6]. The pH of the solution was not controlled during the course of the reaction and adjusted only before irradiation using HCL and NaOH with concentration of 1M. The effect of pH on the photocatalytic degradation of chlorpyrifos was investigated in the pH range from 2.5 to 11 at constant concentration of chlorpyrifos and catalyst dose 100 mg/L and 0.25 g/L, respectively. The effect of pH can be illustrated on the basis of zero-point charge of TiO_2. The pH of the point of zero charge of the TiO_2 is reported to be about 6.25 [23-24]. As pH decreases below the pH of point of zero charge, the surface of TiO_2 has a net positive charge while the negative charged surface dominates as pH increases above pH of point of zero charge [25]. The ionic form of the organiccompound, anionic or cationic affects the electrostatic attraction or repulsionbetween the catalyst's surface and the organic molecule, which consequently improves or inhibits the photodegradation efficiency. When the initial pH increased from 2.5 to 7, the photodegradation efficiency of chlorpyrifos increased from 88.6 to 100%. At low pH condition the catalyst's surface has a positive charge and the oxidation of pollutants achieved by the photogenerated holes, the oxidizing power of these holes is lower than the hydroxyl radicals [26]. At pH value of 11, the photocatalytic degradation efficiency decreased from 100% to 93.2%. At alkaline medium, a repulsive forces exist between the hydroxyl ions and the catalyst surface with negative charge [6]. This effect, results in the reduction of generatedhydroxyl radical, therefore, photocatalyic degradation efficiency decreases.
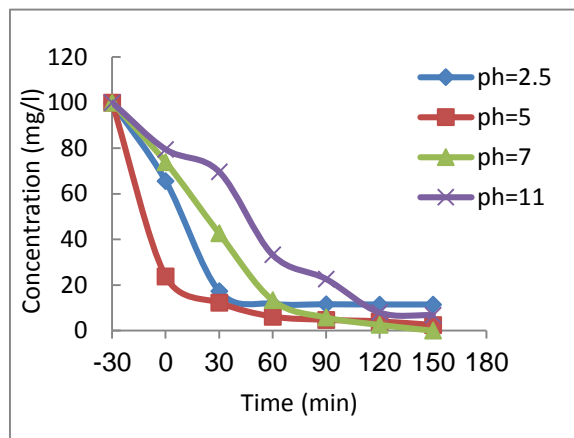
E.Kinetics of photocatalytic degradation of chlorpyrifos

The degradation rate for chlorpyrifos was calculated using Langmuir – Hinshelwood model given as follow [27-28]:

$$r = \frac{K_r \; K_{ad} \; C}{1 + K_{ad} \; C} \qquad (2)$$

Where the rate of degradation is r, concentration of the reactant at time (t) is C, the rate constant is k_r and the adsorption equilibrium constant is K_{ad}. The equ (2) can be simplified to the pseudo- first order kinetics equation with an apparent first-order rate constant k_{app} as the adsorption is very weak in photocatalysis process and/or the concentration of the reactant is very low [27]:

$$Ln \left(\frac{C_o}{C}\right) = K_r \; K_{ad} \; t = k_{app} \; t \qquad (3)$$

Where the initial concentration of chlorpyrifos is C_o and the concentration of chlorpyrifos remaining after time t is C To study the kinetics of photocatalytic degradation of chlorpyrifos, experiments were carried out using TiO_2 dosage of 0.25 g/L, irradiation time 150 min and pH =7 ± 0.5. The concentration of chlorpyrifos after 30 min in the dark was considered the initial concentration for kinetics analysis. Fig. 7 shows the fitting between the model equation and experimental data at various chlorpyrifos solution concentration. Table 1 shows the fitting parameter and the correlation coefficient R^2 for the pseudo first order kinetics. It was demonstrated that the results were validated by pseudo - first order. It was stated that as the initial chlorpyrifos concentrations increases, the reaction rate decreases. This may be due to as the initial chlorpyrifos concentration increases, the path length of photons entering the solution decreases [29-31]. But for low chlorpyrifos concentrations the reverse effect was observed. At high chlorpyrifos concentrations, the chlorpyrifos molecules may absorb a higher amount of light rather than the catalyst

therefore, the catalytic efficiency decreased [32]. Neppolian et al. has the same results using TiO_2 photocatalyst and solar light for the degradation of three commercial textile dyes [33].

TABLE 1
PSEUDO-FIRST ORDER PARAMETERS AND THE CORRELATION COEFFICIENTS
AT VARIOUS CHLORPYRIFOS CONCENTRATIONS

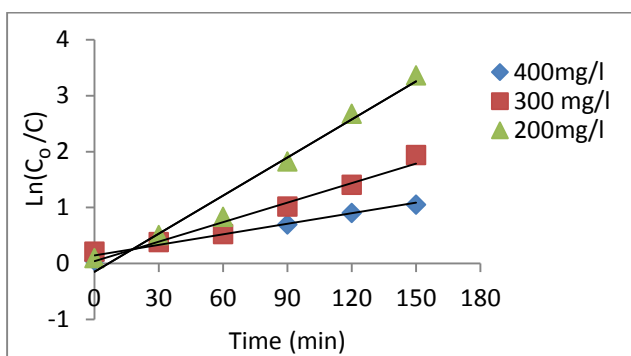| Initial concentration (mg/l)	K (min-1)	R2
200	0.0227	0.9724
300	0.0116	0.9536
400	0.0063	0.9713

Fig. 7. Kinetics analysis of chlorpyrifos using catalyst dose= 0.25 g/L and pH=7 ± 0.5.

F. Optimization of initial chlorpyrifos concentration and illumination time for degradation of chlorpyrifos

The experimental results were used to perform a model that relates degradation efficiency (Y%) and the operational parameters. To determine the reduced model coefficients in the polynomial expression, regression analysis was carried out as shown in equ. (4). The correlation coefficient obtained from regression analysis was 88.45%. Fig. 8 shows the response surface diagram for the optimization of chlorpyrifos concentration and time for photocatalytic degradation of chlorpyrifos at catalyst dose .25 g/l.

$Y\% = 15.3 * (Time)^{0.4} - 0.137033 *(initial\ chlorpyrifos\ concentration) + 0.002455*(catalyst\ dose) + 0.000575$ (4)
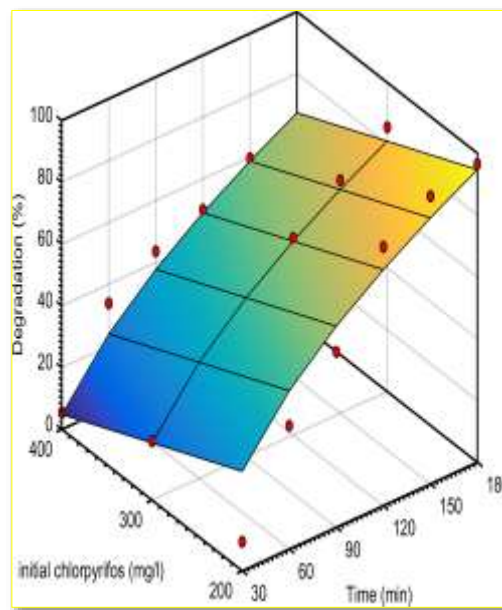

Fig. 8. Optimization of initial chlorpyrifos concentration and time for photocatalytic degradation of chlorpyrifos at catalyst dose .25 g/l using a response surface diagram

IV. CONCLUSIONS

In this study, photocatalytic experiments were performed under various operation conditions using synthesized nano TiO_2 for chlorpyrifos degradation.Chlorpyrifos was successfully degraded by using the synthesized nano TiO_2 in light. The photocatalytic degradation efficiency of chlorpyrifos increased with increasing the illumination time. It was found that as the catalyst dose increased, the chlorpyrifos removal efficiency increased. It was also depicted that the chlorpyrifos removal efficiency was inversely related to the feed chlorpyrifos initial concentration. The highest chlorpyrifos photocatalytic degradation was achieved at neutral media. The data was successfully analyzed with the Langmuir – Hinshelwood pseudo first order kinetic model. A model was performed with regression coefficient of 88.45 % to express the relation between removal efficiency and operational conditions.

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