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Modeling of Chlorpyrifos degradation by TiO_2 photo catalysis under visible light using response surface methodology

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ABSTRACT

Chlorpyrifos has been classified by the Stockholm Convention as priority pesticide under consideration because of its toxicological profile that succinctly characterizes the toxicological and adverse effects on health. TiO_2 photo catalysis of aqueous chlorpyrifos (CPF) solution using a raceway pond, containing total nitrogen and total phosphorus, has been modeled using response surface methodology (RSM). The RSM was used to improve the optimum condition of CPF degradation using R software. The ANOVA, p-value of lack of fit > 0.05 indicated that the equation was well-fitted. 71.09 ± 1.9% of removal was obtained for CPF (2.84 ppm), time (55.15 min) and dosage of TiO_2 (17.07 mg L^{-1}) under TiO_2 visible photo catalysis compared to the 25.6 ± 0.25% by visible photolysis under similar experimental conditions. Nitrogen and phosphorus showed negligible interference on CPF degradation.

Keywords: Chlorpyrifos; TiO_2 catalyst; Photolysis; Visible light; POPs; RSM

1. Introduction

Persistent organic pollutants may impose serious concern at a global scale due to their toxicity, persistence in the environment, bio accumulation, and potential for long-range environmental transport [1]. EPA revised human health risk assessment and drinking water exposure assessment for chlorpyrifos (CPF) in 2015. The revised analysis showed risks from dietary exposure (*i.e.* residues of chlorpyrifos on food crops) and drinking water [2]. Chlorpyrifos is a broad-spectrum organo phosphorus insecticide currently used in the world, and also in Iran, on a variety of crops. Health problems due to chlorpyrifos include myosis, increased urination, diarrhea, diaphoresis, lacrimation, and salivation. Chlorpyrifos enters into the body of people and wildlife through skin contact, ingestion and inhalation [3].

Several studies have reported the use of advanced oxidation processes (AOP) for the degradation of various contaminants including pesticides (e.g. chlorpyrifos) and organic pollutants [4–8].

Ismail et al. [8] studied chlorpyrifos oxidation by ^{60}Co γ-rays and reported that Gamma irradiation showed 100% degradation for a 500 μg L^{-1} of chlorpyrifos at an absorbed dose of 575 Gy. Amalraj and Pius [9] degraded monocro-

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tophos and chlorpyrifos in aqueous solution using TiO_2 under UV radiation. These authors reported that maximum degradation of pesticides was observed using an initial concentration of 2 mg L^{-1}, 100 mg of TiO_2 dose and pH 5 at 60 min. Yadav and collaborators [10] studied the biodegradation of chlorpyrifos using Pseudomonas. According to their results, the optimal conditions for CPF degradation in a batch reactor were: 300 × 10^6 CFU mL^{-1} of inoculum level, 500 mg L^{-1} of CPF concentration, pH 7.5 at 37°C and 5.5 mg L^{-1} of dissolved oxygen (DO). Also, under optimum condition of the batch reactor, the study was operated in a continuous packed bed bioreactor where 91% of CPF removal was observed up to the inlet load of 300 mg L^{-1} d^{-1} [10]. Nevertheless, AOP to remove pesticides from water, are good alternative technologies. AOP represent an excellent process for removing organic pollutants in water since the hydroxyl radicals produced by AOP processes are capable to enhance, in a non-selective manner, both degradation and mineralization of pollutants into CO_2, H_2O and inorganic salts [11]. Among recent technologies, photo catalysis is one of the most advanced and developed process to eliminate contaminants from the environment. Titanium dioxide is nontoxic, stable to photo corrosion, low cost and suitable to work using sunlight as energy source [12]. photo catalyst has been mainly used widely in environmental remediation (*i.e*. wastewater detoxification) and energy conversion [13,14]. When the treatment is aimed at micro pollutant oxidation though, the pollutant concentration is at least a thousand times lower than for macro pollutant oxidation. Therefore, the process needs less hydroxyl radicals and, consequently, less irradiance (less photon) to achieve removal. Up to our study no cases have been published for raceway pond reactors (RPRs) photo-catalyst applications using solar light, which have been widely applied for microalgal mass culture, for pesticide degradation and no one for chlorpyrifos.

This work is aimed at investigating the potential of TiO_2 photo catalysis for chlorpyrifos degradation, under visible light (simulating solar radiation), in water under laboratory conditions at natural water pH (7–7.5). To our knowledge, till now no study has reported a synthetic condition of the real condition for chlorpyrifos removal. A prediction model for chlorpyrifos mineralization is also developed using response surface methodology (RSM) which represents a collection of mathematical and statistical techniques for experimental model building, in which, two steps are necessary, the definition of an approximation function and the design of the plan of experiments. The purpose of RSM application is minimizing the cost of expensive analysis methods and their associated numerical noise [15,16].

2. Experimental

2.1. Standards and reagents

Analytical standard of chlorpyrifos (purchased from Dr Ehrenstorfer, Germany, >99%purity), TiO_2 Aeroxide P25 (Sigma-Aldrich), acetonitrile (chromatography grade, Merck), potassium nitrate, ammonium chloride, nicotinic acid, potassium phosphate and sulfuric acid (high-purity analytical grade reagents, Merck) were used without further purification. All stock aqueous solutions were prepared using deionized water. Chlorpyrifos stock solutions (1000 mg L^{-1}) were prepared by dissolving solid chlorpyrifos in acetonitrile. Various concentration of chlorpyrifos solutions (1 – 4 mg L^{-1}) were prepared in distilled water from stock solution. Fixed concentrations of nicotinic acid as organic source of nitrogen (5 mg L^{-1}), nitrite (10 mg L^{-1}), ammonium (5 mg L^{-1}), and phosphate (1.5 mg L^{-1}) were added to chlorpyrifos aqueous solution to examine their effects on degradation of chlorpyrifos by TiO_2 photo catalysis under visible light. In order to simulate field conditions of CPF oxidation, total nitrogen and phosphate are added in all influent solution of the reactor using neutral conditions.

2.2. Experimental setup

Aqueous solution of chlorpyrifos pesticide (2.5 L), containing total nitrogen and phosphate, was placed in a lab scale fiber glass–RPR (Raceway Pond Reactor) with a maximum capacity of 7.5 L (50 cm x 15 cm x 10 cm). The pH was adjusted to pH 7.3 ± 0.3 using NaOH (0.1 M). It is isolated by a central wall, framing two channels as depicted in Fig. 1. The RPR incorporates a paddle wheel associated with a motor to acquire a blended and homogeneous solution. An halogen lamp (300 W, Osram, Munich, Germany, wavelength range: 400 – 800 nm) was used as the visible light source for the photo catalytic reactions which the solution was exposed up to 1 h. Also the height of the halogen lamp above the RPR was 20 cm. The luminous intensity (lux) was measured using an illumination meter (LX-100S, KIMO, France) to estimate the light intensity, and was then converted to the irradiance unit (in W/m^2) using empirical conversion factors. The light intensity of the light source was estimated to be 697 ± 5.33 lux (7.5×10^{-3} W/m^2), which is much lower than the global average solar irradiance (~10 W/m^2) [17].

2.3. Analytical determinations

Samples were taken at pre-selected time intervals and immediately centrifuge 20 min at 6000 rpm. A Varian chrome pack CP–3800 gas chromatography was used to analyze samples for CPF. The instrument was equipped with 63 Ni electron capture detector (ECD) and a 30 m × 0.32 mm i.d. (0.25 µm film thickness) HP 5 ms fused silica capillary col-

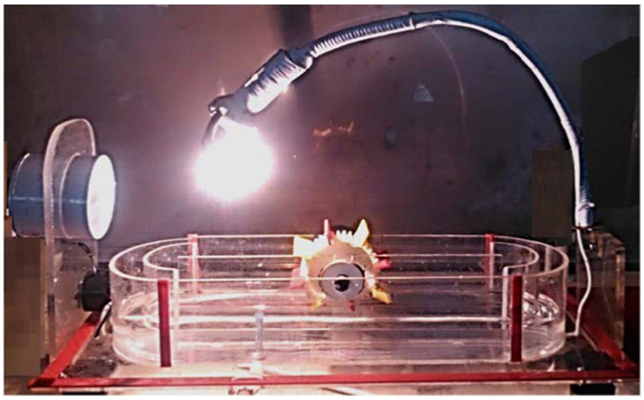

Fig. 1. Experimental set-up of the fiberglass-Raceway Pond Reactor (RPR) with a maximum capacity of 7.5 L.

umn. Nitrogen gas (99.999%) was used as a carrier gas at a flow rate of 1.5 mL/min. Oven temperature was kept at 90°C for 1 min, then increased to 170°C at a rate of 3.5°C/min, and finally to 280°C at a rate of 10°C/min. The injector and the detector temperatures were adjusted to 250°C and 300°C, respectively. 1 µL of each sample was injected to GC-ECD for separation and quantitative analysis. The oxidation of chlorpyrifos (CPF) was followed by Intelligent Professional Ion Chromatography (Metrohm, IC 850). Total nitrogen and total phosphorous were measured using standard methods and standard reagents (Hach test kit, Germany).

2.4. Design of experiment using central composite design (CCD)

Half fractional factorial outline was done to investigate which test factors and their interactions display noteworthy impacts. Then, a central composite rotatable design for three independent variables was employed to design experiments. A five level, three variables central composite rotatable design was employed for optimization with respect to three important reaction variables: CPF concentration (X_1), time (X_2) and TiO_2 dosage (X_3). The R software by RSM package was used for design and statistical analysis [18,19]. The independent variables and their levels are shown in Table 1 for TiO_2 photo catalysis. According to the Montgomery method [20], the total number of experiments carried out was 23 for the photo catalytic CPF oxidation.

The data from the design were used to create a prediction model. The empirical second order polynomial model was shown as follows:

$$Y = \beta_0 + \sum_{j=1}^{K} \beta_j X_j + \sum_{j=1}^{K} \beta_{jj} X_j^2 + \Sigma \sum_{i<j=2}^{K} \beta_{ij} X_i X_j \qquad (1)$$

where Y is the response; X_i and X_j are variables (i and j ranged from 1 to k); β_0 is the constant term; β_j is the linear coefficient, β_{ij} is the interaction coefficient, and β_{jj} is the quadratic coefficient; k is the number of independent parameters ($k = 3$ in this study) [21].

2.5. Statistical analysis

To elucidate the relationship between the independent and dependent variables, a multiple regression analysis through the generalized least square using R software (3.0.3) was used. Also, stationary point in original units, as a result of analysis of variance table in R software, was used to estimate an optimal condition for CPF removal.

Table 1
Independent variables and levels (coded and un coded) of central composite design

TiO_2 solar photo catalysis						
Independent variables	Symbol	Levels of variables				
		–1	–0.59	0	+0.59	+1
Chlorpyrifos concentration (ppm)	X_1	1.0	1.6	2.5	3.4	4.0
Time (min)	X_2	5.0	16.0	32.0	49.0	60.0
TiO_2 dosage (mgL^{-1})	X_3	0.0	10.0	25.0	40.0	50.0

3. Results and discussion

3.1. Model fitting and statistical analysis

CCD can be developed proficiently using a second-order model [20]. It is first-order (2^N) designs which increased by additional center and axial points, to permit estimation of the tuning parameters of a second-order model. According to the created design, Fig. 2 shows good agreement between the removal estimation and the experimental data. In the correlation of the removal efficiency of CPF (Y), using TiO_2 photo catalysis with other independent variables (Table 2), response surface function was utilized (in terms of actual factors), as shown by Eqs. (2)–(4):

$$\mathbf{Y}\left(\textbf{CPF removal } (\%)\right) = 37.44760 - 17.82315 * X_1 + 21.64548 * X_2 \qquad (2)$$

$$\mathbf{Y}\left(\textbf{CPF removal } (\%)\right) = 80.52034 - 28.83402 * X_1 + 14.52152 * X_2 + 5.18115 * X_3 - 7.43750 * X_1 * X_3 - 13.42520 * X_1^2 - 12.08671 * X_2^2 - 42.78020 * X_3^2 \qquad (3)$$

$$\mathbf{Y}\left(\textbf{CPF removal } (\%)\right) = 59.89992 - 3.98966 * X_1 + 28.03456 * X_2 - 6.48744 * X_3 - 21.63649 * X_2 * X_3 - 8.77387 * X_1^2 - 21.18524 * X_2^2 - 38.32613 * X_3^2 \qquad (4)$$

The fit of the model was verified by the coefficient of determination R^2 and p-value for lack of fit. As appeared in Table 3 the R^2 value was 0.987 which indicated that 98.7% of the variations could be clarified by the anticipated model separately. To evaluate correlation between the observed and predicted values of three designed model, R^2-adj estimation confirms it (0.981).

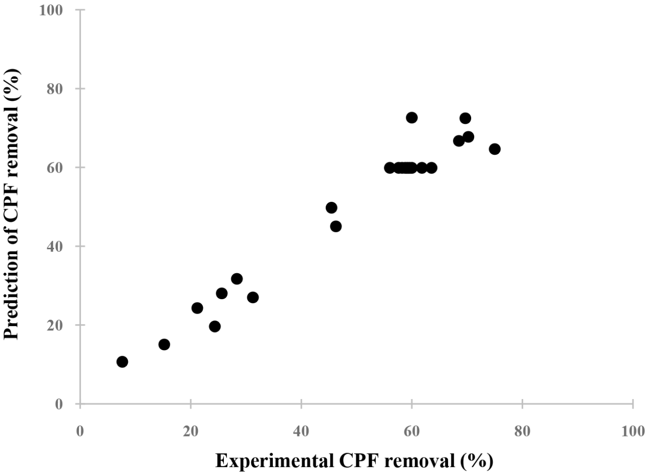

Fig. 2. Experimental versus simulated chlorpyrifos (CPF) removal values.

Table 2
Estimated regression coefficients for removal efficiency by TiO_2 solar photo catalysis

Coefficients:					
	Estimate	SE	t	P	
(Intercept)	59.89992	0.90907	65.8915	< 2.2e–16	***
X_1	–3.98966	1.23513	–3.2301	0.0056068	**
X_2	28.03456	1.23508	22.6986	5.005e–13	***
X_3	–6.48744	1.23529	–5.2517	9.762e–05	***
X_2:X_3	–21.63649	2.67914	–8.0759	7.664e–07	***
x_1^2	8.77387	1.92869	4.5491	0.0003839	***
X_2^2	–21.18524	1.92980	–10.9780	1.445e–08	***
X_3^2	–38.32613	1.92869	–19.8716	3.464e–12	***

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1. where: SE = standard error, t = student test, p = probability

Table 3
Analysis of variance (ANOVA) for the fitted polynomial model for CPF removal using TiO_2 solar photo catalysis

Model formula	Df	Sum Sq	Mean Sq	F value	Pr(>F)
First-order response	3	4027.9	1342.63	180.3467	5.469e–12
Two way interaction	1	485.5	485.55	65.2205	7.664e–07
Pure quadratic response	3	3991.4	1330.46	178.7122	5.844e–12
Residuals	15	111.7	7.44	–	–
Lack of fit	7	71.6	10.23	2.0444	0.1687
Pure error	8	40.0	5.01	–	–

Note: Multiple R2: 0.987, Adjusted R2: 0.981, F–statistic: 163.2 on 7 and 15 DF, p-value: 5.285e–13

In addition to R^2, variance was used to measure the lack of fit between the model and the experimental data which is a good criterion for examining the fitness of the model; this is the sum of the squares of the difference between the response variable and the fitted values predicted by the model. Table 3 shows that there is no significance between observed and model data (p-value of lack of fit > 0.05), all models indicate a good model prediction for CPF removal. A very high F-value (F-statistic = 163.2, much greater than unity) and a very low probability value (p-value = 5.3×10^{-13}) indicate that the models obtained was highly significant.

3.2. Effect of CPF concentration in different time periods

The efficiency of CPF degradation was initially increased by increasing the CPF concentration and reaction time in TiO_2 photo catalysis (Fig. 3a). It means that the RPR designed has a good efficiency in degrading higher CPF concentration. This is attributed to the fact that for the degradation of a greater load of contaminants, more radical species ($\cdot OH$ and $\cdot O_2^-$) are required. Above 3 ppm of CPF, the degradation efficiency decreases since the arrangement of these reactive species on the surface of the catalyst remains constant as a result of the intensity of light, the amount of catalyst and the duration of the irradiation time. Therefore, there are not enough $\cdot OH$ radicals available for a matrix containing a higher concentration of contaminants and the rate of degradation and removal efficiency will be reduced [5,22].

3.3. Effect of TiO_2 dosage in different time periods

The effect of catalyst dose on the degradation efficiency of CPF was studied by varying the TiO_2 dose from 0 to 50 mg L^{-1}. It was observed that, the percentage of degradation was improved by increasing the amount of catalyst and the reaction time, until a decrease was observed when more than 40 mg L^{-1} of TiO_2 was used, as shown in Figs. 3b and 3c. By increasing the dose of TiO_2, the number of CPF molecules adsorbed on the surface of the catalyst was increased, which leads to an increase in the photo catalytic reaction rate. However, above a certain catalyst dose agglomeration (particle-particle interaction) of catalyst occurs; hence, it causes a decrease in the number of active sites on its free surface and, therefore, a drop in speed of the photo catalytic degradation. In consequence, the decrease in CPF degradation is attributed to a decrease in the surface area of the TiO_2 due to catalyst agglomeration. In addition, an increase of suspension turbidity by higher dose of photo catalyst causes a decrease in the penetration of visible photons, light scattering and screening effects; hence, the catalyst photo activation also decreases [5,23,24]. Fig. 3a, also indicates that by increasing the time, CPF concentration was decreased due to the creation of more reactive species. It is important to mention that

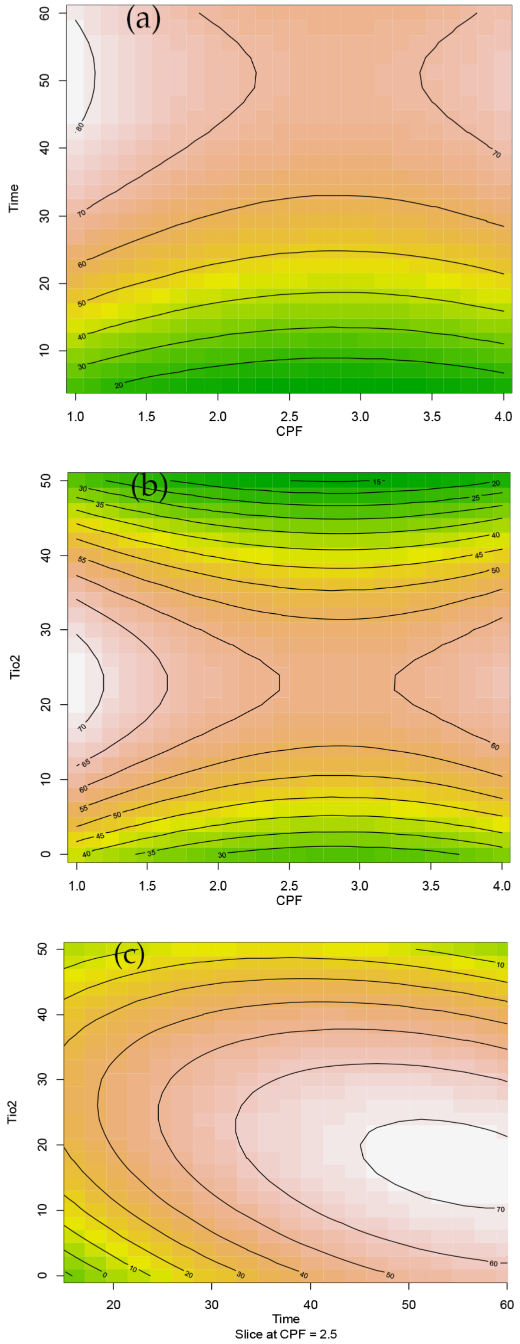

Fig. 3. Second-order response surface plot for CPF removal (%) using TiO_2 photocatalysis at pH 7. (CPF(mg L^{-1})(X_1), (Time (min) (X_2), TiO_2(mg L^{-1})(X_3)).

25.6 ± 0.25% CPF oxidation was achieved by visible photolysis (in the absence of TiO_2 catalyst).

3.4. Influence of ionic species CPF degradation

The effect of some interference on the optimal condition of degradation of CPF was investigated using TiO_2 photo catalysis, as shown in Table 4. This table shows the interference concentration of species such as nitrate, ammonium, nicotinic acid and phosphate under optimum conditions for CPF photo catalytic removal. Based on the removal results, the presence of these anions and cations did not interfere with the pesticide degradation. Under the optimal conditions for the runoff of real agriculture with Total Nitrogen (TN) = 1.8 ± 0.16 mg L^{-1} and Total Phosphorous (TP) = 0.34 ± 0.01 mg L^{-1}, the efficiency for the removal of CPF is 76.42 ± 0.98. Although, according to t-test, there is no significant difference between the experimental and actual condition in the removal of CPF. The efficiency of the real agriculture runoff is higher than the experimental one. This is because of a greater concentration of anions present in the experimental runoff than to the actual runoff.

Table 4
Interference parameter in optimum CPF removal by TiO_2 photo catalysis

Under visible irradiation		
Parameters	C_o	C_f
Ammonium + Nicotinic acid (mg L^{-1} as N)	10.00	6.10
Nitrate (mg L^{-1} as N)	10.00	12.00
Phosphate (mg L^{-1} as P)	1.50	1.70
Cl^- (mg L^{-1})	0.00	38.00
SO_4^{2-} (mg L^{-1})	0.00	0.25

C_o: initial concentration, C_f: final concentration

Oliveira et al. [25] examined the influence of ions such as chloride (Cl^-), nitrate (NO_3^-), phosphate (PO_4^{3-}), and bicarbonate (HCO_3^-) at final concentrations of the pesticide and observed no significant influence on CPF removal by UVC combined with H_2O_2. Although, some researchers reported negative effects of ions on the photo catalytic activity [26], others have reported no significant effect on it [27,28]. In addition, its effectiveness is related to the initial concentration of ion interference. It would be expected that increasing the concentration of ions would inhibit the rate of degradation of CPF, which is attributed to the competition of ions for active sites on the surface of TiO_2 [29].

3.5. Validation of the model

The optimal oxidation conditions (X_1 = (2.84 ppm (0.23)), X_2 = (55.15 min (0.82)) and X_3 = (17.07 mg L^{-1} (–0.32))) for the CPF removal were suggested by Analysis of Variance Table of R software. The theoretical CPF removal that was predicted under the above conditions was 71.09 ± 1.9%. This set of conditions was determined to be optimal by the RSM optimization approach and was also used to experimentally validate and predict the values of the responses using the model equation. The average removal efficiency for CPF was 69.3 ± 2.76 (n = 3), which corresponds well to the predicted value of the model equation, which confirmed that the response model was adequate for the optimization.

4. Conclusions

This study shows the rewarding utilization of the photo catalytic procedure for the treatment of CPF contamination in aqueous solutions containing nitrogen and phosphates, which was effectively improved by CCD. The TiO_2 photo ca talysis under visible irradiation shows a good performance in the degradation of CPF. According to the stationary point in original units, the optimum condition for 71.09 ± 1.9% of CPF removal was CPF (2.84 ppm (0.23)), time (55.15 min (0.82)) and dosage of TiO_2 (17.07 mg L^{-1} (–0.32)) by TiO_2 photo catalysis under visible light. Negligible interference of the ion species on CPF degradation was observed. This research provides the basis for further research on other range of variables (such as liquid depth of the reactor and visible light intensity).

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