PHOTOCATALYTIC DEGRADATION OF LINDANE AND DDT USING TiO_2/SOLAR LIGHT BY RESPONSE SURFACE METHODOLOGY

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ABSTRACT: *Heterogenous photocatalysis is a promising technology used to remove various organic compounds present in very low concentrations. Two of the most persistent organochlorine pesticides that are lindane and DDT was chosen to be eliminated using the photocatalysis process in a* $TiO_2/UV/O_2$ *system. In order to maximize the process efficiency, Response Surface Methodology (RSM) was used by considering three independent variables of pH (A),* TiO_2 *concentration (B), and initial concentration (C). The application of this treatment process was more favourable in the photodegradation of DDT compared to lindane which resulted 73-87% and 36-68% of removal respectively. Good agreement between the experimental and predicted values verified the adequacy and the quality of fit of the quadratic polynomial models. Results showed the optimum degradation can be achieved at* $A = 7$, $B = 1.5$ g/L, and C = 125 µg/L. *Besides that, the degradation of lindane and DDT confirms the feasible use of natural sunlight as the UV source for the photocatalysis process to take place. This process can be an advantageous technique to be applied since high energy consumption can be hindered, thus, ensuring an ecological environment in the water purification industries.*

Keywords: *organochlorine pesticides; photocatalysis; pH; UV source*

1. INTRODUCTION

The determination of organochlorine pesticides (OCPs) in the environment has received great attention not only because of their persistence and toxicity, but also because of their wide usage around the world [1]. Organochlorines are considered a major breakthrough because they are very persistent, that they degrade very slowly in the environment, thus working for very long periods of time [2]. Pesticides can enter the atmosphere through a number of ways, such as spray drift, volatilization from contaminated sites and by re-suspension of soil particles onto which they are adsorbed. Since different pesticides are used for crop protection, there is a great chance that non-point source of pollution comes from the leaching of pesticides from the agricultural fields [3].

World Health Organization (WHO) has listed 12 persistent organic compounds, two of which are a major concern in this study: lindane and DDT. According to [4], both compounds are urgently needed to be eliminated due to their toxicity. Thus, it is important to carry out an efficient treatment in order to get rid of these pesticides before remains in the environment [5]. In the recent years, photocatalytic water treatment has become a promising technology for eliminating organic compounds of low concentrations. Photocatalysis is based on the absorption of a photon from a UV source on a semiconductor surface, mostly used is titanium dioxide (TiO_2), to convert the organic compounds into harmless end products [6]. Many other semiconducting oxides have been tested as catalysts; however, TiO_2 in the anatase form performed the most interesting and efficient features such as high stability, good performance, low toxicity and low cost [7].

Most of the previous studies used UV lamps as the source of the UV light. However, in this study, natural sunlight was used in order to promote an environmentally friendly concept since UV source from the solar energy is unlimited and ecological, thus maintaining a sustainable surrounding condition. Performing a process at optimum conditions has many advantages such as low consumption of energy and higher efficiency of the response outputs. Therefore, response surface methodology (RSM) was used in this study to maximize the efficiency of the treatment method used. In the best knowledge of the authors, statistical analysis of photocatalytic degradation of lindane and DDT from water and wastewater have not been reported.

The specific objectives of this study are to evaluate the values of predicted and experimental output responses using efficiency test, and to investigate the effects of three independent variables: pH (A), TiO_2 concentration (B), initial concentration (C); on the removal efficiency of lindane and DDT via response surface methodology.

2. MATERIALS AND METHODS

2.1 Standard and Materials

Analytical standards of lindane (γ-HCH) and DDT were purchased from Sigma-Aldrich (Steinhelm, Germany) with a purity ranged of 99.8% and 98.7% respectively. Methanol and dichloromethane used as the organic solvent and GC eluent were of the analytical residue grade and obtained from Systerm. Titanium dioxide (Degussa P25) used is a known mixture of 70% anatase and 30% rutile, has a 99.5% purity with mean particle size of 30 nm and surface area of 50 m^2/g, was supplied from R&M Marketing, Essex, U.K. Other chemicals were used without further purification. Deionized and doubly distilled water was used throughout this study.

2.2 Photocatalytic Experimental Work

Stock solutions prepared by dissolving the powdered standard of lindane and DDT with the combination of methanol and dichloromethane were stored at 4°C. The mixture was prepared by diluting a certain amount of stock solutions with deionized water to a 15 L volume of the mixture. The initial concentration of each compound in the solution were the same, and tested from 50 to 200 µg/L. Required amount of TiO_2 was added to the aqueous solution. The suspension was then exposed to natural sunlight using Compound Parabolic Collecting Reactor (CPCR). The solution was sampled after 30 minutes of irradiation time and delivered to the laboratory for the analytical testing purposes.

2.3 Extraction Step and Preparation of Standard Solutions

The concentrations of the two targeted compounds were obtained by using the liquid-liquid extraction method: 100 mL of the sample was transferred into a conical flask and mixed with 100 mL of dichloromethane. The mixtures were shaken in a shaking incubator at room temperature for two hours with 120 rpm of shaking speed. After 30 minutes, the two layers were formed. The mixtures were transferred into a separating funnel. From the separating funnel, the lower layer that formed the organic layer was collected and evaporated to dry. After being dried, the extract was mixed with 1 mL of dichloromethane and ready to be analysed by GC-MS.

Standard solutions of lindane and DDT were prepared by diluting the stock solutions with dichloromethane at concentration of 200000, 20000, 2000, 200, and 20 µg/L.

2.4 GC-MS Analysis

The quantification of lindane and DDT was conducted using an Agilent 6890N Series GC System coupled with Agilent 5973 Inert Mass Selective Detector. In order to quantify the concentration of lindane and DDT, the efficiency test was carried out to determine the effectiveness of the photocatalysis treatment process in degrading lindane and DDT. The degradation percentage was defined as in Eq. 1 below:

$$\text{Degradation }\% = \frac{C_o - C_e}{C_o} \text{ x } 100 \qquad (1)$$

Where C_o is the initial concentration and C_e is the final concentration of the compound.

3. RESULTS AND DISCUSSION

In order to describe the effects of the independent variables on the degradation percentage of lindane and DDT, a standard response surface method called central composite design (CCD) was employed. The experimental ranges and levels of the independent variables used in this study were given in Table 1. The independent variables were varied over three levels (-1, 0, and +1), and the range was all determined from the previous studies [4, 9].

The experimental design, also the obtained output responses of experimental and predicted results were presented in Table 2. The experimental output responses of lindane and DDT were calculated based on the efficiency test using Eq. 1. From the results shown in the table, it was observed that higher degradation removal was obtained for DDT (73-87%) compared to lindane (36-68%). Nevertheless, there was not much difference in the removal percentage of DDT throughout the selected range of experimental variables. The responses and corresponding parameters were analyzed using analysis of variance (ANOVA) to further estimate the significance of the variables and models involved in this study.

Table 1: Experimental ranges and levels of the independent variables (α=1)

Variables	Coded values		
	-1	0	+1
pH, A	5	7	9
TiO_2 Concentration, B (g/L)	1	1.5	2
Initial Concentration, C (µg/L)	100	125	150

Table 2: Experimental design, experimental and predicted degradation values

Run No.	A	B (g/L)	C (µg/L)	Lindane (%) Experimental	Lindane (%) Predicted	DDT (%) Experimental	DDT (%) Predicted
1	5	1	100	42	45	76	76
2	9	1	100	42	42	83	84
3	5	2	100	52	50	75	75
4	9	2	100	42	45	87	86
5	5	1	150	40	37	70	70
6	9	1	150	36	37	76	75
7	5	2	150	40	40	76	75
8	9	2	150	42	38	83	83
9	5	1.5	125	57	60	79	80
10	9	1.5	125	57	57	87	88
11	7	1	125	52	51	75	75
12	7	2	125	50	54	75	78
13	7	1.5	100	70	67	80	80
14	7	1.5	150	53	59	73	75
15	7	1.5	125	68	66	81	80
16	7	1.5	125	66	66	81	80
17	7	1.5	125	68	66	81	80
18	7	1.5	125	67	66	80	80
19	7	1.5	125	67	66	81	80
20	7	1.5	125	68	66	80	80

While analyzing the ANOVA results of lindane and DDT, evaluation of the *p*-value parameter obtained for interaction terms were greater than 0.05. Thus, interaction terms were removed from the initial models. The final equations generated in terms of coded factors for both models are as follows:

$$Y\ (\text{lindane}) = 66.29 - 1.20\,A + 1.40\,B - 3.70\,C - 7.73\,A^2 - 13.73\,B^2 - 3.23\,C^2 \quad (2)$$

$$Y\ (\text{DDT}) = 79.93 + 4.00\,A + 1.60\,B - 2.30\,C + 4.18\,A^2 - 3.82\,B^2 - 2.32\,C^2 + 1.25\,BC \quad (3)$$

A positive sign in front of the terms indicates a synergistic effect, whereas a negative sign indicates an antagonistic effect. Equation (2) shows that TiO_2 concentration (B) has apositive effect on the degradation removal of lindane compared to the other two factors. On the other hand, equation (3) shows that pH has the most significant positive effect on the degradation efficiency of DDT, followed by TiO_2 concentration. Tables 3 and 4 below provide ANOVA results for the modified quadratic model for the removal of lindane.and DDT respectively.

The statistical significance was checked by the F-value of the model. For lindane, the F-value of 37.50 implies that the model is significant for the degradation efficiency. So as for DDT, an F-value of 17.21 shows that the model is significant to be used for DDT degradation. Values of *p*-value less than 0.05 indicate that the model terms are significant. As can be seen in Tables 3 and 4, the model terms included for DDT are rather significant than the model terms included for lindane. In addition to the regression coefficient, residual value shows the difference between the experimental and predicted response values. The standard deviation obtained for lindane is higher than DDT. It is noteworthy that the smaller the standard deviation, the better the model is because it gives predicted values that are closer to the actual values for the response. The coefficient of variance (C.V.) of lindane and DDT are 6.20 and 2.12 respectively. The CV value must be lesser than 10, otherwise the proposed model cannot be considered reproducible [10]. The quality of the fit of polynomial model was evaluated by the coefficient of determination R^2 and adjusted R^2. It is known that R^2 increases in accordance to the number of additional terms to the model, whereas the adjusted R^2 does not. Thus, the adjusted R^2 is often smaller than R^2 ($0.92 < 0.95$ for lindane; $0.86 < 0.91$ for DDT). Figure 1 shows the predicted and actual degradation percentage of both lindane and DDT.

Table 3: ANOVA results for the removal of lindane

Source	Sum of Squares	Degree of Freedom	Mean Square	F-value	*p*-value	
Model	2515.60	6	419.27	37.50	< 0.0001	significant
A	14.40	1	14.40	1.29	0.2769	
B	19.60	1	19.60	1.75	0.2083	
C	136.90	1	136.90	12.24	0.0039	
A^2	164.20	1	164.20	14.69	0.0021	
B^2	518.20	1	518.20	46.35	< 0.0001	
C^2	28.64	1	28.64	2.56	0.1335	
Residual	145.35	13	11.18			
Std. Dev.	3.34	R-Squared		0.95		
C.V.	6.20	Adj R-Squared		0.92		

Table 4: ANOVA results for the removal of DDT

Source	Sum of Squares	Degree of Freedom	Mean Square	F-value	*p*-value	
Model	337.34	7	48.19	17.21	< 0.0001	significant
A	160.00	1	160.00	57.13	< 0.0001	
B	25.60	1	25.60	9.14	0.0106	
C	52.90	1	52.90	18.89	0.0010	
A^2	48.09	1	48.09	17.17	0.0014	
B^2	40.09	1	40.09	14.31	0.0026	
C^2	14.78	1	14.78	5.28	0.0404	
BC	12.50	1	12.50	4.46	0.0563	
Residual	33.61	12	2.80			
Std. Dev.	1.67	R-Squared		0.91		
C.V.	2.12	Adj R-Squared		0.86		

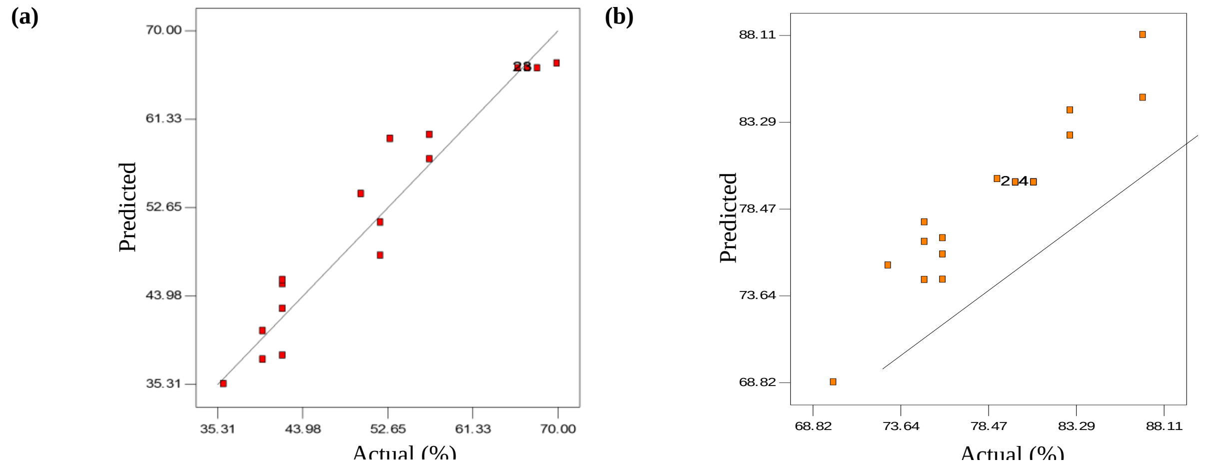

Figure 1: The actual and predicted degradation percent of (a) lindane (b) DDT

In Figure 2, the effects of pH and TiO$_2$ concentration on the degradation of lindane are shown, whereas the initial concentration of lindane was equal 125 µg/L. In this study, it can be seen that pH 7 exhibited the highest photodegradation removal of lindane. Variation of pH changes the surface charge of TiO$_2$ and also shifts the potentials of photocatalytic reactions. Literature reveals that TiO$_2$ has a point of zero charge (PZC) at pH 6.3, which means TiO$_2$ surface remains positively-charged at pH < 6.3 and negatively-charged at pH > 6.3 [11-12]. Akpan and Hameed [13] reported that the adsorption of the pollutant is known to be maximum near the PZC of the catalyst, because at low pH, the positive holes are the major oxidation species, while at neutral or high pH levels, hydroxyl radicals are considered as predominant species. In the mechanism of photocatalysis, it is a fundamental knowledge to know the process that triggers the degradation of the contaminant molecules is the production of hydroxyl radicals.

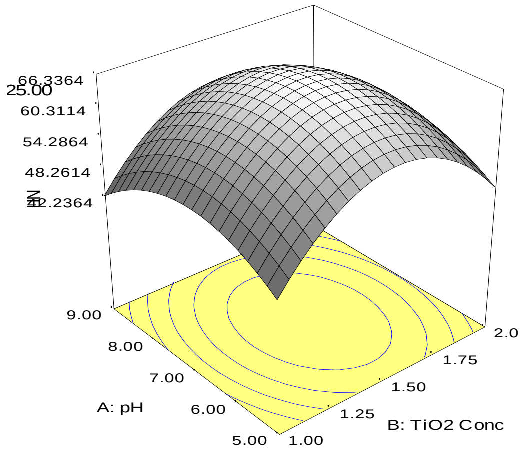

Figure 2: Response surface plot of the degradation percentage of lindane; with C = 125 µg/L

On the other hand, the increment of TiO$_2$ loading shows higher percentage removal of lindane, until it reached the optimum amount of 1.5 g/L. Further increment in the dosage of TiO$_2$ then contributed to a reduction in the degradation percentage of lindane. This finding could be attributed to the availability of the active sites on the TiO$_2$ surface and the penetration of the solar light into the suspension. When the availability of the active sites is more than the light penetration itself, this would create a screening effect and opacity of the suspension [4, 14].

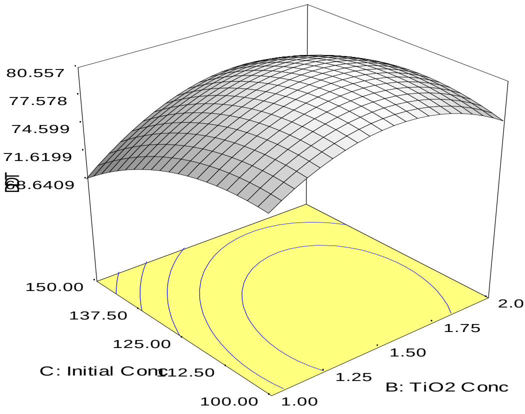

Figure 3: Response surface plot of the degradation percentage of DDT; with A = 7

In Figure 3, the effects of TiO$_2$ concentration and initial concentration on the degradation of DDT are shown, whereas the pH of the aqueous solution was equal to 7. The effect of TiO$_2$ concentration towards the photocatalytic activity of DDT is the same as for lindane. Addition of TiO$_2$ concentration also increases the removal of DDT until its optimum point of 1.5 g/L, and further increment resulted in a lower degradation removal. The initial concentration of DDT was varied from 100 to 150 µg/L. From the graph below, it was observed that 125 µg/L of DDT initial concentration has the highest degradation rate. This result is in agreement to [15], which concluded that at higher initial amount of DDT, the active sites of the TiO_2 surface were covered with DDT molecules and thus, decreasing the path length of photons entering the solution.

4. CONCLUSION

In this study, the photocatalytic degradation of lindane and DDT in TiO_2/UV system was analyzed by using RSM. CCD was applied by considering three independent variables of pH (A), TiO_2 concentration (B), and initial concentration (C). The application of this treatment process was more favorable in the photodegradation of DDT compared to lindane which resulted 73-87% and 36-68% of removal respectively. The models evaluated for lindane and DDT were significant based on the quadratic polynomial regression. ANOVA showed that the experimental and predicted values in this study were close to each other, owing to the low values of standard deviation of lindane and DDT that are 3.34 and 1.67, respectively. The quality of fit of the polynomial model was in accordance to the appropriate coefficients of adjusted R^2 is smaller than R^2 ($0.92 < 0.95$ for lindane; $0.86 < 0.91$ for DDT). Also, the optimum values of A, B, and C for both lindane and DDT models were 7, 1.5 g/L, and 125 µg/L, respectively. According to these results, photocatalytic process can be an appropriate treatment method for maximizing the removal efficiency of organic contaminants at low concentrations. Also, the use of natural sunlight was suitable to be employed as lindane and DDT happened to be degraded throughout this process. Heterogenous photocatalysis can be an advantageous technique for purifying water and wastewater containing organic contaminants, especially in remote arid sunny places, where water supply will be a crucial problem in the future. Furthermore, the use of unlimited natural sunlight as the UV source can hinder the high consumption of energy, thus maintaining a sustainable environment in the water treatment industries.

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