

Optimization of GAC supported TiO₂ photocatalytic process for competent carbofuran removal from an aqueous system

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The present study employed central composite design (CCD) and response surface methodology (RSM) to evaluate the carbofuran removal by photo catalytic process. The carbofuran removal process was carried out in a batch reactor with granular activated carbon (GAC) supported TiO₂ (GAC-TiO₂) as the photo catalyst. The influence of operating parameters such as initial carbofuran concentration, TiO₂ concentration and pH was modelled using CCD and RSM with 11 experimental runs. In the experimental runs, the carbofuran concentration was carried from 1 to 250 mg L⁻¹, TiO₂ concentration was ranged from 5 to 75 mg L⁻¹ and pH was varied from 3-11. The experimental outcomes from CCD revealed an increased carbofuran removal with increase in pH. Complete removal of carbofuran was observed within 240 min in all the runs except in those with higher carbofuran concentration (i.e., 250 mg L⁻¹) and lower pH (i.e., 3). Furthermore, Polynomial equations were developed to predict the carbofuran removal under different operating conditions. The result indicated that the carbofuran concentration and pH as well as the interaction term of TiO₂ concentration and pH had significant effect on the removal process. Good correlation between observed and predicted values indicated that the developed model can be used to predict the carbofuran removal under different operating conditions within the range that is analysed in this particular study. The optimum conditions for carbofuran removal were observed for a carbofuran concentration of 50 mg L⁻¹, TiO₂ concentration of 5 mg L⁻¹ and pH 7.9. These observations revealed that the carbofuran removal was probably due to the adsorption of carbofuran on the GAC surface and subsequent accelerated degradation of carbofuran on the GAC/GAC-TiO₂ surface. Therefore, the adsorbent medium and the adsorbent supported catalyst could be effectively used for efficient treatment of carbofuran contaminated water in a batch-mode photocatalysis system.

Keywords: Carbofuran, GAC supported TiO₂ catalyst, Central composite design, adsorption photocatalysis.

Introduction

The presence of pesticides and phenolic compounds in wastewater has become the major concerns over public health due to their higher toxicity effects and persistent in nature^{1,2}. The wide usage of pesticides in agriculture practice has lead to the increase in intense development of the variety of new chemicals and enhanced distribution of agrochemicals in the environment³. Carbofuran (2,3-dihydro-2,2-dimethylbenzofuran-7-yl methylcarbamate) is a broad spectrum carbamate pesticide and nematicide, is included in the general group of carbamate derivative pesticides. It is widely used to control many soil-borne insects and nematodes present in several fruit and vegetable crops. Recently, the employment of carbofuran has become the major concern not only because of its

heavy usage but also due to its soaring oral toxicity effect^{4,5}. Therefore, a potential technique for the degradation of carbofuran is needed. Advanced oxidation processes (AOPs), like H₂O₂/UV, O₃/UV and H₂O₂/O₃/UV, heterogeneous photocatalysis, homogeneous photo-Fenton, etc., have been effectively tested for the elimination of pesticides⁶. In the present study, the adsorptional photocatalytic degradation (APD) and granular activated carbon supported TiO₂ (GAC-TiO₂) catalyst was subjected to carbofuran removed in a batch mode operation. The influence of various operating variables like initial carbofuran concentration, TiO₂ concentration and pH on the degradation of carbofuran was studied using Central composite design (CCD) method. Response surface methodology (RSM) was chosen to evaluate the effects of photocatalysis of carbofuran and to develop the polynomial equations in terms of carbofuran removals at different reaction times. Moreover, the objective of this study was extended to

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explore the favorable carbofuran concentration, TiO_2 concentration and pH using the experimental design, and to investigate the adsorptional photocatalytic degradation (APD) of carbofuran contaminated wastewater in a batch mode photocatalytic system using granular activated carbon supported TiO_2 (GAC- TiO_2) catalyst.

Materials and Methods

Chemicals and reagents

Carbofuran (Sigma-Aldrich, India) was used as received (HPLC grade >98% purity). 99.9% pure metal basis Titanium tetra isopropoxide, 37% hydrochloric acid (HCl, reagent grade), $\geq 99\%$ pure absolute ethanol and the granular activated carbon (GAC) with a particle size fraction between 0.6 mm and 2.38 mm was supplied by Southern Carbon and Chemicals, India.

Preparation of GAC- TiO_2 catalyst

The GAC- TiO_2 catalyst was synthesized using a wet chemical process⁷. TiO_2 sol gel solution was prepared using 5 mL of titanium isopropoxide mixed with 50 mL of absolute ethanol and 1 mL HCl (37%), followed by the addition of 250 mL double distilled water and a desired stoichiometric amount of prewashed GAC. Then the preparation was homogenized using a magnetic stirrer for 30 min. The resulting mixture was kept in a water bath at 80°C for 2 h, cooled to room temperature, and washed with deionized water. Subsequently, the GAC- TiO_2 was dried at 100°C, and calcined at different temperature under nitrogen atmosphere. The prepared catalyst was analyzed using scanning electron microscopy with Electron dispersive spectroscopy (SEM-EDS) to verify the catalyst support on the GAC surface⁸.

Experimental set-up

The photocatalytic degradation experiments were performed in a specially designed cylindrical double walled batch reactor of 9 cm outer diameter and 34 cm height, incorporated with UV lamps, overhead stirrer and sample collection ports⁸. The working volume of the reactor was maintained as 1.9 L. The source for the UV irradiation was provided through 4 low pressure mercury UV lamp (254 nm, Hitech Ultraviolet, Mumbai) with maximum output of 14W and an intensity of 40 mWcm^{-2} for each lamp. The entire reactor system was covered with aluminium foil to prevent UV light leakage.

Experimental procedures

A stock solution containing 250 mg L^{-1} of carbofuran was prepared in double distilled water and diluted to the required concentrations. Exactly 1.9 L of diluted carbofuran solution corresponding to a predetermined initial concentration (based on experimental design) was added into reactor. The initial pH was adjusted to the designed value using 0.1N NaOH or 0.1N H_2SO_4 . Subsequently, a designed quantity of TiO_2 was added into the reactor and the UV irradiation was provided by 4 low pressure mercury UV lamp (254 nm, Hitech Ultraviolet, Mumbai) with maximum output of 14 W (intensity of each lamp $\sim 40 \text{ mWcm}^{-2}$). During the experimental period, the contents were mixed continuously using electronic overhead stirrer at the rate of 200 to 300 rpm thoroughly. At regular intervals, 8 mL of sample was withdrawn from the reactor and filtered through a 0.25 μm filter. Finally, the samples were analyzed for carbofuran concentration.

Analytical Techniques

The collected samples from the reactor were analyzed for carbofuran concentration in a high performance liquid chromatography (HPLC) (Shimadzu, Japan) equipped with Photo Diode Array (PDA) UV detector and a C-18 column (250 mm x 4.6 mm ID). Exactly, 20 μL of the sample was injected manually and analyzed at 280 nm. The mobile phase was composed of methanol, water and Acetonitrile (20:20:60, v/v), and run in isocratic mode pumped at a flow rate of 1 mL min^{-1} . Under these separation conditions, the retention time of carbofuran was observed around 3.8 - 4 min. Throughout the study, the reaction pH and temperature were monitored continuously using calibrated pH and temperature meters (Hanna-3121, Germany). The surface properties of GAC- TiO_2 catalyst were observed using a Variable Pressure Field Emission Scanning Electron Microscope (FESEM, Hitachi SU6600) and the elemental properties of the catalyst was analysed by Energy Dispersive Spectroscopy (Horiba, EMAX, 137 eV).

Experimental design and data analysis

The photocatalytic carbofuran degradation experiments were designed as per central composite design (CCD) using MINITAB 16 statistical software. In the CCD, initial carbofuran concentration (X_1), TiO_2 concentration (X_2), initial pH of reaction mixture (X_3) were kept as independent variables and the degradation percentage of the carbofuran after 15 min and 240 min of irradiation was chosen as the response

Table 1—Coded levels and natural values of the independent variables

Experimental runs	Coded Value			Actual Value		
	X ₁	X ₂	X ₃	X ₁ (mg L ⁻¹)	X ₂ (mg L ⁻¹)	X ₃
1	0	0	0	125.5	40	7
2	+1	-1	-1	250.0	5	3
3	-1	-1	+1	1.0	5	11
4	0	0	0	125.5	40	7
5	0	0	0	125.5	40	7
6	-1	+1	-1	1.0	75	3
7	+1	-1	+1	250.0	5	11
8	-1	-1	-1	1.0	5	3
9	+1	+1	+1	250.0	75	11
10	-1	+1	+1	1.0	75	11
11	+1	+1	-1	250.0	75	3

factor, i.e. dependent variable. The coded values and natural values of the independent variables are presented in Table 1. Totally, 11 experiments were performed in the present study with three replications at the center point. A polynomial equation and its corresponding estimated coefficients were obtained from the experimental data using the software. The study was performed with a confidence level of 95%.

Results and Discussion

Characterization of GAC-TiO₂

The SEM/EDAX analysis was performed to analyze the distribution of TiO₂ on GAC as well as the surface morphology of the prepared catalyst. Fig. 1.a & b. shows the SEM of the TiO₂-coated granular activated carbon used in this study. Fig. 1.a indicates the TiO₂ particles adsorbed onto the activated carbon and distributed over the adsorbent surface. Moreover, the well developed pore structure is clearly visible in Fig. 1.b. On the other hand, the EDAX result confirms that the TiO₂ was adsorbed over the activated carbon surface (Fig 1.c) and the Fig. 1.d. shows the retention of TiO₂ on the activated carbon after the degradation process.

Photocatalytic Degradation of Carbofuran

Effect of initial pH of the reaction mixture

The solution pH is an important variable in the assessment of aqueous phase intercede photocatalytic reactions. The pH of the solution has major consequences adsorption and dissociation of the

Table 2—Carbofuran removal by photocatalytic process under different experimental conditions

Experimental runs	Actual Value			Carbofuran Removal (%) at various time	
	X ₁ (mg L ⁻¹)	X ₂ (mg L ⁻¹)	X ₃	15 min	240 min
1	125.5	40	7	37	100
2	250.0	5	3	4.1	77
3	1.0	5	11	76	100
4	125.5	40	7	36	100
5	125.5	40	7	37	100
6	1.0	75	3	67	100
7	250.0	5	11	32	100
8	1.0	5	3	37	100
9	250.0	75	11	25	100
10	1.0	75	11	100	100
11	250.0	75	3	8.5	74

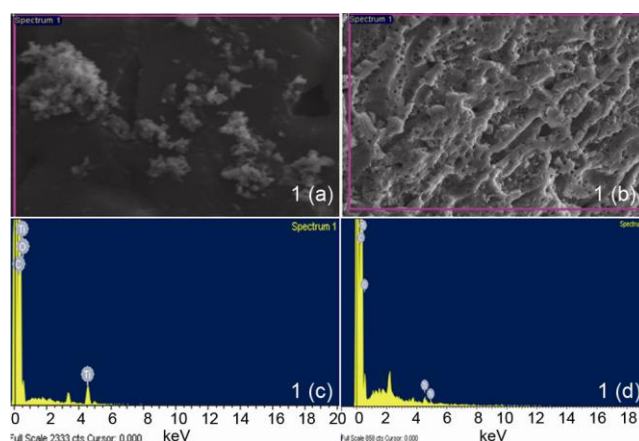


Fig. 1—1(a), 1(b) and 1(c), 1(d) shows the SEM and EDAX images of GAC-TiO₂ before and after photocatalytic experiments

substrate, catalyst surface charge, oxidation potential of the valence band and other physico-chemical properties of the system⁹. The effects of various experimental conditions are given in Table 2. In Runs 3, 6, 8 and 10, the complete carbofuran degradation was achieved with an initial pH of 3 and 11 at various catalyst dosages (5 and 75 mg L⁻¹) for lower carbofuran concentration, which indicates that the complete degradation is possible in the photocatalytic system at lower carbofuran concentrations. Runs 1, 4 and 5, indicates the centre point runs with the initial pH of 7, catalyst dosage of 40 mg L⁻¹ and intermediate concentration of carbofuran (i.e., 125.5 mg L⁻¹). In Run 2 and 11, at the fixed pH value of 3 and highest carbofuran concentration (i.e., 250 mg L⁻¹) the carbofuran removal are 77 % and 74% was observed with the TiO₂ concentration

of 5 and 75 mg L⁻¹ respectively. This indicates that acidic pH is not favourable for photocatalytic carbofuran removal for higher concentrations. At comparably low pH values, carbofuran might be protonated at the nitrogen or at the carbonyl oxygen of the carbamate group. Such protonation could stimulate revulsion between the substrate and catalyst¹⁰. In run 7 and 9, with higher concentration of carbofuran (i.e., 250 mg L⁻¹) and higher initial pH value (i.e., 11), complete carbofuran removal was observed with different catalyst dosage 5 and 75 mg L⁻¹. It can be seen that the carbofuran removal % is increased under the alkaline pH. Similar results were observed by Remya and Lin in the microwave-assisted carbofuran degradation study⁵. As a whole, the photocatalytic treatment can be successfully carried out under higher concentration of carbofuran 250 mg L⁻¹ and with lower TiO₂ concentration of 5 mg L⁻¹ for higher initial pH values.

Effect of Carbofuran Concentration

Experiments are conducted with carbofuran concentration varying from 1 to 250 mg L⁻¹ in order to analyze the degradation efficiency of the process and to understand the effect of lower and higher initial carbofuran concentration in photocatalytic process. Table 2 shows the reaction condition of three variables for 11 runs; The center point was repeated three times (Runs 1, 4 & 5) at an initial concentration of 125.5 mg L⁻¹ to check the repeatability of the experiments. The profiles of the carbofuran remaining with respect to time in various runs are shown in Fig. 2. Thereafter, applying the experimental data in Minitab 16, the response surface plot was prepared as shown in Fig. 3. From the experimental results almost complete removal and mineralization was observed in Run 10 (carbofuran of 1 mg L⁻¹, TiO₂ of 75 mg L⁻¹ and pH of 11) within 15 min of reaction, Run 3

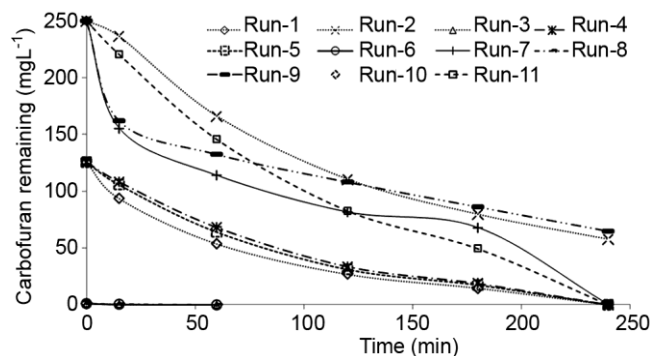


Fig. 2—Profile of carbofuran remaining in the aqueous phase during CCD Experiments

(carbofuran of 1 mg L⁻¹, TiO₂ of 5 mg L⁻¹ and pH of 11), Run 6 (carbofuran of 1 mg L⁻¹, TiO₂ of 75 mg L⁻¹ and pH of 3) and Run 8 (carbofuran of 1 mg L⁻¹, TiO₂ of 5 mg L⁻¹ and pH of 3) within 60 min of reaction. However, complete carbofuran removal was observed after 240 min for Run 7 (carbofuran of 250 mg L⁻¹, TiO₂ of 5 mg L⁻¹ and pH of 11), Run 9 (carbofuran of 250 mg L⁻¹, TiO₂ of 75 mg L⁻¹ and pH of 11) as well as the center point runs (i.e., Runs 1, 4 and 5 with carbofuran of 125.5 mg L⁻¹, TiO₂ of 40 mg L⁻¹ and pH of 7). This indicates that the photocatalytic process is useful for degrading the carbofuran at higher concentration under alkaline pH. On the other hand with higher concentration of carbofuran and lower reaction pH, the removal efficiency was 77% and 74% with a TiO₂ dosage of 5 mg L⁻¹ & 75 mg L⁻¹ respectively (Runs 2 & 11). This may be due to the protonation and decrease in the performance of the catalyst at lower pH. Similar results were observed in the degradation of carbofuran in a microwave assisted system⁵. On the other hand, the conversion of hydroxyl ion to hydroxyl radical might have resulted in improved carbofuran removal at higher pH. Moreover, the adsorption of carbofuran on GAC surface accelerates the photocatalyst degradation process in a GAC- TiO₂ system.

Optimization of photocatalytic carbofuran degradation conditions

The initial carbofuran concentration, catalyst concentration and initial pH of the solution are three of the most important parameters in the evaluation of photocatalytic degradation¹¹. In order

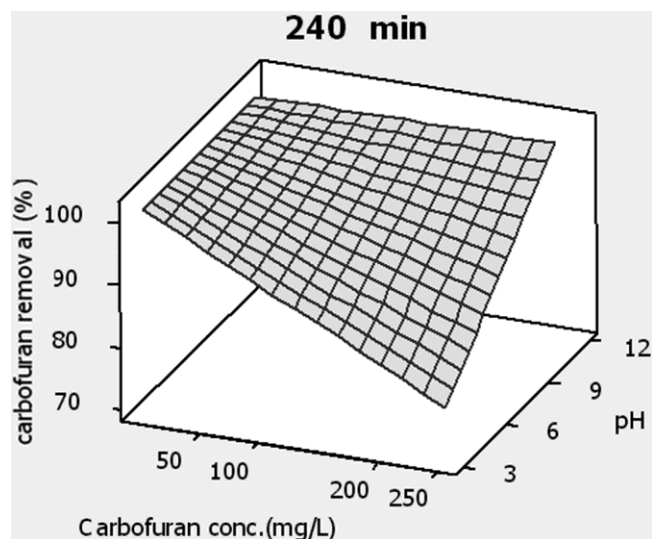


Fig. 3—Response Surface plot for carbofuran removal with initial concentration of carbofuran (mg L⁻¹) versus pH at 240 min

to evaluate the influence of these three parameters on the photocatalytic degradation of carbofuran, a factorial design was implemented using the Minitab 16 software. The factorial design is considered to be the most suitable design for obtaining beneficial and analytically significant models of a phenomenon by doing a minimum set of well-chosen experiments when the study is directed towards gaining knowledge of the influence of the variables on the process¹⁰⁻¹². The Table 2 shows the experimental conditions and the responses of each experiment, defined as the carbofuran removal efficiency after 240 min of treatment. It is understood that carbofuran concentration and pH has a significant effect on the affect the degradation efficiency of carbofuran in the photocatalytic system. A three factors CCD was carried out through carbofuran concentration from 1 to 250 mg L⁻¹, TiO₂ concentration from 5 to 75 mg L⁻¹ and pH ranging from 3 to 11 to investigate their influence on carbofuran degradation under the photo catalytic experiments. Carbofuran removal (%) is the dependent variable of photo catalytic process including with different reaction times are shown in Table 2. The influences of carbofuran concentration, TiO₂ concentration and pH were determined by carbofuran removals at 15 and 240 min. The center point was repeated three times (Runs 1, 4 and 5) to check the propagation of experimental error in the CCD results. The coefficients of the polynomial equation corresponding to each dependent variable were developed by factorial design using the MINITAB 16 statistical software. Carbofuran removal at 15 min (Y₁) and 240 min (Y₂) were expressed as a function of X₁, X₂ and X₃ as per Eqs.(1)–(2). The experimental results are in good concurrence with the values calculated by the polynomial equations. Based on Eqs.(1) and (2) the dependent variable are more influenced by carbofuran concentration and pH.

$$Y_{1, 15\text{min}} = 29.6022 - 0.146862 X_1 + 0.520470 X_2 + 4.56440 X_3 - 0.00154116 X_1 X_2 - 0.00189687 X_1 X_3 - 0.0225280 X_2 X_3 + 0.000027969 X_1 X_2 X_3 \dots (1)$$

$$Y_{2, 240\text{min}} = 101.913 - 0.147311 X_1 - 0.002514 X_2 - 0.01411 X_3 + 0.00251434 X_1 X_2 + 0.0141064 X_1 X_3 + 0.0003715 X_2 X_3 - 0.000371486 X_1 X_2 X_3 \dots (2)$$

The R² values for Eqs. (1) – (2) were 0.9862 and 0.9170, respectively. The R² of 0.9862 for Eq. (1) was considered relatively high, indicating that there was a good concurrence between the experimental and the

predicted in the in the removal of carbofuran from this model. The R² of 0.9170 for Eqs. (2) were considered high, indicating that there was an agreement between the experimental and the predicted values in the removal of carbofuran from this model. The adequacy of the models was further justified through analysis of variance (ANOVA). The ANOVA for the factorial design model of carbofuran removal (%) is Y₁, Y₂ are listed in Table 3¹³. The experimental results procured for each experiments were probabilistically analyzed by analysis of variance (ANOVA) using the MINITAB 16 described previously. The ANOVA results are shown in Table 3. The assurance level chosen in this experiment was 95%, which means that the implication level for analyzing the ANOVA table was 0.05. Finally, P values, significant probability values, were also estimated. If the P value is lesser than 0.05, this indicates the model terms are very significant and must be considered in the model¹⁴. From this Table 3, the variables of X₁ and X₃ and the interaction term X₂ X₃ are significant as their P values are as 0.001, 0.022 and 0.044 respectively. Therefore the response factors Y₁ and Y₂ representing the carbofuran removals are significantly affected by the factors X₁ and X₃ (i.e.,) carbofuran concentration & pH respectively and the effect of term X₂ (i.e.,) catalyst concentration was less significant in the photocatalytic degradation of carbofuran using GAC-TiO₂ system.

Estimation of Carbofuran Sorption on GAC-TiO₂

The outcome of the adsorption photocatalytic degradation of carbofuran using GAC-TiO₂ carried out under a 56 W UV power. 100% carbofuran removal was observed at 240 min in the 56 W GAC-TiO₂ photocatalytic systems. The reason for the stimulation in the removal rates in the GAC-TiO₂ system could be the superior photocatalytic efficiency of GAC-TiO₂ for carbofuran degradation owing to its large adsorption potential. The mechanism underlying TiO₂ degradation on GAC can be explained as follows: (i) during the synthesis of GAC-TiO₂, GAC scatters the deposited TiO₂ particles, preventing their agglomeration and thus improves their excitation under UV irradiation. (ii) during the degradation process, GAC could concentrate the target carbofuran molecules adjacent to the TiO₂ loaded sites and subsequently endorse the reaction between carbofuran and the hydroxyl radicals produced on the surface of the excited TiO₂ under UV irradiation and result in the improved carbofuran removal (%). Thus, the combined effect of adsorption-photocatalysis

Table 3–ANOVA results for carbofuran removal (%) at 15 min and 240 min

S.No	Time (min)	Source	Sum of squares	Degree of freedom	Mean square	F value	P value
1	15	X ₁	5371.66	1	5371.66	154.86	0.001
2		X ₂	247.53	1	247.53	7.14	0.076
3		X ₃	664.30	1	664.30	19.15	0.022
4		X ₁ X ₂	291.61	1	291.61	8.41	0.063
5		X ₁ X ₃	331.53	1	331.53	9.56	0.054
6		X ₂ X ₃	387.81	1	387.81	11.18	0.044
7		X ₁ X ₂ X ₃	148.78	1	148.78	4.29	0.130
8	240	X ₁	300.125	1	300.125	11.00	0.045
9		X ₂	1.125	1	1.125	0.04	0.852
10		X ₃	300.125	1	300.125	11.00	0.045
11		X ₁ X ₂	1.125	1	1.125	0.04	0.852
12		X ₁ X ₃	300.125	1	300.125	11.00	0.045
13		X ₂ X ₃	1.125	1	1.125	0.04	0.852
14		X ₁ X ₂ X ₃	1.125	1	1.125	0.04	0.852

phenomena of GAC-TiO₂ has enhanced the target carbofuran molecules. The 56 W GAC-TiO₂ system has showed higher carbofuran removals, i.e. 100% at 240 min of reaction. Overall, the GAC-TiO₂ photocatalyst proved highly effective and resulted in superior removal efficiencies compared to TiO₂ photocatalysis of carbofuran¹⁵.

Conclusions

The performance of adsorptional photocatalytic degradation of carbofuran was evaluated in a laboratory-scale batch mode photo catalytic reactor system through CCD experiments. The polynomial equations for carbofuran removal at different reaction times have been successfully developed. The influence of parameters like carbofuran concentration, TiO₂ concentration and pH were analyzed for the carbofuran removal process. Carbofuran concentration and initial pH have significant effects on removal of carbofuran. The increase in carbofuran concentration (1-125.5-250 mg L⁻¹), pH from 3-11 as well as TiO₂ dosages (5-40-75 mg L⁻¹) resulted in increased carbofuran removal efficiency. Based on the results the optimum conditions for carbofuran removal was observed as carbofuran concentration of 50 mg L⁻¹, TiO₂ concentration of 5 mg L⁻¹ and pH of 7.9. As a whole, the adsorption photocatalysis using GAC-TiO₂ is suitable for carbofuran contaminated water treatment owing to high carbofuran removal and superior catalyst separation from the effluent stream.

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