Photochemical degradation of toluene in gas-phase under UV/visible light graphene oxide-TiO₂ nanocomposite: influential operating factors, optimization, and modeling

Faramarz Azimi¹ · Ramin Nabizadeh^{1,2} · Mohammad Sadegh Hassanvand^{1,2} · Noushin Rastkari² · Shahrokh Nazmara¹ · Kazem Naddafi^{1,2}

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Abstract

The current study aimed to investigate the removal efficiency of toluene using synthesized titanium dioxide-graphene oxide composites under visible light and UV irradiation. The characterization of synthesized composites was examined by field emission scanning electron microscope equipped with energy dispersive, X-ray diffraction and fourier transforms infrared. In order to find the optimum of the main experimental parameters affecting the removal efficiency of toluene including the length of the reactor, initial concentration, and flow rates, central composite design together with response surface methodology with R software was used. The initial concentration of toluene in the inlet of the reactor as well as its concentration in the outlet was measured using gas chromatography with the flame ionization detector. Analysis of variance results for the quadratic model showed that the highly significant and simple linear regression was established as a predicting model. Multiple and adjusted R² were 0.965 and 0.974 for UV irradiation GO-TiO₂ model and 0.951 and 0.959 for visible light GO-TiO₂ model, respectively. As such, the differences less than 0.2 between multiple and adjusted R² in two models indicate that two examined models were fitted well. The highest removal efficiency of toluene using UV irradiation GO-TiO₂ and visible light GO-TiO₂ was obtained at optimum condition; length of reactor 40 cm, initial concentration of 0.1 ppm, and flow rate equal to 1 l min⁻¹, with 97.7 and 77.2%, respectively. The results indicated that the removal efficiency of toluene increased considerably with rising the length of the reactor, decreasing flow rates, and initial concentration.

Keywords Photocatalysis · Graphene oxide · Toluene · Response surface methodology · Optimization

Introduction

Ambient air pollutants have a profound effect on human health [1–3]. Among the gaseous air pollutants, benzene, toluene, ethylbenzene and meta-, para- and ortho-xylene (BTEX) is the most notable group of volatile organic compounds (VOCs) due to their abundance in ambient air and their function as the major ozone precursors in atmospheric

chemistry [4–6]. Based on the International Agency for Research on Cancer and the U.S. EPA, benzene is classified as a carcinogenic compound for humans (Group 1) [7–10]. Furthermore, toluene is a potent teratogenic compound for human and affects the reproductive and central nervous systems [11–13]. There are several main sources for these compounds as follows: vehicle exhausts, gasoline evaporation, solvent use, natural gas emissions, industrial activities and combustion for domestic heating, to name but a few [14–17]. It should be noted that approximately 50% of the total VOCs emissions are benzene and toluene [18]. Unfortunately, exposure to these compounds is an inseparable part of the human societies owing to the presence of them in ambient air and various indoor microenvironments [19–22]. According to above-mentioned concerns, over the past decades, the interest in VOCs, particularly BTEX, have intensified in order to identify the concentration of them in both

✉ Kazem Naddafi
knadafi@tums.ac.ir

¹ Department of Environmental Health Engineering, School of Public Health, Tehran University of Medical Sciences, Tehran, Iran

² Center for Air Pollution Research (CAPR), Institute for Environmental Research (IER), Tehran University of Medical Sciences, Tehran, Iran

indoor and ambient air and to investigate the methods to remove them [23, 24]. To date, several methods have been applied to remove VOCs, which each has its own advantages and drawbacks. Adsorption, absorption, incineration, ozonation and catalytic oxidation have been proven to abate the VOCs emissions to secure levels [25]. Catalytic oxidation taking advantages of high efficiency in low temperature would be a promising technology to convert VOCs to mineral and safe products like CO₂ and H₂O [26]. Among available applied methods to treat environmental pollution, photocatalysts have received great attention in comparison with other methods. In this process, generally TiO₂ particles with high-energy photons, as semiconductor materials, is used to leave electron holes h⁺ (Reaction 1) by raising electrons; e⁻; from the valence band to the conduction band. After that, the pairs of mobile charges; high-energy photons and their holes; can locate on the surface of the TiO₂ and other semiconductor particles and initiate a reduction-oxidation process [27]. Moreover, as illustrated in the Reactions 2 and 3, through reactions with the water adsorbed from the surrounding air (Reaction 2) and the oxygen (Reaction 3), reactive oxygen species, including HO[•] and O₂^{•-} are produced and act as strong oxidants which have a high potential to decompose or mineralize a wide range of compounds [28–31].

There were several disadvantages for application of TiO₂ as a catalyst as follows: firstly, low quantum efficiency an adsorption capacity; secondly, high recombination rates of electron-hole pairs, and last but not least, high band gap energy [32]. Consequently, in relation to improving the photodegrade ability of semiconductor oxide photocatalysts, for instance, TiO₂, the following efficient techniques have mainly used: doping with metal ions, coupling with a second semiconductor, and anchoring TiO₂ particles onto large-surface-area materials, including mesoporous materials, zeolites or carbon-based materials. As one of the most important derivatives of graphene, graphene oxide (GO) is an excellent carbon material with high specific surface area, good dispersion, and a surface rich in functional groups; thus, the material has attracted the interest of researchers from various fields. Go presents an abundance oxygen-containing functional groups (e.g., hydroxyl, epoxide, carbonyl and carboxyl) on its basal plane and edges; these groups allow the combination of GO with other modified nanomaterials and provide vast opportunities for constructing GO-based hybrid nanocomposites [33]. Additionally, a combination of TiO₂ and graphene oxide and/

or graphene; GO; is believed to have synergetic effects and consequently improve the photodegradation of organic compounds in both gaseous and aquatic media. In this case, adsorbent ability and efficient charge transfer rate are enhanced. Few studies published have investigated the efficacy of the synthesis of such graphene-based composites with TiO₂ photocatalyst regarding the removal of toxic vaporous aromatic pollutants [34]. For instance, the effective degradation of toxic vaporous aromatic pollutants using the GO-TiO₂ composites supported by Pyrex tubes has reported by Wan-Kuen Jo [32, 35]. It is difficult to determine the effect of design factors and how their efficiencies in a complex system. In order to deal with this problem, in such cases, the mainly full factorial design of the experiment is utilized to examine all possible combinations of various factors. As such, this experimental design method is often the only choice when researchers are interested in accurate results under various operating conditions and when the responses are expected to change in unforeseen ways. It is bearing in mind that this method mostly requires a large number of experimental trials that may be unnecessary in practice because the number of trials rises geometrically with the number of factors to be investigated. Moreover, the interpretation of a large measurement dataset is difficult, because particularly in engineering and practical applications, focus on trends in how different factors affect system responses can be sufficient. Therefore, response surface methodology (RSM) coupled with central composite design (CCD) is introduced as an efficient method for exploring associations between examined factors and system response [36]. In reality, RSM uses various mathematical and statistical techniques to lower the number and consequently cost of experiments [37].

Based on the above-mentioned reasons, the main objectives of the current study are **1)** optimization of toluene removal efficiency and **2)** investigation of effects of the primary factors affecting removal efficiency, including the length of reactor, initial concentration, and air flow rates.

Materials and methods

Synthesis and characterization of GO-TiO₂ composites

In order to synthesize graphite oxide from commercial graphite (<20 μm, Merck, Germany) was used the modified Hummers method as follows [38]: firstly, the mixture of commercial graphite (2 g), concentrated H₂SO₄ (120 mL, 98%, Merck, Germany) and H₃PO₄ (13 mL, Merck, Germany) were stirred at controlled temperature (50 °C) for 1 h; secondly, KMnO₄ (6 g, Merck, Germany) was added together with stirring, so that the temperature of the mixture was fixed at 50 °C; thirdly, the mixture was stirred at 50 °C for 24 h, after which 500 mL de-ionized water was slowly added. After that, 2 mL

of H_2O_2 (30%) was slowly added. In final, to form graphene oxide nanosheets, the prepared solution washed with HCl (5%, Merck, Germany) and deionized water in ultrasonic.

To synthesize GO-TiO₂ composite, we provided the TiO₂ nanoparticles from the commercial source (Degussa Co., Ltd., Germany), as shown in following link: (<https://www.nanoshel.com/product/degussa-tio2-p25>). at first stage, 0.5 g graphene oxide was added to a mixture of ethanol and water with a ratio of 1:1 under sonication condition. Moreover, 0.05 g TiO₂ nanopowder was added to the mixture of graphene oxide and solvent and placed under sonication condition at 25 °C for 2 h. The resulting mixture was transferred to an autoclave. In the next stage, the mixture was placed in furnaces at 150 °C for approximately 4 h. Then, the mixture was cooled at room temperature. GO-TiO₂ composite was separated with centrifuging at 6000 rpm and washed with ethanol and water. Finally, the prepared product was dried with an oven at 60 °C for 24 h.

Characterization

To characterize prepared GO-TiO₂ composites, a field emission scanning electron microscope (FE-SEM) equipped with energy dispersive was used (EDX; FE-SEM-TESCAN MIRA3). Additionally, X-ray diffraction (XRD) was used to study the surface morphology of the coatings and the elemental analysis of the deposited layer. XRD patterns were obtained over the diffraction angle range (2θ) of 4–80° using an XRD (Rigaku Ultima IV X-ray Diffractometer, Italy) diffractometer with Cu K α irradiation at a scan speed of 0.05 s^{−1},

Fourier transforms infrared (FTIR) spectroscopy was conducted on a Nicolet 380 FTIR spectrometer (Spectrum One, Perkin-Elmer®, USA) using KBr pellet technique.

Experimental setup for evaluating the toluene removal efficiency

The experimental setup for measuring the removal efficiency of toluene is given in Fig. 1. This experimental setup includes: (1) primary sampling valve in order to sampling, (2) gas inlet port, (3) multiple annular reactor, (4) Teflon connector, (5) secondary sampling valve, (6) UV and visible lamps, (7) adapter (8) Tedlar bag in order to storage, (9) SKC pump with flow rate in the range 1–5 l min^{−1}, (10) Lamp holder, and (11) Steel and pyrex tubes.

The photocatalytic performance of the GO-TiO₂ composites was evaluated using annular-type Pyrex tubes 5 cm in diameter, fitted and fixed in a stainless steel tube with an inside diameter of 6 cm with inner-walls that each had been coated with the photocatalyst. A UV-light lamp 43 cm was placed inside the annular-type Pyrex tube. Visible and UV irradiation were provided using the 15 W fluorescent lamps (Hitachi F15 T8/D, 700 lm) and UV lamps (LT15wT8/UVc, Narva, Germany) with a spectrum in the range of 400 to 720 nm and a peak intensity of 254 nm, respectively. In addition, the light intensities for UV irradiation, and Visible light were 2.4, 2.1 mW/cm², respectively.

In the current study, the effect of three factors including FR (1–5 l min^{−1}), LoR (20–40 cm), and IC of toluene (0.1–1 ppm, 99.7%; Merck, Germany) on VOCs removal was investigated

Fig. 1 The Photocatalyst reactor used in the toluene removal

(Table 1). As shown in Table 1, coded values for the range of each investigated factor were considered from +1 to −1. Here, zero code represents the center point for each examined factor. The following equation was used to conduct coding of variables:

$$X_i = \frac{X_0 - X_1}{\Delta X} \quad (4)$$

Where X_i (dimensionless) is a coded value for each factor, X_0 is the encoded value for the test factor at the center point and X_2 is the center point value of X_i , and ΔX is the step change value.

Before entering the synthetic air (toluene vapor) into a reactor, the inside wall of the reactor was coated with nano-sized GO-TiO₂ composites. To coat the walls of the reactor with GO-TiO₂ composites, 0.4 g of nano-sized composite was mixed in 2 mL of ethanol (>99.8%, Merck, Germany). The prepared mixture was applied for covering the different length of reactor (0.4 g of nano-sized composite per each 10 cm of reactor). As mentioned earlier Table 1, we used 0.8, 1.0, 1.2, 1.4 and 1.6 g of nano-sized composite for the length of 20, 24, 30, 36 and 40 cm of reactor, respectively. Then, the reactor was placed at 80 °C for 12 h. Moreover, the synthesized vapor was stored in a 3-L Tedlar bag (SKC Inc., USA). Furthermore, the bag was connected to the SKC air-sampling pump (SKC Model 224-PCXR8, USA) and the flow rate was adjusted. To ascertain the removal efficiency, the synthesized vapor was sampled before and after of reactor with a 1 mL syringe (gas-tight, Hamilton, Reno, NV, USA) and measured with GC-FID (Varian CP 3800, USA), the method detection limit for toluene analysis was 25 ppb.

Design of experiment using CCD

In the current study, to investigate the toluene removal, CCD was used. Also, RSM was applied to determine the interaction effects of each considered factors including FR (X1), LoR (X2), IC of toluene (X3) on the toluene removal efficiency (Y). Additionally, RSM was used to optimize three process variables in order to enhance the removal efficiency of toluene. Collectively, 22 runs were performed. The analysis of variance (ANOVA) test was utilized to evaluate the data

validation and to survey the significant level of suggested model coefficients. The data from the design were used to create a prediction model. The following equation is the empirical second-order polynomial model. All the design of experiments and statistical calculations were performed using the R software, RSM package [39–41]:

$$Y = \beta_0 + \sum_{j=1}^k \beta_j x_j + \sum_{j=1}^k \beta_{jj} x_j^2 + \sum_{i < j=2}^k \beta_{ij} x_i x_j + \varepsilon \quad (5)$$

Where, Y is the response (removal efficiency of toluene); 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 (in the present study, k was considered equal to 3) and ε is the error of the model.

Results and discussion

Structural properties of GO-TiO₂ composites

Figure 2 shows the SEM images of the GO and GO-TiO₂ composites. As shown in Fig. 2 (a, b), the SEM image of GO reveals various graphene sheets, reflecting its folding nature and a crumpled surface structure along with a typical layered structure. Figure 2 (c,d) illustrates the SEM image of GO-TiO₂ composite. As can be seen in Fig. 2 (c, d), the microstructure of sheet layers of GO-TiO₂ composite has been disappeared. The TiO₂ nanoparticles; small sphere-like particles; approximately uniformly distributed on the wrinkled surface of GO layers with an appropriate density. Indeed, GO in composite structure caused to increase dispersion, resulting in reduced-particle agglomeration. Figure 2 (e, f) provides the EDX spectrum of treated GO with TiO₂ nanoparticles. As can be noticed in Fig. 2 (e, f), the presence of C, O, and Ti in the sample of two composites reveal that the formation of GO/TiO₂ nanocomposite was successful.

Figure 3 compares the phase structures of as-synthesized GO-TiO₂ composites and GO described by XRD patterns. As provided in the Fig. 3, prepared composites have several diffraction peaks at $2\theta = 27.58^\circ, 36.30^\circ, 41.30^\circ, 54.82^\circ, 62.86^\circ$, and 65.66° where attributed to the planes of rutile TiO₂ (JCPDS Card No. 21–1276), whereas the peak at 37.86°

Table 1 Experimental ranges and independent variable levels used in CCD design

Original factors	Unit	Symbol	Coded levels				
			1	+0.59	0	−0.59	−1
Flow Rate (FR)	(l min ^{−1})	X1	5	4.18	3	1.82	1
Length of Reactor (LoR)	(cm)	X2	40	36	30	24	20
Initial Concentration of Toluene (IC)	(ppm)	X3	1	0.82	0.55	0.288	0.1

Fig. 2 FESEM image of GO (a, b) and GO-TiO₂ (c, d) composites, EDX of GO (e) and GO-TiO₂ composites (f)

Fig. 3 XRD patterns of TiO_2 - GO composites and GO

may be attributed to the (004) plane of anatase TiO_2 (JCPDS Card No. 21–1272). The weak characteristic peaks about 12° were determined within the XRD pattern of GO- TiO_2 composites, which is related to GO. In GO- TiO_2 composite, s, XRD patterns, sharp peak of GO disappeared.

The FT-IR spectra of GO and TiO_2 - GO composites are shown in Fig. 4. In all samples, a broad peak at around 3300 and 1600 cm^{-1} , representing the O–H stretching vibration (Fig. 4) [42]. A small peak at around 1720 and 1230 cm^{-1} observed for GO- TiO_2 composites was representative to the C–O stretching of carboxylic groups at the surface of GO [32]. The bands at 1410 and 1333 cm^{-1} attributed to carboxyl C–O and tertiary C–OH groups, respectively [43]. The strong absorption bands observed in the range of 400 – 1000 cm^{-1} in GO- TiO_2 composites corresponded to Ti–O–Ti banding. A broad peak at 730 cm^{-1} was observed for GO/Ti as-prepared TiO_2 –GO composites. This represents the combined effects of Ti–O–C and Ti–O–Ti bands in the GO- TiO_2 composites, confirming the chemical interaction between TiO_2 and functional groups of GO [40].

Model fitting and statistical analysis

Table 2 shows the experimental data utilizing in the toluene removal process using UV irradiation GO- TiO_2 and visible light GO- TiO_2 . Also, the predicted results produced by the corresponding model are shown in Table 2. Toluene removal efficiencies using UV irradiation GO- TiO_2 were between 42 and 82%, whereas for visible light GO- TiO_2 ranged from 36 to 73% (Table 2). Table 3 compares the results of the effect of each factor (X_1 , X_2 , and X_3 represent FR, LoR, and IC of toluene, respectively) on toluene removal efficiency using UV irradiation GO- TiO_2 and visible light GO- TiO_2 . A glance at Table 3 provided reveals that all factors at the first order model had a statistically significant effect on toluene removal efficiency using both UV irradiation GO- TiO_2 and visible light GO- TiO_2 . As highlighted in Table 3, amongst all examined variables at the first-order model, the LoR had the highest effect on the removal efficiency of toluene using both UV irradiation GO- TiO_2 and visible light GO- TiO_2 , with T-value and coefficient estimate 12.8285 and 12.68470, 15.5022 and

Fig. 4 FTIR spectra of GO and GO- TiO_2 composites

Table 2 CCD experimental design for toluene removal

Run order	Coded levels of variables			Block	Level of variables			Response toluene removal %	
	X1	X2	X3		FR ^a (l min ⁻¹)	LoR ^b (cm)	IC ^c (ppm)	UV Irradiation GO-TiO ₂ Experimental	Visible light GO-TiO ₂ Experimental
1	0	0	0	1	3.00	30	0.55	60	56
2	0.59	-0.59	-0.59	1	4.19	24	0.288	57	53
3	0.59	0.59	-0.59	1	4.19	36	0.288	69	63
4	-0.59	0.59	-0.59	1	1.81	36	0.288	78	68
5	0	0	0	1	3.00	30	0.55	57	55
6	-0.59	0.59	0.59	1	1.81	36	0.82	68	63
7	0.59	0.59	0.59	1	4.19	36	0.82	53	52
8	0	0	0	1	3.00	30	0.55	58	55
9	0	0	0	1	3.00	30	0.55	59	54
10	0.59	-0.59	0.59	1	4.19	24	0.82	42	36
11	-0.59	-0.59	0.59	1	1.81	24	0.82	48	45
12	0	0	0	1	3.00	30	0.55	57	52
13	0	0	0	1	3.00	30	0.55	61	55
14	-0.59	-0.59	-0.59	1	1.81	24	0.288	60	56
1	0	0	-1	2	3.00	30	0.1	82	73
2	0	0	0	2	3.00	30	0.55	60	56
3	-1	0	0	2	1.00	30	0.55	64	59
4	0	0	0	2	3.00	30	0.55	58	53
5	0	1	0	2	3.00	40	0.55	74	70
6	0	-1	0	2	3.00	20	0.55	49	42
7	1	0	0	2	5.00	30	0.55	48	44
8	0	0	1	2	3.00	30	1	51	50

^a Flow Rate, ^b Length of the reactor, ^c Initial Concentration

12.68987, respectively. Indeed, the removal efficiency of toluene increased with the increase of the LoR. Furthermore, as shown in Table 3, the results of this work indicated that the other investigated factors such as IC of toluene and flow rate had the inverse effect on the removal efficiency of toluene. In reality, the removal efficiency declined with the rising of IC of toluene and FR. Of these two factors, the IC of toluene with T-value and coefficient estimate -13.0790 and -12.86885 for UV irradiation GO-TiO₂ and -12.4274 and -10.12295 for

visible light GO-TiO₂ had the lowest negative effect on removal efficiency of toluene as compared with FR (Table 3). In the interaction model for the removal of toluene using irradiation GO-TiO₂, as shown in Table 3, only the interaction of FR and LoR was statistically significant.

Moreover, invisible lights GO-TiO₂ model for removal of toluene, the interaction of length of the reactor and initial concentration of toluene, and flow rate and initial concentration of toluene was statistically significant (Table 3). As

Table 3 Estimated regression coefficients for experimental toluene removal %

Model term	Coefficient estimate	Standard error coefficient	T-value	P value	Significant level
UV irradiation GO-TiO ₂					
(Intercept)	59.15202	0.67648	87.4414	< 2.2e-16	***
X1	-7.37449	0.98879	-7.4581	2.020e-06	***
X2	12.68470	0.98879	12.8285	1.727e-09	***
X3	-12.86885	0.98393	-13.0790	1.321e-09	***
X1:X2	-5.29624	2.17068	-2.4399	0.0275833	*
X1:X3	-3.15126	2.14672	-1.4679	0.167836	Non-significant
X2:X3	0.35014	2.14672	0.1631	0.873150	Non-significant
X1^2	-4.06798	1.56058	-2.6067	0.0198321	*
X2^2	1.47780	1.55706	0.9491	0.361295	Non-significant
X3^2	6.41656	1.55537	4.1254	0.0008987	**
Visible light GO-TiO ₂					
(Intercept)	54.63063	0.56003	97.5488	< 2.2e-16	***
X1	-6.55188	0.81859	-8.0039	2.224e-06	***
X2	12.68987	0.81859	15.5022	9.190e-10	***
X3	-10.12295	0.81457	-12.4274	1.372e-08	***
X1:X2	-1.41233	1.79704	-0.7859	0.4460036	Non-significant
X1:X3	-4.20168	1.78206	-2.3578	0.0347201	*
X2:X3	4.20168	1.78206	2.3578	0.0347201	*
X1^2	-4.17901	1.29195	-3.2346	0.0065180	**
X2^2	0.33125	1.34195	0.2468	0.8092042	Non-significant
X3^2	5.80329	1.28764	4.5069	0.0005898	***

*** < 0.001; ** < 0.01; * < 0.1

shown in Table 3, amongst quadratic of examined factors for removal of toluene in two models UV irradiation GO-TiO₂ and visible light GO-TiO₂, only the effect of length of the reactor was statistically non-significant, whereas the effect of two other factors on the removal of toluene was significant. Based on the aforementioned results, the quadratic of investigated factors for removal of toluene in two models UV irradiation GO-TiO₂ and visible light GO-TiO₂ was selected.

The analysis of variance (ANOVA) for the response surface quadratic model is presented in Table 4. A glance at Table 4 provided reveals that in the obtained model in the present work has a significant relationship between the examined variables and the removal efficiency of toluene as the response, because of the P- value less than 0.05 and high T- and F-value. Moreover, Multiple and adjusted R² were 0.965 and 0.974 for UV GO-TiO₂ model and 0.951 and 0.959 for visible light GO-TiO₂ model, respectively, since the difference between multiple R² and adjusted R² (0.951) was less than 0.2, the predicted model showed an excellent relationship between the independent variables and the response; removal efficiency of toluene (Table 4). As discussed earlier, the quadratic model was selected to examine the effect of each variable on toluene removal, because this model could properly foresee the effects of independent parameters on the toluene removal efficiency. Also, P value for non-significant lack of fit for UV irradiation GO-TiO₂ and visible light GO-TiO₂ in order to remove toluene were 0.075 and 0.145 (> 0.05), respectively. In addition, a very high F-statistic 70.27 and 62.77 for UV irradiation GO-TiO₂ and visible light GO-TiO₂ and a very low probability value 3.975e-10 and 3.876e-09 indicated that the

models were statistically significant and could appropriately estimate the toluene removal.

According to the results from obtained regression coefficients (Table 3), an experimental relationship between the response; removal efficiency of toluene; and independent examined variables was achieved and expressed by the following equation of quadratic regression model (Eq. (6) for UV irradiation GO-TiO₂ and Eq. (7) for visible light GO-TiO₂:

$$Y = 24.48 + 10.35X_1 + 2X_2 - 63.45X_3 - 0.26X_1X_2 - 1.01X_1^2 + 31.68X_3^2 \quad (6)$$

$$Y = 45.73 + 5.56X_1 + 0.75X_2 - 68X_3 - 4.66X_1X_3 + 0.93X_2X_3 - 1.01X_1^2 + 28.65X_3^2 \quad (7)$$

Effect of independent variables for removal toluene

Figure 5 compares the effect of each factor on the removal efficiency of toluene by UV irradiation GO-TiO₂ (a, b, c) and visible light GO-TiO₂ (d, e, f). As shown in the Fig. 5a and d, the removal efficiency of toluene using UV irradiation GO-TiO₂ (Fig. 5a) and visible light GO-TiO₂ (Fig. 5d) at IC 0.55 ppm increased from 40.3 and 31.2 to 80.4 and 69.7% with the rising length of the reactor and decreasing the FR. Indeed, the highest removal efficiency of toluene using UV irradiation GO-TiO₂ and visible light GO-TiO₂ was found in the LoR and the FR 40 cm and 1 l min⁻¹, respectively, whereas the lowest removal toluene was observed in 20 cm and

Table 4 ANOVA results for toluene removal

UV irradiation GO-TiO ₂ *					
Model formula in RSM (X1, X2, X3)	DF	Sum of square	Mean square	F-value	Pr > F***
First-order response (X1, X2, X3)	3	1848.46	616.15	130.4185	5.732e-11
Two way interaction (X1, X2, X3)	1	28.13	28.13	5.9531	0.027583
Pure quadratic response (X1, X2, X3)	2	115.32	57.66	12.2045	0.000714
Residuals	15	70.87	4.72		
Lack of fit	8	55.37	6.92	3.1255	0.075489
Pure error	7	15.50	2.21		
Visible light GO-TiO ₂ **					
Model formula in RSM (X1, X2, X3)	DF	Sum of square	Mean square	F-value	Pr > F
First-order response (X1, X2, X3)	3	1485.65	495.22	152.94	2.181e-10
Two way interaction (X1, X2, X3)	3	38	12.67	3.91	0.034208
Pure quadratic response (X1, X2, X3)	3	102.26	51.13	15.79	0.001516
Residuals	13	42.09	3.24		
Lack of fit	6	28.09	4.68	2.34	0.145205
Pure error	7	14	2		

* R² = 0.965, Adjusted R² = 0.951, F-statistic = 70.27 on 6 and 15 DF, p value = 3.975e-10

** R² = 0.9748, Adjusted R² = 0.9592, F-statistic = 62.77 on 8 and 13 DF, p value = 3.876e-09

***Values of "Pr > F" less than 0.05 indicate model terms are significant

Fig. 5 Contour plots for the effect of each factor on the toluene removal by UV irradiation GO-TiO₂ (a, b, c) and visible light GO-TiO₂ (d, e, f), LoR (cm) versus and FR l min⁻¹ (a and d), IC of toluene (ppm) versus the FR (b and e), IC of toluene versus LoR (c and f)

Table 5 Predicted and coded experimental values for the highest toluene removal

Coded levels of Variables			Level of Variables			Toluene removal %	
X1	X2	X3	FR ^a (l min ⁻¹)	LoR ^b (cm)	IC ^c (ppm)	UV irradiation GO-TiO ₂	Visible light -GO-TiO ₂
-1	1	-1	1	40	0.1	97.73	77.21

^a Flow Rate, ^b Length of the reactor, ^c Initial concentration

Fig. 6 Scatter plot of the removal efficiency of toluene using both UV irradiation GO-TiO₂ (a, R^2 : 0.95, Adjusted R^2 : 0.94) and Visible light GO-TiO₂ (b, R^2 : 0.91, Adjusted R^2 : 0.9) at experimental runs and predicted

5 l min⁻¹. With respect to the effect of the IC of toluene and the FR on the removal efficiency of toluene by UV irradiation GO-TiO₂ (Fig. 5b) and visible light GO-TiO₂ (Fig. 5e) at the LoR 30 cm, the results indicated that the removal efficiency of toluene increased considerably with decreasing FR and IC. Moreover, as can be noticed in Fig. 5b and e the removal efficiency of toluene by UV irradiation GO-TiO₂ and visible light GO-TiO₂ ranged from 41.3 to 81.7% and 35.4 to 68.7%, respectively. In reality, the highest removal efficiency of toluene by two models was found in the IC of toluene 0.1 ppm and FR 1 l min⁻¹. Addressing the effect of the interaction of the IC

of toluene and the LoR at the stable FR 3 l min⁻¹ on the removal efficiency of toluene at two models (Fig. 5c and f), the results confirmed that the toluene removal increased remarkably with decreasing the IC of toluene and rising the LoR. A glance at Fig. 5c and f provided reveals that the highest removal efficiency of toluene for UV irradiation GO-TiO₂ (91.1%) and visible light GO-TiO₂ (79.1%) was found at the IC of toluene 0.1 ppm and the LoR 40 cm. Furthermore, the lowest removal for two mentioned models (40.1 and 33.4%) was recorded at the IC of toluene 1 ppm and the LoR 20 cm. Observed high efficiency for the removal of

Table 6 Validation of the studied parameters and the results of the two models

Run order	Coded levels of Variables			Level of Variables			Response toluene removal %			
	X1	X2	X3	FR(l min ⁻¹)	LoR (cm)	IC of toluene (ppm)	UV Irradiation GO-TiO ₂		Visible light GO-TiO ₂	
							Experimental (%)	Predicted (%)	Experimental (%)	Predicted (%)
1	-1	1	0.33	1	40	0.7	75	76.86	72	69.76
2	-0.5	-1	0.18	2	20	0.63	38	44.4	37	42.18
3	0	-0.5	0.71	3	25	0.87	42	46.9	39	42.52
4	-1	0.5	0.04	1	35	0.57	69	70.88	62	63.19
5	-0.5	0	-0.40	2	30	0.37	64	67.99	58	60.99
6	1	0.5	-0.98	5	35	0.11	73	70.12	66	67.74
7	1	1	-0.51	5	40	0.32	61	63.35	59	63.27
8	0.5	0.5	0.51	4	35	0.78	51	54.56	47	52.99
9	-0.5	1	-0.07	2	40	0.52	68	65.38	68	63.57
10	1	-0.5	0.76	5	25	0.89	40	37.95	34	28.45

toluene can be attributed to a combination of greater numbers of active sites related to higher surface area [40], decreased the bulk mass transport of toluene due to declined FR, and higher the ratio of the aggregation of reactive species and active sites to pollutant molecules in the lower initial concentrations. In reality, high FRs decrease the toluene residence time in the reactor that leads to decline toluene transfer from the gas-phase to the surface of the GO-TiO₂ composites. This represents lower contact time between air pollutant molecules and reactive species including hydroxyl radicals and superoxide anion as the most common reactive species. As mentioned earlier, the removal efficiency of toluene for UV irradiation GO-TiO₂ is higher as compared with visible light GO-TiO₂, mainly because of higher light intensity as well as the higher generation of photons and consequently $e^- - h^+$ pairs. To sum up, higher residence time and light intensity, lower toluene concentration and shorter light source wavelength favor the removal efficiency of toluene and its mineralization to CO₂ [31, 32, 44–47].

Parameter optimization

To optimize the values of process parameters in the quadratic model in Eqs. 6 and 7, the excel solver was used to obtain the highest removal efficiency of toluene (Table 5). As showed in Table 5, the predicted optimum operating conditions were as follows: FR equal to 1 l min⁻¹, LoR equal to 40 cm, and IC of toluene equal to 0.1 ppm. In reality, in the mentioned condition, the highest removal efficiency of toluene in two studied model; UV irradiation GO-TiO₂ (97.73% removal) and visible light GO-TiO₂ (77.21% removal).

Validation of the studied models

To determine the validation of two investigated models; UV irradiation GO-TiO₂ and visible light GO-TiO₂; as well as in order to compare the removal efficiency of toluene obtained at experimental runs with predicted by model, ten runs were randomly examined and their results were compared by simple regression (Fig. 6 and Table 6). As shown in Fig. 6 and Table 6, a statistically significant correlation between the removal efficiency of toluene using both UV irradiation GO-TiO₂ and visible light -GO-TiO₂ at experimental runs and predicted by the model was found.

Conclusions

The findings revealed that the photocatalytic degradation of toluene by both models UV irradiation GO-TiO₂ and visible light GO-TiO₂ is feasible, in which increasing LoR and decreasing IC and FR resulted in enhanced removal efficiency of toluene. According to the optimum operational conditions, the

highest efficiency toluene removal using both UV irradiation GO-TiO₂ model and visible light GO-TiO₂ model was found at the following conditions: FR equal to 1 l min⁻¹, LoR equal to 40 cm, and IC of toluene equal to 0.1 ppm that were 97.73 and 77.21%, respectively and highest efficiency toluene removal were at condition FR equal to 5 l min⁻¹, LoR equal to 20 cm, and IC of toluene equal to 1 ppm, 33.8 and 18.5% respectively.

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Compliance with ethical standards

Conflict of interest All authors declare that they have no conflict of interest.

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