*Research Article*

# RSM-Based Optimization of the Parameters Affecting TiO$_2$-Mediated UV Photocatalysis of Vehicular Emissions in Enclosed Parking Garages

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In the preceding times, the number of enclosed parking garages has increased significantly in developing nations. The toxic emissions from vehicular exhausts are expected to drastically compromise the environmental conditions of the parking garages. Subsequently, exposure of humans to these accumulated pollutants is also expected to degrade their health. Therefore, in the present investigation, efforts were made to estimate the applicability of TiO$_2$-mediated UV photocatalysis in degrading the concentration of vehicular emissions, viz., NO$_x$ and SO$_2$, in the enclosed parking garages (EPGs). In this regard, an artificial EPGs' environment was created and experiments were designed using the Box-Behnken design in combination with response surface methodology. The process parameters chosen for maximizing the degradation of the pollutants were a concentration of TiO$_2$ emulsion (20 to 120 ml/m$^2$), UV irradiance (1 to 5 mW/cm$^2$), and relative humidity (10 to 50%). Optimization of the laboratory experiments revealed that at optimal conditions of the process parameters, i.e., a concentration of TiO$_2$emulsion = 77.50 ml/m$^2$, intensity of UV irradiance = 3 mW/cm$^2$, and relative humidity = 43.2%, maximum degradation of the NO$_x$ and SO$_2$, i.e., 61.24% and 55.05%, respectively, was achieved. Further, it was revealed that relative humidity may prove to be the limiting factor while using the TiO$_2$-mediated UV photocatalysis in humid areas. Findings of this study may prove beneficial in urban planning as it may assist scientific auditory and local authorities in identifying the applicability of TiO$_2$-based photocatalysis in mitigating the impacts of vehicular emissions.

# 1. Introduction

Anthropogenic activities involving the combustion of fossil fuels contribute significantly to the air pollution content of the world [1]. Among the various emission sources, industrial emissions and vehicular emissions are the most prominent ones [2]. With the recent advancements in technology, the obsolescence rate of the vehicles has tremendously increased owing to lower prices of the vehicular technology in the developing countries. In this way, a substantial increase in the vehicular density of the developing countries such as India, Kuwait, and Prishtina has also been reported [3–6]. Further, the number of vehicles owned by a single citizen of these nations has also increased. The sudden surge in the number of vehicles on the roads of these nations has put forward an issue of management of vehicular density among the urban planners. Also, due to the lack of parking space, in urban residential areas, the vehicles are generally parked on the road sides, leading to traffic congestion and accidents. To overcome these issues, in recent years, the citizens of these nations have initiated adopting the provisions of the enclosed parking garages (EPGs) in their residencies [7].

In order to cut the cost involved in construction and operation, these EPGs are generally designed with natural ventilation. However, studies have reported that the vehicular emissions generated in the EPGs are not efficiently dispersed using natural ventilation [8, 9]. In this way, several toxic pollutants, viz., PM, $NO_x$, $SO_2$, CO, $CO_2$, poly-aromatic hydrocarbons (PAHs), and volatile organic carbons (VOCs), are accumulated inside the EPGs [9–12]. These pollutants were reported to have several deteriorating health impacts on human beings [13, 14]. Therefore, the working staff in the EPGs, such as security guards and cleaner, is exposed to these pollutants and consequent health impacts can be speculated. Thus, these EPGs may act as hot spots of the air pollutants which may compromise the human health [15–17]. Therefore, it is imperative to identify an innovative and cost-effective approach to reduce the vehicular pollution inside the EPGs [18].

With a motive to reduce vehicular pollution, in ambient air, studies have identified the usage of photocatalytic material, i.e., $TiO_2$, on the asphalt roads, as significantly efficient [19, 20]. It has been reported that when applied on the surface of the roads, $TiO_2$ can significantly reduce the concentration of several pollutants, viz., organic carbon, $NO_x$, $SO_2$, and volatile organic carbons (VOCs) [21–23]. To reduce the ambient air pollution, many countries, around the world have also adopted the usage of $TiO_2$ in the construction of pavements, buildings, windows, etcetera [20, 24, 25]. However, studies proving the applicability of photocatalysis in reducing the vehicular pollution, inside the EPGs, are scanty. Moreover, there is still a research gap for identifying the utility of response surface methodology (RSM) in efficiently optimizing the $TiO_2$-mediated UV photocatalytic treatment of pollutants inside the EPGs.

Therefore, in this study, efforts were made to conduct a laboratory experiment and understand the applicability of $TiO_2$-mediated photocatalysis in reducing the concentration of $NO_x$ and $SO_2$. Impacts of concentration of $TiO_2$ emulsion, UV irradiance, and relative humidity (RH) were estimated in a closed reaction chamber. Further, optimal conditions, for achieving the maximum reduction of $NO_x$ and $SO_2$, were estimated using Box-Behnken design (BBD) in combination with RSM. The findings, of this study, may prove beneficial in the scientific quest for finding an appropriate solution for air pollution-related problems arising from uncontrolled vehicular emissions in the EPGs.

# 2. Materials and Methods

*2.1. Site Configuration.* The brief sketch of the site, where all the experiments were conducted is shown in Figure 1.

As shown in Figure 1, the experiments were conducted inside cemented and empty rooms which had the volume of $812 \, m^3$. These rooms were termed as a reaction chamber in this manuscript. The inner side of the walls and the roof were sprayed with $TiO_2$ emulsion which was prepared by mixing the required amount of $TiO_2$ in deionized water. The $TiO_2$ emulsion was sprayed in crosshatch formation. UV lamps (Mazda/36 W/2500 lm), which acted as a source of UV-A radiation, were installed on all the four walls and the roof. The irradiance inside the reaction chambers was estimated using pyranometers (model: LPPYRA, SolUrja, India), which were placed near the active surfaces of the reaction chamber. The variations in the irradiance were adjusted by removing the required number of UV lamps. In order to investigate the impact of relative humidity on the depollution process, relative humidity, inside the reaction chamber, was estimated using a hygrometer (model: Traceable, Fisher Scientific, USA). Further, variations in the relative humidity were made by using a humidifier and dehumidifier (AC4081/20, Philips, India).

A Bharat Stage-4 and gasoline-driven car was used to generated $NO_x$ and $SO_2$. The car was kept outside the reaction chamber, and its emissions were introduced in the middle of the reaction chamber using a pipe attached to the car's exhaust pipe. Concentrations of $NO_x$ and $SO_2$ inside the reaction were estimated using a chemiluminescent $NO_x$ and $SO_2$ analyzer (Rosemount Analytical; model 951C and 890). On the basis of the standardized permissible limits for indoor environments, the initial concentrations of $NO_x$ and $SO_2$, for present investigation, were chosen to be $40 \, \mu g/m^3$ [26, 27]. Therefore, the car was kept on an idle mode, until concentrations of $NO_x$ and $SO_2$, inside the reaction, reached the required limits.

*2.2. Statistical Analysis.* Optimization was performed using Stat-Ease Design Expert (version 8.0.7.1) regression software. In this analysis, the impacts of process parameters on response parameters were assessed. The process parameters chosen in this study were a concentration of $TiO_2$ emulsion, UV irradiance, and relative humidity of the reaction chamber. Similarly, the response parameters, chosen in present investigations, were the % change in the concentrations of the $NO_x$ and $SO_2$. Three levels of the process parameters, viz., low, medium, and high, finalized for the optimization process are described in Table 1.
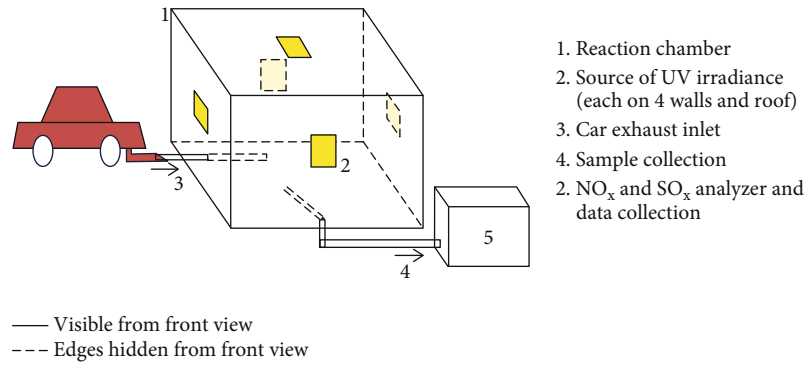
Figure 1: Brief sketch of the experimental site.

Table 1: Three levels of the process parameters used during the optimization process.

| S. no. | Process parameters | Symbolic representation | Units | −1 (low) | Coded values 0 (medium) | +1 (high) |
|---|---|---|---|---|---|---|
| 1 | Concentration of TiO$_2$ | $X_1$ | ml/m$^2$ | 20 | 70 | 120 |
| 2 | UV irradiance | $X_2$ | mW/cm$^2$ | 1 | 3 | 5 |
| 3 | Relative humidity | $X_3$ | % | 10 | 30 | 50 |

As mentioned in Table 1, the three levels of $X_1$ were decided on the basis of findings of the previous scientific literature. However, levels of $X_2$ were chosen considering the average intensity of UV-A light received by landmass of the Earth [28]. Similarly, relative humidity, inside the reaction chamber, was decided as per the required range of the relative humidity in the indoor environments [26].

In statistical investigations, the relationship between the process and response parameters was generated using a multivariate statistical approach, which is faster and more user friendly as compared to the one-variable-at-a-time (OVAT) approach. This statistical approach designed the experiments using the response surface methodology (RSM) involving the Box-Behnken design (BBD). In case of three process parameters and two response parameters, a total of 17 experimental results are required to run this application. After providing the results of 17 experiments, adopted statistical approach derived different types of associations between the response and process parameters, which can generally be described using equation (1) as follows:

$$Y = c_o + c_1 X_1 + c_2 X_2 + c_3 X_3 + c_{12} X_1 X_2 + c_{13} X_1 X_3 + c_{23} X_2 X_3 + c_{11} X_1^2 + c_{22} X_2^2 + c_{33} X_3^2, \quad (1)$$

where $Y$ depicts the response parameter(s), $X_1$ to $X_3$ are the process parameters, and $c_i$ is the response function coefficients which are determined using Stat-Ease Design Expert (version 8.0.7.1) regression software. This software was further used to evaluate the accuracy of the generated models using analysis of variance (ANOVA). The various parameters estimated for checking the adequacy were correlation regression coefficients, adjusted regression coefficients, and goodness of fit. After all the statistical analyses, 3D plots of the results were also generated using RSM. Eventually, opti-

mum conditions, of the process parameters, for achieving maximum degradation of NO$_x$ and SO$_2$, were evaluated.

## 3. Results and Discussion

*3.1. Model Equations and Regression Analysis.* Based on the experimental results, two quadratic models were generated which depicted the relation between the response and process parameters. These quadratic models are described in equation (2) as follows:

$$Y_1 = 50 + 4.75 X_1 + 13.5 X_2 + 6.5 X_3 + X_1 X_2 + 0.5 X_1 X_3 + 2 X_2 X_3 - 20 X_1^2 - 5.5 X_2^2 - 6.5 X_3^2,$$

$$Y_2 = 44 + 5 X_1 + 12.25 X_2 + 7 X_3 - 0.5 X_1 X_2 + 1.5 X_1 X_3 + 3 X_2 X_3 - 19.25 X_1^2 - 5.25 X_2^2 - 6.75 X_3^2,$$

$$(2)$$

where $Y_1$ and $Y_2$ indicate the response parameters, i.e., percentage removal of NO$_x$ and SO$_2$, respectively; $X_1$ to $X_3$ depict the process parameters, i.e., concentration of TiO$_2$ emulsion, UV irradiance, and relative humidity. Response parameters $Y_1$ and $Y_2$ showed negative and positive correlations with certain terms which indicated an antagonistic and synergistic association, respectively. Further, with an objective of assessing the reliability of the models, the results generated using these models were compared with the experimental values. The outcomes of this comparison are shown in Table 2.

Table 2 compares the 17 experimental responses to the predicted responses, with respect to different conditions of the process parameters. In Table 3, it is evident that a significant correlation existed between the experimental

TABLE 2: Comparison of experimental and predicted responses.

| S. no. | Process parameters | | | Experimental responses | | Predicted responses | |
|---|---|---|---|---|---|---|---|
| | $TiO_2$ $X_1$ ml/m² | UV irradiance $X_2$ mW/cm² | RH $X_3$ % | $Y_1$ % | $Y_2$ | $Y_1$ % | $Y_2$ |
| 1 | 70 | 5 | 50 | 64 | 60 | 60 | 54.25 |
| 2 | 20 | 3 | 50 | 21 | 14 | 24.75 | 18.5 |
| 3 | 70 | 5 | 10 | 42 | 34 | 43 | 34.25 |
| 4 | 70 | 1 | 10 | 16 | 10 | 20 | 15.75 |
| 5 | 120 | 3 | 50 | 34 | 30 | 35.25 | 31.5 |
| 6 | 120 | 5 | 30 | 41 | 32 | 43.75 | 36.25 |
| 7 | 20 | 3 | 10 | 14 | 9 | 12.75 | 7.5 |
| 8 | 120 | 1 | 30 | 15 | 14 | 14.75 | 12.75 |
| 9 | 70 | 3 | 30 | 50 | 44 | 50 | 44 |
| 10 | 120 | 3 | 10 | 25 | 19 | 21.25 | 14.5 |
| 11 | 70 | 3 | 30 | 50 | 44 | 50 | 44 |
| 12 | 70 | 3 | 30 | 50 | 44 | 50 | 44 |
| 13 | 20 | 5 | 30 | 32 | 26 | 32.25 | 27.25 |
| 14 | 70 | 1 | 50 | 30 | 24 | 29 | 23.75 |
| 15 | 20 | 1 | 30 | 10 | 6 | 7.25 | 1.75 |
| 16 | 70 | 3 | 30 | 50 | 44 | 50 | 44 |
| 17 | 70 | 3 | 30 | 50 | 44 | 50 | 44 |

TABLE 3: Optimum conditions for $TiO_2$-based UV photocatalytic degradation of the pollutants.

| S. no. | Control parameters | Symbolic representation | Units | Maximum values for responses % degradation of $NO_x$ and $SO_2$ ($Y_1 = 61.24\%$ & $Y_2 = 55.05\%$) | |
|---|---|---|---|---|---|
| | | | | Coded values | Actual values |
| 1 | Concentration of $TiO_2$ | $X_1$ | ml/m² | +0.15 | 77.5 |
| 2 | UV irradiance | $X_2$ | mW/cm² | +1.00 | 5 |
| 3 | Relative humidity | $X_3$ | % | +0.66 | 43.2 |

and predicted values. These results were further augmented by estimating the correlation (at confidence interval of 95%) between the experimental and predicted responses, as shown in Figure 2.

In Figure 2, it can be implied that the results predicted using the models are significantly correlated with the experimental results. The correlation coefficients for $NO_x$ removal and $SO_2$ removal were 0.96 and 0.93, respectively, i.e., almost equal to 1. Hence, it can be said that the models can be relied to generate appropriate results. Further, the adequacy and applicability of the models were verified using ANOVA.

3.2. Analysis of Variance (ANOVA). Reliability, of the outcomes predicted via the generated models, was verified using ANOVA-based analysis. Findings of the ANOVA-based analysis, of the experimental and predicted outcomes, at 95% confidence level, are shown in Table 4.

In Table 4, it can be seen that the $p$ values of the models were less than 0.05, and hence, it can be depicted that the models generated in Design Expert software were adequate for predicting the optimal values of the process

and response parameters. Also, the $p$ values for the process parameters, i.e., concentration of $TiO_2$ emulsion, UV irradiance, and relative humidity, were reported to be significant. Regression coefficient, being close to 1, shows that variations observed among experimental and predicted results are insignificant and models are adequate for the present analysis (Kiely 1997; Ehrig and Stegmann 1992) [29, 30]. It can also be illustrated that the generated models can be used to analyze the responses from even more variations in the designed experiments (i.e., more than 17), as the values of correlation coefficients were observed to be very close to adjusted correlation coefficients ($R^2_{adj}$) [29].

Moreover, the $p$ values can also be used to identify the significant effect of the different terms of the model on response parameters. In the present investigation, the model terms having a $p$ value > 0.05 were considered as having insignificant effect on the response parameters. In this way, it can be observed that only $X_1$, $X_2$, $X_3$, $X_1^2$, $X_2^2$, and $X_3^2$ were having $p$ values > 0.05 and hence have significant effect on the response parameters. The rest of the terms, i.e., $X_1$
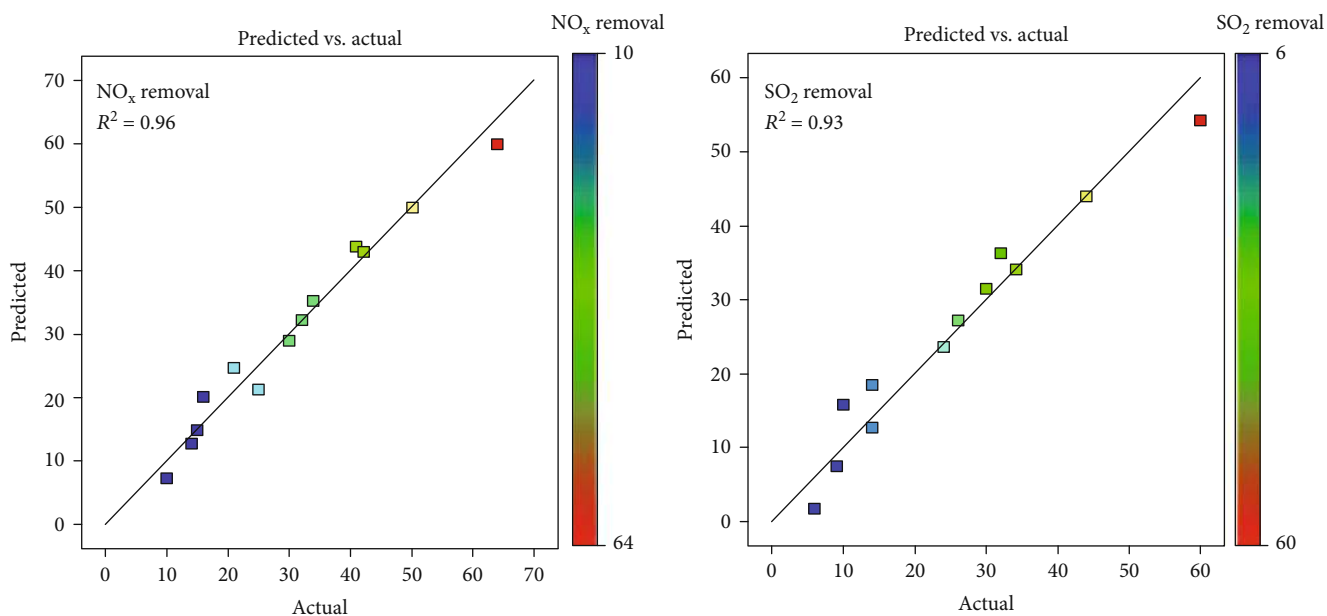
FIGURE 2: Predicted versus actual plots for decontamination of $NO_x$ and $SO_2$.

TABLE 4: ANOVA test for response parameters.

| Source | Sum of squares | | df | Mean square | | F value | | p value | |
|---|---|---|---|---|---|---|---|---|---|
| | $Y_1$ | $Y_2$ | $Y_1$ & $Y_2$ | $Y_1$ | $Y_2$ | $Y_1$ | $Y_2$ | $Y_1$ | $Y_2$ |
| Model | 4128 | 3843 | 9 | 458 | 427 | 39.89 | 19.86 | <0.0001 | <0.0001 |
| $X_1$ | 180.5 | 200 | 1 | 180 | 200 | 15.70 | 9.30 | 0.0054 | 0.0005 |
| $X_2$ | 1458 | 1200 | 1 | 1458 | 1200 | 126.78 | 55.84 | <0.0001 | <0.0001 |
| $X_3$ | 338 | 392 | 1 | 338 | 392 | 29.39 | 18.23 | 0.0010 | 0.0006 |
| $X_1X_2$ | 4 | 1 | 1 | 4 | 1 | 0.3 | 0.04 | 0.5739 | 0.8354 |
| $X_1X_3$ | 1 | 9 | 1 | 1 | 9 | 0.08 | 0.42 | 0.7760 | 0.5383 |
| $X_2X_3$ | 16 | 36 | 1 | 16 | 36 | 1.39 | 1.67 | 0.2767 | 0.2367 |
| $X_1^2$ | 1684 | 1560 | 1 | 1684 | 1560 | 146.45 | 72.57 | <0.0001 | <0.0001 |
| $X_2^2$ | 127 | 116 | 1 | 127 | 116 | 11.08 | 5.40 | 0.0126 | 0.004 |
| $X_3^3$ | 178 | 191 | 1 | 178 | 191.8 | 15.47 | 8.92 | 0.0057 | 0.003 |
| Residual | 10.5 | 15 | 7 | 11.50 | 21.5 | | | | |
| Lack of fit | 10.5 | 15 | 3 | 26.83 | 50.17 | | | 0.07 | 0.09 |
| Pure error | 0 | 0 | 4 | 0 | 0 | | | | |
| Total (Corr) | 4209 | 3993 | 16 | | | | | | |

$X_2$, $X_1 X_3$, and $X_2 X_3$, was eliminated from the model, for further analysis. Moreover, as a p value for lack of fit (LoF) was observed to be >0.05, therefore, it can be depicted that the models generated are suitable for predicting the response parameters. After verifying the accuracy and adequacy of the models, they were further used to generate the response surface plots.

*3.3. Response Surface Plots and Optimization.* After assessing the adequacy of the models, Design Expert software was further used to plot 3-dimensional surface plots for all the operating parameters. The RSM approach was used

to draw these plots and the generated plots are shown in Figure 3.

Analysis of the surface plots, as shown in Figure 3, and derived maximum degradation of the $NO_x$ and $SO_2$, that assisted in identifying the optimum conditions for $TiO_2$-based UV photocatalytic degradation of the $NO_x$ and $SO_2$ which, are shown in Table 3.

In Table 3, it can be implied that under optimized conditions, i.e., concentration of $TiO_2$ emulsion = 77.5 ml/m$^2$, UV irradiance = 3 mW/cm$^2$, and RH = 43.20%, the % degradation of $NO_x$ and $SO_2$ was reported to be 61.24% and 55.05%, respectively. Hence, the experiments designed in this
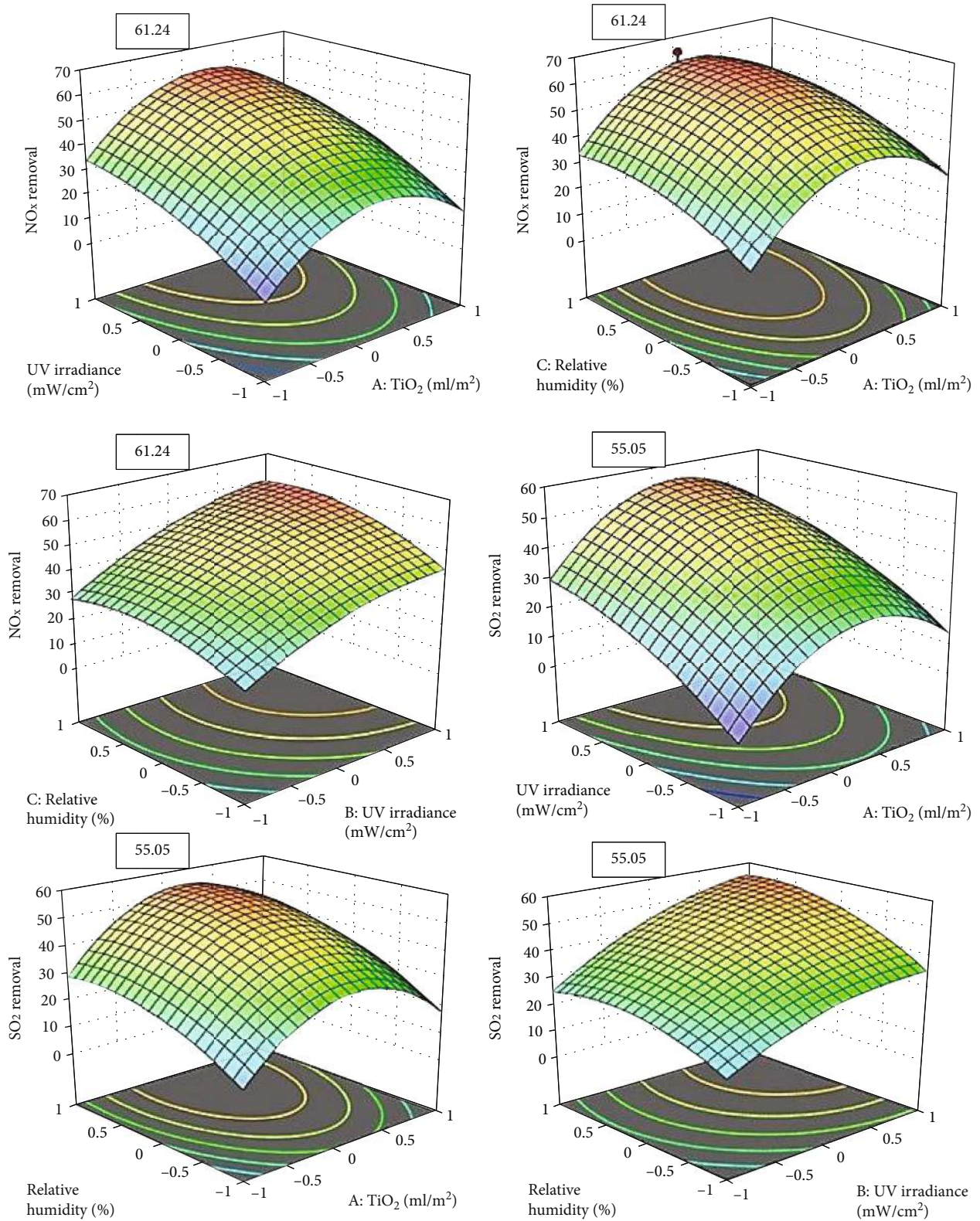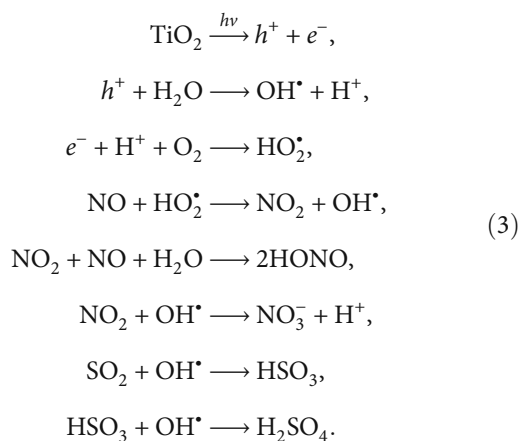
FIGURE 3: Response surface plots.

investigation using the Design Expert software were found to be suitable in deciding the optimal conditions of the process parameters under which significant degradation of the air pollutants could be achieved.

*3.4. Impacts of $TiO_2$.* In Figure 3 and Table 4, it is evident that the concentration of $TiO_2$ emulsion has a significant influence ($p$ value > 0.05) on the decontamination of $NO_x$ and $SO_2$ in the reaction chamber. In the reaction chamber, $TiO_2$

particles get excited after getting in contact with the photon-embedded light, emitted from the UV lamp. Excited $TiO_2$ particles generate free electrons and holes that further react with the water molecules and eventually initiate the decontamination process. These charged particles, in the reaction mixture, assist in enhancing the degradation process of $NO_x$ and $SO_2$. The free electrons react with oxygen molecules and generate oxidizing radicals. On the other hand, holes lead to oxidation of gaseous molecules by producing hydroxyl radicals from water molecules. The overall reactions taking place during photocatalysis-induced decontamination of $NO_x$ and $SO_2$ are described in equation (3) as follows:

$$TiO_2 \xrightarrow{hv} h^+ + e^-,$$
$$h^+ + H_2O \longrightarrow OH^{\bullet} + H^+,$$
$$e^- + H^+ + O_2 \longrightarrow HO_2^{\bullet},$$
$$NO + HO_2^{\bullet} \longrightarrow NO_2 + OH^{\bullet},$$
$$NO_2 + NO + H_2O \longrightarrow 2HONO, \quad (3)$$
$$NO_2 + OH^{\bullet} \longrightarrow NO_3^- + H^+,$$
$$SO_2 + OH^{\bullet} \longrightarrow HSO_3,$$
$$HSO_3 + OH^{\bullet} \longrightarrow H_2SO_4.$$

In equation (3), it can be seen that during the $TiO_2$-mediated UV photocatalysis, hydroxyl radicals react with $NO_x$ and $SO_2$ and finally degraded them into nitrates and sulphates, respectively. Subsequently, it can also be seen in Figure 3 that with the increase in concentration of the $TiO_2$ solution, the degradation of $NO_x$ and $SO_2$ also increased. It can be attributed to the accelerated generation of hydroxyl radicals. However, such a scenario was observed till the concentration of $TiO_2$ solution was $77.50 \, ml/m^2$, after which a continuous slight decrease was reported. One of the various promising explanations of such a trend could be the decreased exposure of $TiO_2$ particles to UV light caused by obstruction in the passage of light due to agglomeration of $TiO_2$ particles.

It has also been reported that overdosing of the $TiO_2$ particles lead to intershifting of charge among the ground state and activated particles [31, 32]. In this way, lesser electrons and holes are available for generating the hydroxyl radicals [33, 34]. Moreover, with a larger concentration of the $TiO_2$ solution, the solvent may seep the particles deeper into the walls, where they could not get exposed to the UV light. Similar observations had also been reported in studies conducted using $TiO_2$-mediated photocatalysis to degrade contaminants such as toluene (Morteza [35]) and benzene [36]. In a similar study, Hussein et al. [24] estimated the photocatalytic efficiency of $TiO_2$ particles by spraying its 3% solution ($w/v$) on the concrete surface. It was revealed that surface coating of concrete led to 98.85% reduction of nitric oxide. In another

study, it was estimated that surface coating of concrete with 5% $TiO_2$ reduced approximately 60% of $NO_x$ (Guo et al. [37].

### 3.5. Impact of UV Irradiance.

Response surface plots, as shown in Figure 3 and Table 4, clearly indicate that a significantly positive ($p$ value > 0.05) and quadratic association exits between the UV-A irradiance and the decontamination of gaseous pollutants. In the present investigation, the % decontamination of the $NO_x$ and $SO_2$ gases was observed to increase with the increase in UV irradiance and maximum % decontamination of the $NO_x$ and $SO_2$ gases was reported at $5 \, mW/cm^2$ of UV irradiance. A promising explanation to this could be that on increasing the intensity of UV-A light, at a surface of catalyst-covered walls, the rate of generation, of free electrons and holes from the $TiO_2$ particles, escalated. These excited particles further increase the generation of hydroxyl radicals that finally oxidized the $NO_x$ and $SO_2$ molecules. In a similar study done by Hüsken et al. [38], increase in the decontamination of $NO_x$ was reported till the UV irradiance was increased up to $13 \, W/m^2$. The findings of Ballari et al. [39] also support such an association between UV irradiance and gaseous decontamination argument. However, disagreement exists while deciding the linear or quadratic relation between the decontamination of the pollutants and intensity of the UV-A irradiance [40–42]. These studies explained that linearity exists when electron holes are stabled on reacting with pollutants at the photocatalytic surface rather than recombining with the electrons. However, in case of quadratic relation, opposite phenomenon existed and holes are filled largely by recombination. In the present investigation, the impact of UV irradiance on the photocatalysis is depicted to follow the latter phenomenon.

Also, while evaluating the impact of UV irradiance on efficiency of photocatalysis, it was observed that maximum % decontamination was observed at $5 \, mW/cm^2$. However, it can be depicted that further increase in the UV irradiance could have increased the decontamination. Therefore, it is suggested that further research is required to conclude the optimum value of UV irradiance by increasing its range.

### 3.6. Impact of Relative Humidity.

Relative humidity inside the reaction chamber was also observed to impact the $TiO_2$-based UV photocatalytic degradation of $NO_x$ and $SO_2$. As shown in Figure 3, the maximum degradation of $NO_x$ and $SO_2$ was achieved when RH of the reaction chamber was 43.2%. Also, as mentioned in Table 4, the decontamination process of the pollutants showed a significantly positive ($p$ value > 0.05) and quadratic relation with the relative humidity of the reaction chamber. It was observed that with the increase in RH, till 43.2%, the degradation of the pollutants also increased.

Discussion on the interaction of water molecules and holes generated in $TiO_2$ particles made it evident that RH is a crucial factor for deciding the degradation efficiency of $TiO_2$-mediated UV photocatalysis. In an enclosed reaction chamber like EPGs, generation of hydroxyl radicals is majorly limited by the content of reaction chamber's RH. Due to hydrophilic nature of the surface of $TiO_2$ particles, the water molecules initially form a monolayer on the $TiO_2$

particles [43]. This interaction between the $TiO_2$ particles and water molecules initiates the photocatalytic degradation of the $NO_x$ and $SO_2$ molecules. However, with the increase in RH, the number of layers of water molecules also increases on the $TiO_2$ particles [44]. Consequently, the interaction of $TiO_2$ particles with the gaseous molecules decreases and adsorption stops.

Moreover, this phenomenon also assisted in higher generation of free radicals further leading to radical scavenging. In case of radical scavenging, free radicals, instead of causing decontamination, are indulged in generating water molecules, as described in equation (4) as follows:

$$H_2O_2 + {}^*OH \longrightarrow HO_2^* + H_2O,$$
$$HO_2^* + {}^*OH \longrightarrow H_2O + O_2. \tag{4}$$
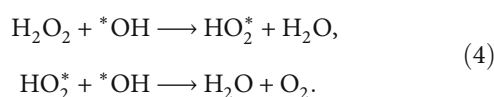
In this way, the increase in RH of the reaction chamber, after a certain amount, leads to hinder the photocatalysis of the gaseous molecules. Therefore, in present investigation, the maximum degradation of the gaseous pollutants was observed at RH = 43.2%. Increasing the RH beyond this content could have increased the competition between the water and gaseous molecules for getting attached to the active sites of the $TiO_2$ particles. Therefore, it can also be implied that in humid areas, the RH could prove to be a limiting factor for $TiO_2$-mediated UV photocatalysis of air pollutants. Sleiman et al. [45] and Rismanchian et al. [46], also observed the photocatalytic degradation of Toluene in the 20% to 80% of RH and reported that maximum degradation was achieved at RH = 40%.

## 4. Conclusions

The findings of the present investigation proved that $TiO_2$-mediated UV photocatalysis can be used as a promising technology for the decontamination of $NO_x$ and $SO_2$ in the enclosed parking garages. A comprehensive approach of RSM-BBD showed that at optimized conditions of the process parameters, i.e., concentration of $TiO_2$ emulsion = 77.5 ml/m$^2$, UV irradiance = 3 mW/cm$^2$, and relative humidity = 43.20%, concentrations of $NO_x$ and $SO_2$ can be degraded up to 61.24% and 55.05%, respectively. In this way, accumulation of pollutants in the EPGs and associated human health impacts can be prevented.

## Data Availability

Data will be made available on demand.

## Conflicts of Interest

The authors would like to declare that they do not have any conflict of interest.

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