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Research Article

Assessing the Applicability of Photocatalytic-Concrete Blocks in Reducing the Concentration of Ambient NO_2 of Chandigarh, India, Using Box–Behnken Response Surface Design Technique: A Holistic Sustainable Development Approach

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Anthropogenic emissions, such as industrial, vehicular, biomass burning, and coal combustion, play a significant role in degrading the atmospheric conditions of India. Therefore, in the present study, applicability of the photocatalytic-concrete blocks was estimated in improving the ambient environment of Chandigarh, India. The photocatalytic-concrete blocks were prepared by mixing the TiO_2 particles with cement. All the experiments, designed in accordance with the Box–Behnken approach, in combination with response surface methodology, were performed in a batch reactor. Further, the process parameters, namely, concentration of TiO_2 (1 to 5 g), UV-A irradiance (1 to 5 mW/cm^2), and relative humidity (RH) (10 to 70%), were optimized to achieve maximum degradation of NO_2. Outcomes of batch experiments depicted that the maximum degradation of NO_2, that is, 68.32%, was attained at 3.35 g of TiO_2, 5 mW/cm^2 of UV-A irradiance, and 64.60% RH. The findings of batch experiment were further theoretically applied to degrade the ambient NO_2 concentration of Chandigarh, India. It was estimated that using the photocatalytic concrete for construction of Chandigarh's pavements may reduce the ambient NO_2 concentration of Chandigarh, India, to an average of 5.80 μg/m^3. Afterwards, reusability of photocatalytic-concrete blocks was also assessed, and it was made evident that after five cycles, their efficiency was reduced by only 7.15%. Subsequently, it was revealed that hydrogen peroxide-based treatment of photocatalytic-concrete blocks could completely regenerate its treatment efficiency. Therefore, it is expected that the findings of this study may prove beneficial in urban planning, as it may assist scientific auditory in identifying the applicability of TiO_2-based photocatalysis in mitigating the impacts of vehicular emissions.

1. Introduction

It is irrefutable that a comprehensive development of any nation is depicted by the extant of its road network. Therefore, in the race of development, all the developing nations are expanding their road network by laying more roads. However, it is also evident that with an efficient road network, the number of fossil fuels' powered vehicles also increases [1]. In this way, the emissions attributed to vehicular exhausts also increase and degrade the environmental conditions of the nation [2]. In certain areas, such as rural areas, seashores, and mountainous terrains, these pollutants are easily dispersed, and hence impacts were reported to be minimal. However, in urban areas, construction of tall buildings, such as houses, shopping malls, and offices, creates a street canyon conditions. Consequently, the dispersion of vehicular emissions is limited, and several associated environmental implications, such as photochemical smog, tropospheric ozone, acid rain, and secondary aerosols, could be speculated [3–5]. Poor environmental conditions, of the urban areas, expose its residents to several toxic pollutants, namely, particulate matter, heavy metals, NO_x, CO, O_3, and volatile organic compounds (VOCs). Studies have also reported that owing to the exposure to such pollutants, the residents of urban areas are more susceptible to respiratory diseases as compared to the residents of rural areas of developing nations [6, 7]. Therefore, it is imperative to identify an innovative way of reducing the ambient concentration of vehicular emissions [8].

Several technologies have recently been developed to decontaminate the environment of urban areas, namely, installation of smog towers, air purifiers, and water sprinklers. However, due to the drawbacks of these technologies, such as high installation cost and poor efficiency, they are less preferred [9–13]. On the other hand, applications of photocatalysis have already been studied vastly in oxidation of pollutants in different environmental media, such as air, water, and soil [14, 15]. Among the various oxidation agents, such as TiO_2, ZnO, Ag_3PO_4, CuO, AgI, and Cu_2S, TiO_2-based photocatalysis was reported to be most advantageous because of its high efficiency, easier mobilization on different substrates, lower operational cost, and no damage to environment and living beings [16, 17]. Therefore, in recent years, scientific community is also working towards exploring the applicability of photocatalysis in reduction of urban-air pollution [18–20]. In this regard, several surfaces of the global-urban areas, namely, buildings, roads, and monuments, were reported to be laden with different photocatalysts, and significant reduction in concentration of air pollutants was also reported [19].

However, in developing nations such as India, where the air quality is generally poor, the studies, emphasizing the use of photocatalysis in reducing the air pollution, are scanty [21, 22]. Although few studies estimated the treatment efficiency of TiO_2 for different pollutants, they merely optimized the treatment process using conventional one-variable-at-a-time approach [18–20]. Moreover, research gap still exists in identifying the use of response surface methodology in photocatalysis-based reduction of air pollution. Scientometric analysis of the last eight years' research trends of photocatalytic-concrete blocks has been performed using VOSviewer (version 1.6.16) analytical tool. Figure 1 plots the network of keywords for the last eight years developed using Scopus database. The study indicates strong network relationship between photocatalysis, titanium dioxide, and nitrogen oxides which has also been found in literature review [16, 17]. Recently, titanium dioxide nanoparticles, zinc oxide, and oxide minerals are used for manufacturing of concrete blocks. However, the role of these chemicals in air purification is less reported. Hence, there is need to investigate the impact of photocatalytic concrete on air purification of air, and scope for reduction of toxic pollutants must be ascertained.

Therefore, in this study, efforts were made to conduct a laboratory experiment and assess the applicability of photocatalytic concrete in reducing the concentration of NO_2 and SO_2. Also, optimal conditions, for achieving the maximum reduction of NO_2, were estimated using Box–Behnken design (BBD) in combination with response surface methodology (RSM). The findings of this analysis were further used to estimate the efficiency of photocatalytic concrete in reducing the ambient NO_2 levels of Chandigarh, India. It is expected that this study may prove beneficial in the scientific quest for finding the solution for air pollution-related problems arising from uncontrolled vehicular emissions in developing nations.

2. Materials and Methods

2.1. Study Area. In the present study, Union Territory of Chandigarh, India, was chosen for estimating the application of photocatalytic concrete in reducing the concentration of ambient NO_2. Currently, almost all the roads in Chandigarh are made up of asphalt. However, in recent years, the authorities of Chandigarh have identified the importance of concrete roads and also constructed some roads in Sectors 31, 32, and 39 using concrete. Considering the benefits of concrete roads, the regional authorities have also decided to further increase the area of concrete roads in Chandigarh, India. The city's roads are categorized into seven types, that is, V_1 up to V_7. With the total length of 3.15×10^6 m, the city's road network comprises national highways, intercity roads, and rural roads. Initially, the roads of Chandigarh were designed to manage the road congestion. However, in the last decade, vehicular density, within the study area, has increased substantially which further led to frequent events of traffic jams [23]. Consequently, the various emissions, from fossil fuel-powered vehicles, have degraded the ambient air quality of the study area [24].

The geographical location of Chandigarh, India, also plays a crucial role in impacting its atmospheric conditions. The study area falls in the Indo-Gangetic Plains (IGPs) where major agrarian states of India, that is, Punjab, Haryana, and Uttar Pradesh, are located. In the IGPs, crop residue burning is the most popular way of managing the crop stubble [25]. Subsequently, the atmospheric concentration of NO_2 was reported to increase in the IGPs after the

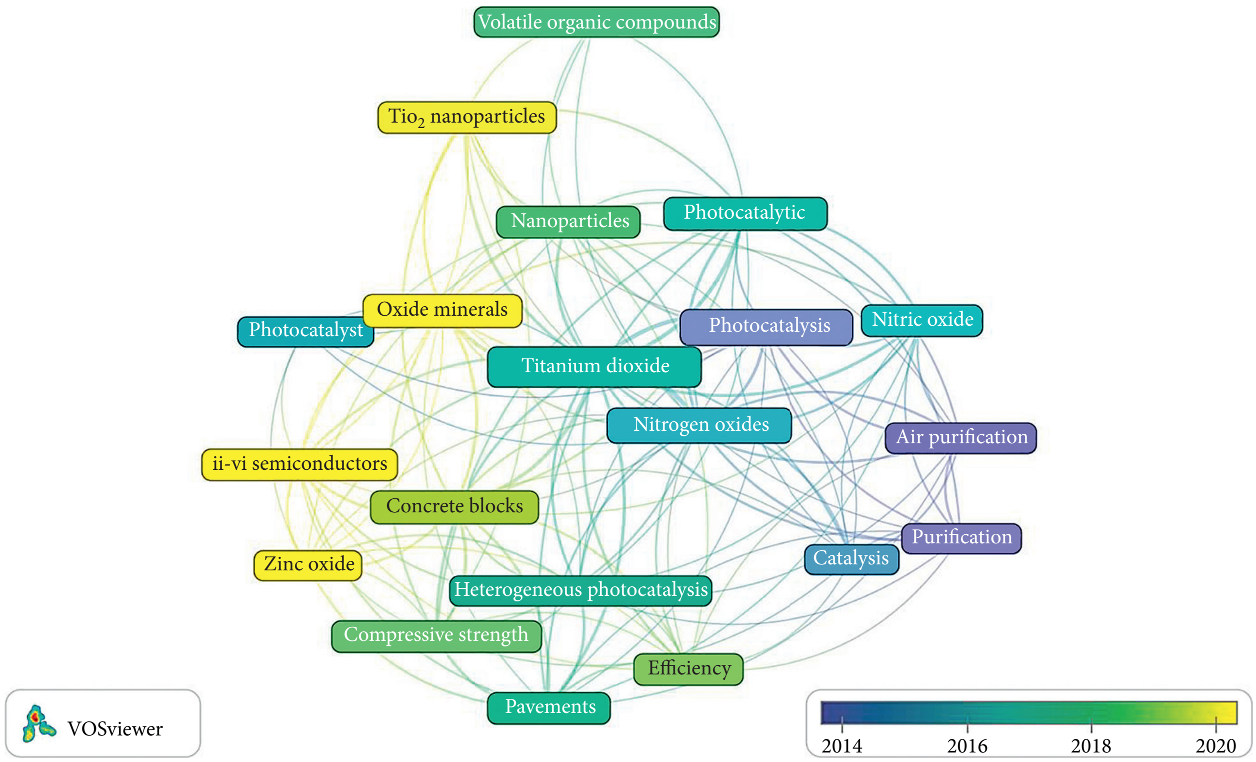

Figure 1: Scientometric analysis of research trends of photocatalytic-concrete blocks.

harvesting season [26, 27]. Such deteriorating atmospheric conditions of the study area may significantly impact the health of its residents [28]. Hence, it is imperative to develop an innovative technique to improve the air quality of the study area.

In order to regularly monitor the air quality of the city, five monitoring stations are installed around the city by the authorities of Chandigarh Pollution Control Board (CPCB). The location for these five monitoring stations is industrial area, Kaimbwala village, Sector 17, Sector 32, and Sector 12. These locations were chosen on the basis of the type of the nearby source of air pollution, that is, industries and vehicles. Brief layout of the road network in the study area, generated using Arc GIS software (version 10.1), is shown in Figure 2.

2.2. Preparing the Specimen of Photocatalytic Concrete. The laboratory specimens of photocatalytic concrete were prepared in the form of slabs and their dimensions were 152 mm × 152 mm × 25 mm. These slabs were prepared by mixing 624 kg/m^3 of cement, 262 kg/m^3 of water, and 1412 kg/m^3 of the fine aggregates. The proportion of the various components of the specimen was decided on the basis of their specific proportion in the concrete roads of the study area. The fine aggregates, used in the present study, were extracted from the demolition waste. Constituents of demolition waste, which passed through the 2.36 mm sieve but retained on the 75-micron sieve, were used as fine aggregates. The fine aggregates, extracted in this way, were hard, durable, dry, and free from dust. The coarse aggregates were not used while preparing the specimen as the volume of the slabs was small. Further, the photocatalytic activity was induced in the concrete slabs by mixing the required amount of TiO_2 catalyst (anatase) with the cement. The slabs were prepared using a two-lift procedure, according to which the TiO_2-free cement was used in the bottom half of the slab, and the upper-half slab contains the TiO_2-laden cement. Proportion of the depth of the bottom half and upper half of the concrete slabs was maintained as 2 : 1. After pouring the slab material, the specimen-blocks were left undisturbed for 24 h after covering them with a plastic sheet and damp cloth. After 24 h of initial curing, the specimen blocks were removed from the molds and kept in a container with 100% relative humidity for the next 16 h. Similarly, the blank samples were also prepared without adding TiO_2. The procedure of preparing the photocatalytic-concrete specimen was acquired from the International Organization of Standardization (ISO) standard 22197-1:2007 (E) [29].

2.3. Laboratory Analysis. The brief layout of the laboratory setup used for conducting the experiments is shown in Figure 3.

As shown in Figure 3, the laboratory setup comprised gas cylinders, zero air source, humidifier, UV-A source, reaction chamber, and chemiluminescent NO_2 analyzer (Rosemount Analytical; Model 951C and 890). The specimen of photocatalytic concrete was placed in an enclosed reaction chamber with preinstalled UV-A lamps (Mazda/36 W/2500 lm). The irradiance inside the reaction chambers was estimated using pyranometers (Model: LPPYRA, SolUrja,

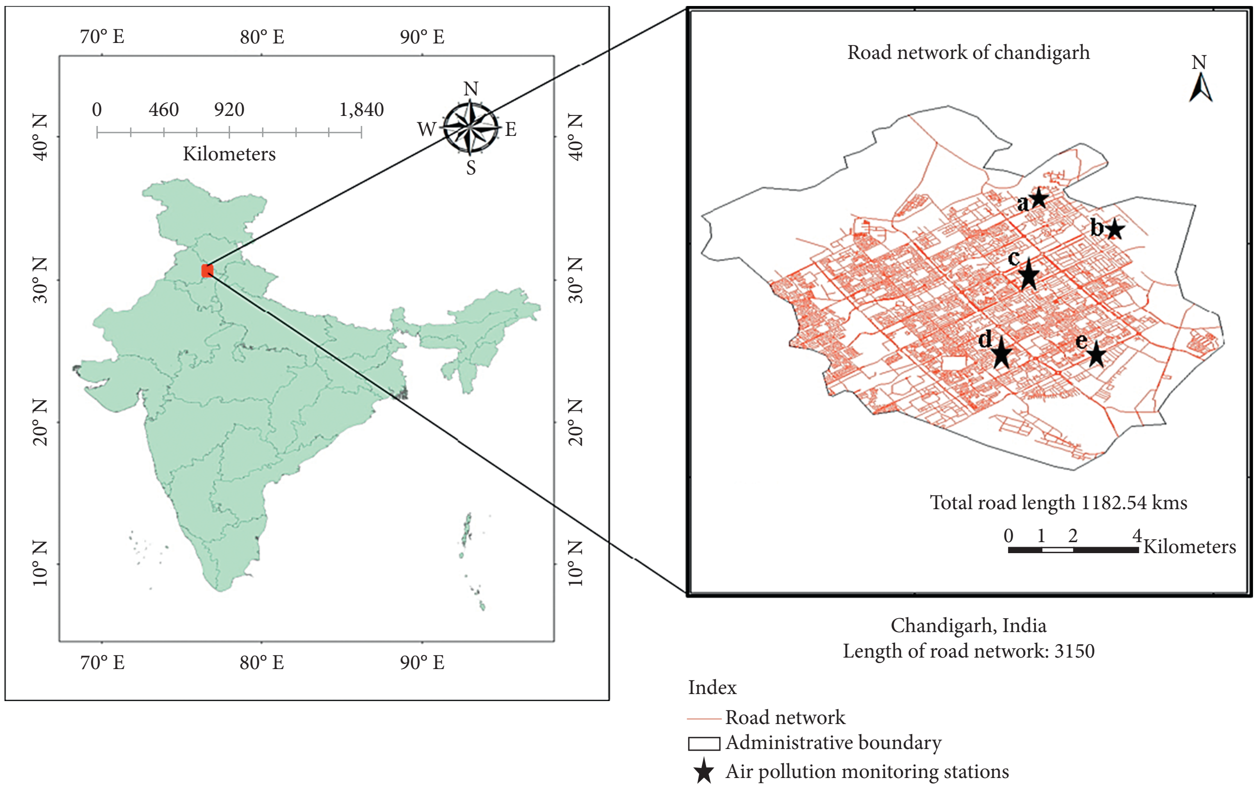

FIGURE 2: Geographical location of the study area (generated by Arc-GIS software).

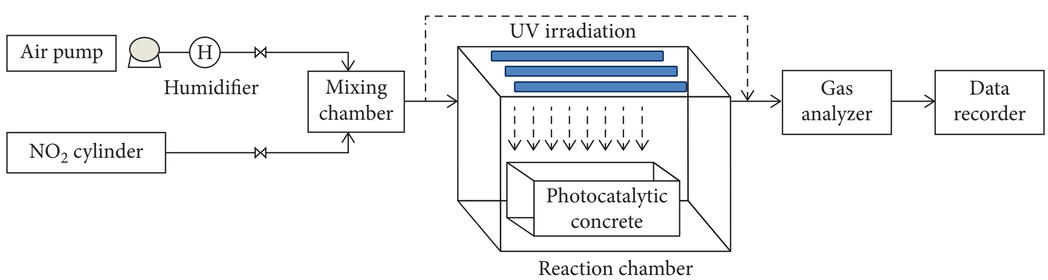

FIGURE 3: Sketch of the laboratory setup.

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-A lamps. In order to investigate the impact of relative humidity (RH) on the depollution process, an insider of the reaction chamber was continuously monitored using hygrometer (Model: Traceable, Fisher Scientific, USA). Further, RH of the reaction chamber was changed using a humidifier and dehumidifier (AC4081/20, Philips, India).

NO_2 was pumped inside the reaction chamber, and its concentration inside the chamber was continuously monitored using NO_2 analyzer. After achieving the required concentration of NO_2 inside the reaction chamber, the impacts of photocatalysis were estimated. The concentration of NO_2 was decided in order to meet the atmospheric conditions of Chandigarh, India. In this regard, air pollution data for the study area was procured from https://www.data.gov.co.in, and accordingly annual-average concentration of NO_2 was calculated. Subsequently, 18.31 $\mu g/m^3$ of NO_2 was maintained inside the reaction chamber. Time of reaction, that is, 8 h, was decided on the basis of the duration of exposure of Chandigarh's road to sunlight [30]. After 8 h of reaction, air from the reaction chamber was pumped into the gas analyzers, which analyzed the concentration of the gases after treatment. A T-connection was also provided, which assisted in analyzing the concentration of gases entering the reaction chamber.

Results obtained from the laboratory analysis were statistically analyzed, using a comprehensive approach of RSM and BBD. In statistical analysis, the optimization of process parameters, namely, concentration of TiO_2, intensity of UV-A irradiance, and RH, was done to maximize the degradation of NO_2. These optimized conditions were further used to estimate the applicability of photocatalytic concrete in reducing the ambient NO_2 levels of the study area.

2.4. Reusability of Photocatalytic Concrete. After performing the laboratory assessment of the applicability of photocatalytic concrete in reducing the NO_2, their reusability was estimated. In this regard, the surface of the specimen of photocatalytic concrete was washed with tap water and then H_2O_2. After the surface treatment of photocatalytic concrete, the experiments were repeated. This step was repeated for five times and each time the degradation efficiency of the photocatalytic concrete was noted.

2.5. 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 concentration of TiO_2, intensity of UV-A irradiance, and RH. Similarly, the chosen response parameter was the % change in the concentration of NO_2. The three levels of the process parameters, namely, low, medium, and high, were finalized for the optimization process, and these are described in Table 1.

As mentioned in Table 1, the three levels of X_1 were decided on the basis of the findings of previous scientific literature [21, 22]. However, levels of X_2 were chosen considering the intensity of light received by the study area [30]. Similarly, RH, inside the reaction chamber, was decided as per the required range of the relative humidity in the indoor environments [31].

In statistical investigations, the relationship between the process and response parameters was generated using a multivariate statistical approach. The multivariate statistical approach is faster and more user-friendly as compared to the one-variable-at-a-time (OVAT) approach. This statistical approach designed the experiments using Box–Behnken design (BBD). In case of three process parameters and one response parameter, a total 17 experiments were designed and performed in the reaction chamber. The findings of 17 experiments were further used as an input dataset for the Stat-Ease Design Expert software. Further, associations between the response and process parameters were derived, which can be described using the following:

$$Y = c_o + c_1X_1 + c_2X_2 + c_3X_3 + c_{12}X_1X_2 + c_{13}X_1X_3 + c_{23}X_2X_3 + c_{11}X_1^2 + c_{22}X_2^2 + c_{33}X_3^2, \tag{1}$$

where Y depicts the response parameter (s), X_1 to X_3 represent the process parameters, and c_i shows the coefficients of the process parameters. The accuracy and reliability of the statistical models, generated in this way, were further assessed 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 analysis, 3D plots of the results were also generated using RSM. Eventually, optimum conditions of the process parameters for achieving maximum degradation of NO_2 were evaluated.

3. Results and Discussion

3.1. Model Equations and Regression Analysis. Based on the experimental results, one quadratic model was generated which is described in the following equation:

$$Y_1 = 56 + 5.25X_1 + 12.63X_2 + 6.87X_3 + 1.75X_1X_3 + 0.25X_1X_3 + 2.5X_2X_3 - 20.5X_1^2 - 4.75X_2^2 - 5.75X_3^2, \tag{2}$$

where Y_1 indicates the percentage removal of NO_2 and X_1 to X_3 depict the process parameters, that is, concentration of TiO_2, UV-A irradiance, and RH, respectively. All the variables were mentioned in the equation without considering their respective statistical significance. Response parameter Y_1 showed positive correlation with all the process parameters which indicated a synergistic association [32].

Further, with an objective of assessing the reliability of the model, the results generated using this model 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. From Table 2, it can be seen that responses predicted by the model were similar to the experimental responses. These results were further augmented by estimating the correlation (at confidence interval of 95%) between the experimental and predicted responses, as shown in Figure 4.

From Figure 4, it can be implied that the results predicted using the model were significantly correlated with the experimental results. The correlation coefficient for NO_2 removal was 0.96, that is, almost equal to 1. Hence, it can be said that the model could efficiently generate accurate results [33]. Further, the adequacy of the model was further verified using ANOVA.

3.2. Analysis of Variance (ANOVA). Reliability of the outcomes predicted via the generated model was verified using ANOVA-based analysis. Findings of the ANOVA-based analysis at 95% confidence level are shown in Table 3.

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

S. no.	Process parameters	Symbolic representation	Units	Coded values		
				−1 (low)	0 (medium)	+1 (high)
1	Concentration of TiO_2	X_1	g	1	3	5
2	UV-A irradiance	X_2	mW/cm^2	1	3	5
3	Relative humidity	X_3	%	10	40	70

Table 2: Comparison of experimental and predicted responses.

S. no.	Process parameters			Experimental responses	Predicted responses
	TiO_2 X_1 g	UV-A irradiance X_2 mW/cm^2	Relative humidity X_3 %	Y_1 %	Y_1 %
1	1	3	70	29	31.12
2	3	3	40	56	56
3	3	5	10	48	48.75
4	3	5	70	71	67.50
5	5	1	40	23	21.62
6	5	3	10	30	27.87
7	3	3	40	56	56
8	3	1	70	38	37.25
9	1	3	10	20	17.87
10	3	3	40	56	56
11	3	3	40	56	56
12	5	5	40	49	50.37
13	3	1	10	25	28.5
14	1	1	40	16	14.62
15	5	3	70	40	42.12
16	1	5	40	35	36.37
17	3	3	40	56	56

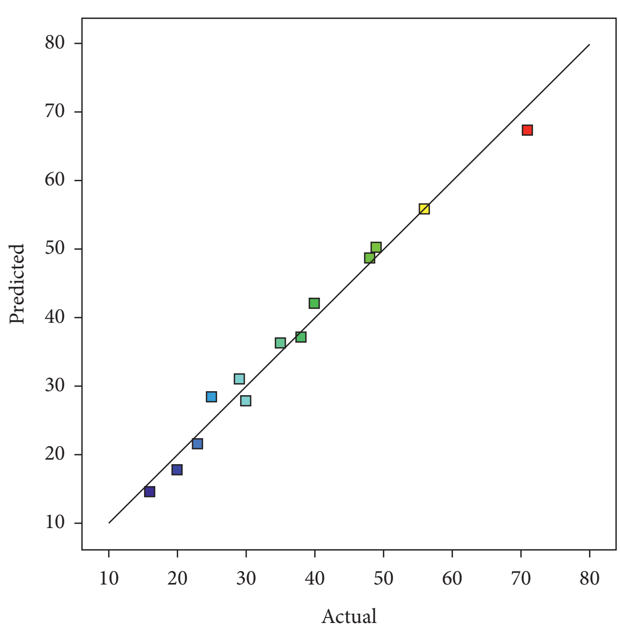

Figure 4: Predicted versus actual plots for degradation of NO_2.

From Table 3, it can be seen that the p values of the models were <0.0001, and hence, it can be depicted that the model generated in Design Expert software was adequate for optimizing the process and response parameters [34].

Table 3: ANOVA test for response parameters.

Source	Sum of squares Y_1	df Y_1	Mean square Y_1	F value Y_1	p value Y_1
Model	4040.87	9	448.99	61.32	<0.0001
X_1	220.53	1	220.50	30.12	0.0009
X_2	1275.13	1	1275.13	174.16	<0.0001
X_3	378.13	1	378.13	51.65	0.0002
X_1X_2	12.25	1	12.25	1.67	0.2368
X_1X_3	0.25	1	0.25	0.0341	0.8586
X_2X_3	25	1	25	3.41	0.1071
X_1^2	1769.47	1	1769.47	241.68	<0.0001
X_2^2	95	1	95	12.98	0.0087
X_3^3	139.21	1	139.21	19.01	0.0033
Residual	15.25	7	7.32		
Lack of fit	15.25	3	17.08		0.017
Pure error	0	4	0		
Total (corr)	4092.12	16			

Similarly, the p values for the process parameters, that is, the concentration of TiO_2, intensity of UV-A irradiance, and RH, were reported to be significant. Moreover, the p values can also be used to identify the significant effect of the different terms of the model on response parameter. 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 parameter [35]. The rest of the terms were eliminated from the model for further analysis. Moreover, as the 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 parameter [36].

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 process parameters. RSM approach was used to draw these plots, and the generated plots are shown in Figure 5.

Analysis of the surface plots, as shown in Figure 5, was used to derive the maximum degradation of NO_2. This further assisted in identifying the optimized conditions for photocatalytic-concrete-assisted degradation of NO_2. The optimized conditions derived in this way are mentioned in Table 4.

From Table 4, it can be implied that under the optimized conditions, that is, concentration of TiO_2 solution = 3.35 g, intensity of UV-A irradiance = 5 mW/cm^2, and RH = 64.60%, the % degradation of NO_2 was 68.32%. Hence, the experiments, designed 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, such as NO_2, can be achieved.

3.4. Impacts of TiO_2. From Figure 5 and Table 3, it is evident that during the process of photocatalysis-induced depollution, the concentration of TiO_2 emulsion could play a significant role (p value >0.05) in the degradation of NO_2. Inside the reaction chamber, TiO_2 particles get excited after getting in contact with the photons of energy, emitted from UV-A lamps. Excited TiO_2 particles generate free electrons and holes, which further react with the water molecules [37]. In this way, the degradation process of NO_2 inside the reaction chamber is initiated. The overall reactions, taking place during photocatalysis-induced degradation of NO_2, are described in the following equations:

$$TiO_2 \xrightarrow{h} v\, h^+ + e^- \quad (3)$$

$$h^+ + H_2O \longrightarrow OH^{\cdot} + H^+ \quad (4)$$

$$e^- + H^+ + O_2 \longrightarrow HO_2^{\cdot} \quad (5)$$

$$NO + HO_2^{\cdot} \longrightarrow NO_2 + OH^- \quad (6)$$

$$NO_2 + NO + H_2O \longrightarrow 2HONO \quad (7)$$

$$NO_2 + e^- \longrightarrow NO_3^- \quad (8)$$

From (3) through (8), it can be seen that during the photocatalytic-concrete-assisted degradation of NO_2, hydroxyl radicals react with the gaseous molecules of the pollutants and degrade them into nitrates and sulphates. Also, from Figure 5, it can be depicted that with the increase in the concentration of TiO_2 emulsion, the degradation of NO_2 also enhanced. It can be attributed to the increase in the generation of hydroxyl radicals with the increased active sites on TiO_2 particles. However, such a trend was observed till the concentration of TiO_2 emulsion reached 3.35 g. Further increase in the concentration of TiO_2 led to decrease in degradation of the pollutant gases. Agglomeration of the TiO_2 particles could be the plausible cause of reduced degradation of NO_2 [38]. In this way, with the increase in number of TiO_2 particles, the obstruction in the passage of UV-A light takes place and lesser number of TiO_2 particles gets excited [39]. Similar behavior of the TiO_2 particles has also been reported in other photocatalysis-based studies, dealing with treatment of different types of contaminants, namely, bisphenol, hematoxylin, chloramphenicol, and paracetamol [40–45].

It has also been reported that overdosing of the TiO_2 particles lead to intershifting of charge among the ground state and activated particles [46]. In this way, lesser electrons and holes are available for generating the hydroxyl radicals [47]. Moreover, with larger concentration of the TiO_2 solution, the solvent may seep the particles deeper into the photocatalytic concrete where they could not get exposed to the UV-A light [48].

3.5. Impact of UV-A Irradiance. Response surface plots, as shown in Figure 5, clearly indicate that a significantly positive and quadratic association exits between the intensity of UV-A irradiance and the decontamination of pollutants. In present investigation, maximum decontamination of the NO_2 molecules was reported at 5 mW/cm^2 of UV-A irradiance. A prominent explanation is the increase in generation of free electrons and holes from the TiO_2 particles on increasing the intensity of UV-A irradiance [49, 50]. In this way, generation of hydroxyl molecules also increases which further enhances the oxidation of the NO_2 molecules [51].

It has been explained that when holes are stabled on reacting with pollutants at the catalyst's surface, a rather than a linear relationship between the degradation and UV-A irradiance exists [52]. However, in case of quadratic relation, opposite phenomenon exists and holes are filled largely by recombination of electrons [53]. In this case, lesser hydroxyl ions are generated which decreases the oxidation rate of pollutant gases [54]. In present investigation, impact of UV-A irradiance on the photocatalysis is supposed to follow the latter phenomenon.

3.6. Impact of Relative Humidity. Relative humidity inside the reaction chamber was also observed to impact the photocatalytic-concrete-assisted degradation of NO_2. As shown in Figure 5, the maximum degradation of NO_2 was achieved when RH of the reaction chamber was 64.60%. Also, as mentioned in Table 3, the decontamination process of the pollutants showed a significantly positive (p value >0.05) and quadratic relation with the RH of the reaction chamber. It was observed that with the increase in RH, till 64.60%, 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 photocatalytic concrete. In an enclosed reaction chamber,

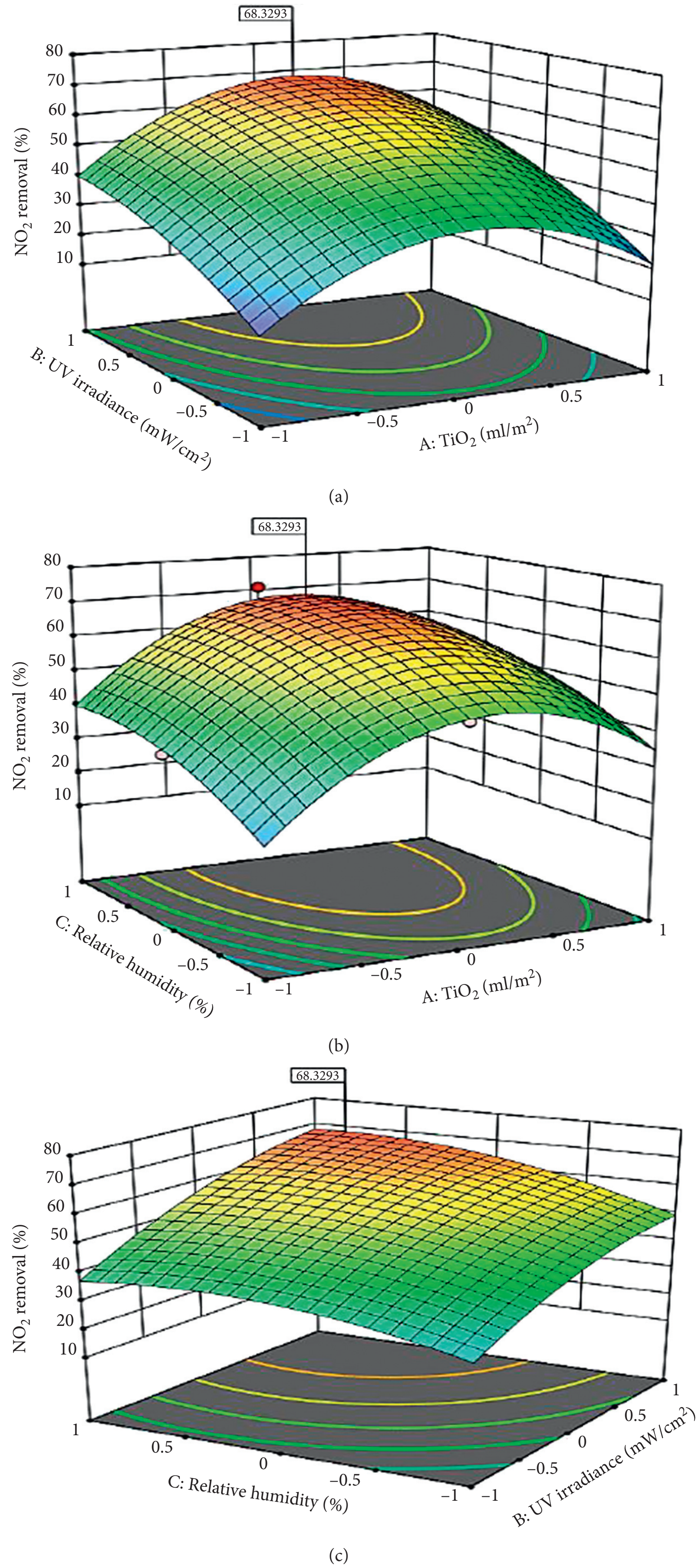

Figure 5: Response surface plots.

Table 4: 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_2 ($Y_1 = 68.32\%$)	
				Coded values	Actual values
1	Concentration of TiO_2	X_1	g	+0.175	3.35
2	UV-A irradiance	X_2	mW/cm^2	+1.00	5
3	Relative humidity	X_3	%	+0.82	64.60

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 [55]. This interaction between the TiO_2 particles and water molecules initiates the photocatalytic degradation of the NO_2 molecules. However, with the increase in RH, the number of layers of water molecules also increases on the TiO_2 particles [56]. Consequently, the interaction of TiO_2 particles with the gaseous molecules decreases and degradation 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 the following equations:

$$H_2O_2 + {}^*OH \longrightarrow HO_2^* + H_2O \quad (9)$$

$$HO_2^* + {}^*OH \longrightarrow H_2O + O_2 \quad (10)$$

In this way, the increase in RH of the reaction chamber, after a certain amount, leads to hindering the photocatalysis of the gaseous molecules. Therefore, in the present investigation, the maximum degradation of the gaseous pollutant was observed at RH = 64.60%. 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 photocatalytic-concrete-assisted degradation of air pollutants. Sleiman et al. (2009) and Rismanchian et al. (2014) also observed the photocatalytic degradation of toluene in the 20% to 80% of RH and reported that maximum degradation was achieved at RH = 40% [57, 58].

3.7. Applicability of Photocatalytic Concrete in Degrading Chandigarh's Ambient NO_2. Analysis of ambient air done at the five monitoring stations of Chandigarh, India, assisted in depicting the concentration of ambient NO_2. In the present study, analysis of the ambient air data of Chandigarh, India, was done from 2005 to 2015. This time duration was chosen on the basis of the availability of the data. Further, information of ambient NO_2 concentration was extracted, compiled, and analyzed. The results of this analysis are shown in Figure 6.

From Figure 6, it can be seen that data from all the five monitoring sites of Chandigarh, India, showed an increasing trend for the concentration of NO_2. However, among the five monitoring sites, the highest average-annual concentration of NO_2 was reported in the decreasing order of industrial area > Sector 17 > Sector 39 > Sector 12 > Kaimbala village. Monitoring sites located in Sector 17, Sector 39, and Sector 12 represent the commercial areas. In these areas, major source of pollution is vehicular emissions. Hence, it can be implied that in Chandigarh, India, the major contributors of NO_2 are emissions from industries and vehicles. These findings can be justified by the fact that Chandigarh has also been reported to have the highest vehicular density in India [23]. The number of registered vehicles (including two and four wheelers) in the study area was also reported to increase by almost 580% since 2005 [23]. Therefore, owing to the increasing vehicular emissions, the ambient air quality of the study area can be speculated to reduce in the coming years. In this regard, the duration was estimated, during which the ambient concentration of NO_2 would cross the regional permissible limits. It was revealed that by the year 2031, the ambient air concentration of the NO_2 in the study area is going to cross the concentration of 40 μg/m^3. However, in case Chandigarh's asphalt roads are replaced with TiO_2-laden concrete roads, its ambient concentration of NO_2 can be reduced to up to 5.80 μg/m^3. In this way, the duration, during which the ambient concentration of NO_2 is going to cross the permissible limits, can be extended and pushed further to 2112.

3.8. Assessing the Reusability. The reusability of the photocatalytic concrete was evaluated for five consecutive cycles. After each cycle, the surface of the photocatalytic concrete was cleaned with distilled water, washed with H_2O_2, and reused. The findings of this analysis are shown in Figure 7.

From Figure 7, it is evident that the photocatalytic concrete can be reused efficiently, for the degradation of NO_2, after treating it with distilled water. It can also be seen that with each cycle, efficiency of the photocatalytic concrete reduces by an average of 0.9%. After consecutive reuse of the photocatalytic concrete, for the five cycles, it was observed that, overall, 7.15% degradation efficiency was reduced. Therefore, it can be implied that the pavements made up of photocatalytic concrete can be reused efficiently for the degradation of NO_2 after washing with H_2O_2. These observations were also augmented by the findings of Gandhi et al. (2012), which compared the various regeneration treatment techniques [59].

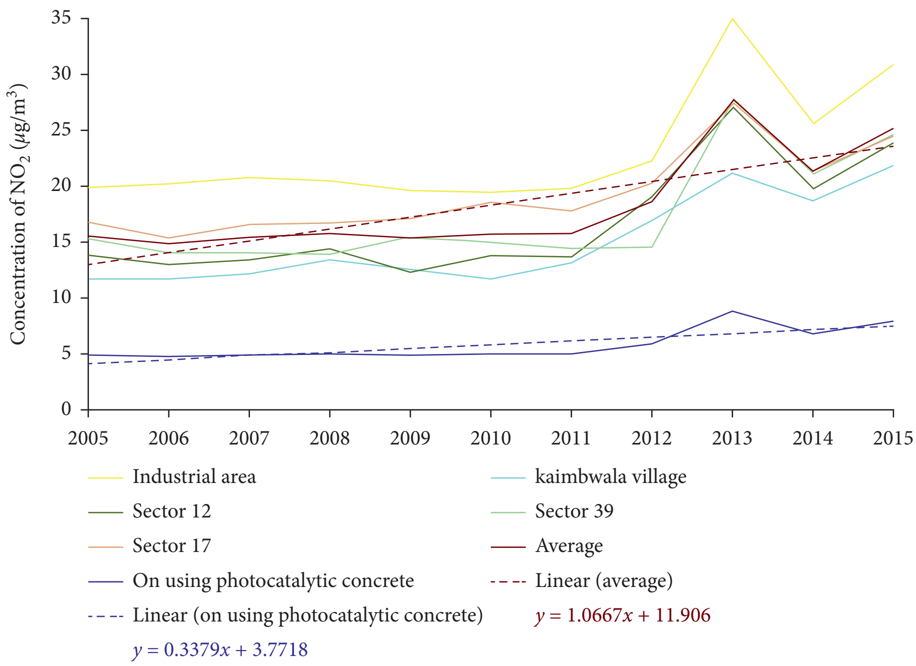

Figure 6: Ambient concentration of NO_2 in Chandigarh, India.

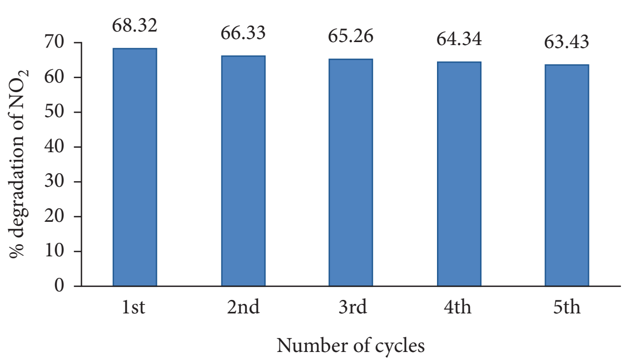

Figure 7: Efficiency of the photocatalytic concrete during five cycles of repeated use.

4. Conclusions

The findings of present study showed that roads made up of photocatalytic concrete can prove to be an efficient way of degrading the concentration of gaseous pollutants. Laboratory-based experiments performed by exposing the photocatalytic-concrete blocks to UV-A irradiance in an enclosed reaction chamber showed a significant reduction in the concentration of NO_2. RSM-based optimization revealed that at optimized conditions, 68.32% degradation of NO_2 could be achieved. Further, it was also estimated that concentration of NO_2 in ambient air of the Chandigarh, India, has substantially increased from 2005 to 2015. This unprecedented increase in NO_2 levels of the study area was attributed to vehicular emissions, and by 2031, it may also cross the regional permissible limit. However, replacing the asphalt roads of Chandigarh, India, with photocatalytic-concrete roads may extend this situation to 2112. Moreover, after five cycles, 7.15% reduction in the degradation efficiency of the photocatalytic concrete proved its applicability for long duration. Therefore, in the northern region of India where vehicular emissions are significantly contributing to the air pollution, TiO_2-based photocatalytic treatment of roads may prove to be an efficient approach. However, to understand the in situ application of the TiO_2-based photocatalytic degradation of air pollutants, it is recommended that a pilot-scale analysis should be done within the study area.

Data Availability

No data were used to support this study.

Conflicts of Interest

The authors declare no conflicts of interest.

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