Research Article

Simultaneous Photocatalytic Reduction of Cr(VI) and Oxidation of Benzoic Acid in Aqueous N-F-Codoped TiO₂ Suspensions: Optimization and Modeling Using the Response Surface Methodology

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The simultaneous photocatalytic reduction of Cr(VI) and oxidation of benzoic acid (BA) in aqueous suspensions using N-F-codoped TiO₂ and simulated solar irradiation were investigated in the present study. Chemometric optimization tools such as response surface methodology (RSM) and experimental design were used to model and optimize selected operational parameters of the simultaneous photocatalytic reduction of Cr(VI) and oxidation of BA. RSM was developed by considering a central composite design with three input variables, that are, N-F-codoped TiO₂ mass, ratio of Cr/BA, and pH. The removal of Cr(VI) and BA in binary systems, containing both Cr(VI) and BA, showed a synergistic photocatalytic decontamination as BA significantly facilitated Cr(VI) reduction, whereas Cr(VI) accelerated also BA degradation. Due to the anionic-type adsorption onto TiO₂ and its acid-catalyzed photocatalytic reduction, the removal of Cr(VI) decreased with increasing pH, while the degradation of BA followed also the same trend. Under the optimum conditions (N-F-TiO₂) = 600 mg L⁻¹, ratio of Cr(VI)/BA = 5, pH = 4, the removal for both Cr and BA followed a pseudo first-order kinetic model. It was found that the selected variables have significant effect both on Cr(VI) removal and BA degradation efficiency. The results revealed the feasibility and the effectiveness of using N-F-codoped TiO₂ as photocatalyst for simultaneous decontamination of Cr(VI) and organic pollutants such as BA due to the appropriate oxidation and reduction ability of the photogenerated h_{VB}⁺-e_{CB}⁻ pairs.

1. Introduction

The increasing level of global industrialization and urbanization has led to the transport and introduction of various contaminants in aquatic environment. The water pollution caused by organic pollutants and heavy metal ions represents an important ecological and health hazard and had gradually gained great scientific interest. Heavy metals enter aquatic environment through the discharge of treated or untreated industrial wastewater and municipal sewage, storm water runoff, acid mine drainage, and other diffuse sources [1]. On the other hand, a wide range of organic micropollutants are derived from a variety of agricultural, municipal, and industrial sources and pathways [2, 3].

Although, the co-existence of organic compounds and metal ions in wastewater is common [4], in conventional methods it is often indispensable to be treated separately, that means complicated process with the requirement of higher cost and more man power [5]. Hence, simultaneous decontamination of heavy metals and organic contaminants constitutes a very interesting and important aspect. In last decades, water pollution had resulted in the development of the so-called advanced oxidation processes (AOPs) as alternative to the conventional water and wastewater treatment methods. These enhanced processes aim to degrade the non biodegradable contaminants of water into harmless species [6]. Among AOPs, heterogeneous photocatalysis employing semiconductor solids has been applied with success for

the oxidation of a variety of organic compounds [7] as well as for the removal/reduction of toxic metals from aqueous solutions [8–10]. Photocatalysis is a well-known and particularly promising method based on the activation of a semiconductor and utilizes the photogenerated positive holes and various oxygen radical species for the oxidation of organic compounds as well as the photogenerated electrons for the reduction of heavy metal ions [11]. Moreover, photoreduction of a metal ion is promoted significantly if it is accompanied by simultaneous oxidation of an organic compound able to act as ligand or as “sacrificial electron donor” [12], because of the enhanced charge separation of photo-induced hole/electron pairs by the simultaneous reduction/oxidation reactions [11].

The application of experimental design methodologies in the development of photocatalytic processes can result in improved remediation efficiency with the lesser number of experiments. Response surface methodology is a powerful and widely used mathematical method suitable for modeling and optimizing chemical reactions and/or industrial processes [13].

In the present study, the simultaneous photocatalytic reduction of Cr(VI) and oxidation of benzoic acid (BA) using N-F-codoped TiO₂ under simulated solar irradiation was studied. Cr(VI) and BA were selected as target compounds since they may be present in a great variety of industrial waste effluents and their simultaneous treatment will show both economical and technological profits. Benzoic acid, the simplest aromatic carboxylic acid, is a model compound representative of the aromatic content typically found in various industrial wastewaters. It also constitutes the parent molecule of various phenolic compounds which are usually low biodegradable and high ecotoxic and are commonly found in agro-industrial effluents [14]. BA is used to produce a broad range of organic chemicals [15]. Furthermore, it has a wide usage as preservative in the cosmetic, drug, and food industry because of its antibacterial and antifungal properties at a pH 4 or lower [16]. Among heavy metals, Cr(VI) is one of the most frequent and toxic contaminants in wastewaters arising from various industrial processes such as electroplating, pigment production, leather tanning, textile dyeing, wood preservation, as well as finishing of metals and plastics [17, 18]. Due to its carcinogenic and mutagenic properties as well as its high mobility, its concentration in drinking water has been regulated in many countries [17]. It is considered to be highly toxic to most of the living organisms when the Cr(VI) concentration level is higher than 0.05 mg L⁻¹ [19]. As a result, the removal of Cr(VI) or its reduction to less harmful and immobile Cr(III) is of great importance. Several studies have reported the simultaneous decontamination of Cr(VI) and organic contaminants such as carboxylic acids, phenols, phthalates, and dyes [11, 20–25]. However, in the above-mentioned researches commercial forms of TiO₂ (anatase, Degussa P25) were used. On the contrary, this study investigates the application of N-F-codoped TiO₂, a photocatalyst with improved photo efficiency and visible light response compared to TiO₂ catalysts [26], for the simultaneous decontamination of organic pollutants and heavy metals. In addition, the

assessment of the beneficial role of N-F-doping for the synergistic removal of Cr(VI) and organic pollutants in aqueous substrates has not been performed so far. The main objectives of this research were (a) to assess the simultaneous removal of an organic micropollutant, benzoic acid, and a toxic heavy metal Cr(VI); (b) to investigate the effect of three parameters (initial ratio Cr/Benzoic acid concentration, pH, catalyst concentration) on the total process efficiency; (c) to model and optimize the photocatalytic procedure by means of a central composite design and response surface methodology.

2. Experimental

2.1. Materials and Reagents. Benzoic acid was residue analysis grade, purchased from Sigma-Aldrich (USA), and Cr(VI) in the form of potassium dichromate was purchased from Fluka and used without further purification. N-F-TiO₂ (Ti : N,F molar ratio 1 : 1, named as TNF) was prepared based on a simple sol-gel impregnation method [26]. Titanium n-butoxide [Ti(OC₄H₉)₄] was used as inorganic precursor and ammonium fluoride (NH₄F) as the source of N and F dopant atoms. X-ray diffraction analysis showed that the photocatalyst crystal phase is anatase with a crystallite size of ≈ 1.8 Å. A band-gap energy of 2.96 eV was determined using diffuse reflectance UV-Vis spectroscopy, while electron pair resonance revealed the presence of N_b[•] and Ti⁺³ photoactive centers. The point-of-zero charge (PZC) was determined at pH = 5.7 using the mass titration method [27]. All solvents used (acetonitrile, methanol and LC-grade water) were pesticide residue analysis grade from Merck (Darmstadt, Germany). HVLP 0.45 μ m filters were supplied by Millipore (Bedford, USA). Ultrapure water was obtained from a Millipore Waters Milli-Q water purification system.

2.2. Irradiation Procedure. Photocatalytic experiments were carried out in a Suntest XLS+ solar simulator (Atlas, Germany) equipped with a vapor xenon lamp (2.2 kW). The light source was jacked with special glass filters restricting the transmission of wavelengths below 290 nm. The temperature of the samples was maintained at 25°C using a tap water cooling circuit preventing any heating of the suspension. The irradiation intensity was measured by internal radiometer supplied by the manufacturer. Irradiation experiments were performed using a 250 mL Pyrex glass UV-reactor containing 250 mL of aqueous solutions at different pH. The pH of solutions was adjusted by H₂SO₄ or NaOH aqueous solutions. The solutions were mixed with the appropriate amount of catalyst and were magnetically stirred before and during the illumination. The suspensions were kept in the dark for 30 minutes, prior to illumination in order to reach adsorption equilibrium onto semiconductor surface. As the reaction progressed, aliquots of 5 mL were withdrawn from the reactor at specific time intervals for further analysis. In order to remove the N-F-TiO₂ particles the solution samples were filtered through a 0.45 μ m filter. Performance of the process was evaluated by analyzing the responses of Cr(VI)

removal and BA degradation percentages after a fixed time of 30 min according to the equation:

$$Y_1(\%) = \left[\frac{(C_0 - C_t)}{C_0} \right] * 100, \quad (1)$$

where C_0 is the initial Cr(VI) or BA concentration and C_t the concentration of Cr(VI) or BA after the photocatalytic treatment.

2.3. Kinetic Studies: Determination of Benzoic Acid and Cr(VI). Benzoic acid concentrations were determined by a Dionex P680 HPLC equipped with a Dionex PDA-100 Photodiode Array Detector using a Discovery C₁₈, (250 mm length $\times$ 4.6 mm ID; 5 μ m particle size) analytical column from Supelco (Bellefonte, PA, USA). The mobile phase was a mixture of LC-grade water H₂O (70%) at pH 3 (adjusted with formic acid) and acetonitrile (30%) with a flow rate of 1 ml/min. Column temperature was set at 40°C. The detection of BA was realized at 228 nm. The concentration of Cr(VI) was determined by the diphenylcarbazide colorimetric method [11] at a wavelength of 540 nm using a UV-Vis spectrophotometer (Hitachi, U-2000).

2.4. Experimental Design: Data Analysis. A central composite design was employed for the optimization of photocatalytic process in the present study. In order to evaluate the influence of operating parameters on the simultaneous photocatalytic efficiency of BA and Cr(VI), three main factors were chosen: catalyst concentration (mg L⁻¹) (x_1), Cr(VI)/BA ratio (x_2), and pH (x_3). A total number of 17 experiments were determined by the expression: $2^n + 2n + 3 = 2^3$ (8 factor points) + 2×3 (6 axial points) + 3 central points, replications) = 17, as shown in Table 1. The three selected experimental parameters were optimized using RSM considering them as independent variables and % Cr(VI) removal and % BA degradation as response variables. The data set obtained from CCD was used for the optimization of the responses and RSM was used to fit the experimental data. A second order model was used to locate the optimum point and can be expressed as follows:

$$Y = \beta_0 + \sum_{i=1}^k \beta_i x_i + \sum_{i=1}^k \beta_{ii} x_i^2 + \sum_{1 \leq i < j}^k \beta_{ij} x_i x_j + \varepsilon, \quad (2)$$

where Y is the response variable of degradation efficiency, β_0 is the constant term, β_i represents the coefficients of the linear parameters, x_i represents the variables, β_{ii} represents the coefficients of the quadratic parameters, β_{ij} represents the coefficients of the interaction parameters and ε is the random error [13]. Experimental data were analyzed using Design Expert V. 7.1.5 (Stat-Ease Inc. 2008, Mn, USA). Data were further estimated and evaluated by the analysis of variance (ANOVA). Correlation coefficients (R^2 , R^2 adj.) were used to evaluate the correlation between the experimental data and the predicted responses and thereby the goodness of the fit for the polynomial models. The statistical significance was also checked by the F value (Fisher variation ratio), probability P value and adequate precision

TABLE 1: Central composite design matrix and experimental results for benzoic acid (BA) and Cr(VI) photocatalytic degradation.

Exper. no.	C _{TiO₂-x₁} (mg L ⁻¹)	Cr/BA ratio-x ₂	pH-x ₃	(%) removal Cr(VI)	(%) degradation BA
1	200	5	10	32.36	2.5
2	600	15	4	55.22	49.47
3	400	1.59	7	100	17.5
4	400	18.41	7	36.41	32.78
5	600	5	10	54.95	5.1
6	600	5	4	100	36.61
7	400	10	1.95	58.9	47.84
8	400	10	7	45.96	9.49
9	200	5	4	76.16	23.07
10	200	15	10	4.58	6.56
11	400	10	12.05	4.85	2.79
12	200	15	4	24.06	30.34
13	400	10	7	45.57	8.18
14	63.64	10	7	18.85	2.7
15	736.36	10	7	65.82	17.24
16	400	10	7	47.44	8.66
17	600	15	10	32.92	12.08

in the same program. The significance of each model term was evaluated based on P value with 95% confidence level ($P > 0.05$). Finally, three-dimensional response surface plots were developed in order to visualize the individual and the interaction effects of the independent variables on degradation efficiency.

3. Results and Discussion

3.1. Preliminary Experiments. Preliminary experiments were carried out, before the development of the experimental design, in order to evaluate the possible synergistic effect of the simultaneous photooxidation-photoreduction of the selected pollutants, Cr(VI) and BA. For this reason, experiments were conducted in single and binary systems at pH = 2, catalyst concentration 500 mg L⁻¹ and UV intensity 750 W m⁻². The initial concentrations used were 0.1 mM Cr(VI) and 0.01 mM BA. Figures 1 and 2 show the reduction of Cr(VI) and oxidation of BA under different conditions, respectively. The adsorbed percentages of Cr(VI) and BA in the binary system were 12.5% and 6%, respectively, while prolonged dark experiments in the presence of N-F-TiO₂ led to neither BA degradation nor metal reduction after 240 min. Direct photolysis in the single systems of Cr(VI) and BA resulted in low removals for both pollutants. Similarly, low removal was observed for both pollutants in the binary system under photolytic treatment, implying no severe interaction between Cr(VI) and BA under direct photolysis. As shown in Figures 1 and 2, in single systems the photocatalytic reduction of Cr(VI) was achieved after 150 min irradiation, whereas the photocatalytic oxidation of BA was much slower and almost complete degradation is

FIGURE 1: Photocatalytic reduction of Cr(VI) in single and binary systems. ($[\text{Cr(VI)}]_0 = 0.1 \text{ mM}$, $[\text{BA}]_0 = 0.01 \text{ mM}$, $\text{pH} = 2$, $\text{N-F-TiO}_2 = 500 \text{ mg L}^{-1}$).

FIGURE 2: Photocatalytic degradation of benzoic acid in single and binary systems. ($[\text{Cr(VI)}]_0 = 0.1 \text{ mM}$, $[\text{BA}]_0 = 0.01 \text{ mM}$, $\text{pH} = 2$, $\text{N-F-TiO}_2 = 500 \text{ mg L}^{-1}$).

accomplished after 240 min of irradiation time. On the other hand, the simultaneous photocatalytic treatment of Cr(VI) and BA in the binary system significantly enhanced the reduction/oxidation of substrates each other. In the binary system, the coupled oxidation of the BA consumes photo-generated holes and/or $\cdot\text{OH}$ radicals efficiently, blocking the electron-hole recombination and thus, increasing the total efficiency. Moreover, the enhancement of the rates confirmed that Cr(VI) acted as an efficient scavenger of the photogenerated electrons. The results obtained, revealed not only the simultaneous decontamination of two pollutants but also the synergistic effect between the photocatalytic redox reactions.

3.2. RSM Modeling and Optimization for Cr(VI) Photocatalytic Removal. The design matrix and experimental

results obtained for the Cr(VI) photocatalytic degradation are depicted in Table 1. The step-wise model fitting was employed in order to find the best model fitted. The quadratic model was selected to describe the relationship of operational parameters and photocatalytic removal based on lack-of-fit analysis and model summary statistics. The quadratic model obtained for the response of % Cr(VI) removal in terms of coded variables can be written as follows (4):

$$\begin{aligned} \% \text{ Removal Cr (VI)} = & + 46.32 + 13.54x_1 - 18.57x_2 \\ & - 16.22x_3 + 1.63x_1x_2 - 0.51x_1x_3 \\ & + 5.88x_2x_3 - 1.41x_1^2 + 7.73x_2^2 \\ & - 5.11x_3^2. \end{aligned} \quad (3)$$

The model adequacy and significance were further checked by ANOVA and the results are shown in Table 2. The ANOVA of the second order quadratic polynomial model showed that the model was highly significant, as the F value for the model was 1841.56 and the corresponding P value was <0.0001 . This means that there was only a 0.01% chance for such model F value due to noise. The non significant lack of fit relative to the pure error also confirmed good predictability of the model. The experimental values plotted against the predicted responses for the degradation efficiency of Cr(VI) (Figure 3) showed good correlation $R^2 = 0.9996$ indicating that the model explained the experimental range studied very well. The high model regression coefficient implied that 99.96% of the variations for % Cr(VI) removal were explained by the model. As well, adjusted correlation coefficient of 0.9990 was also very high to advocate for a high significance of the model. The adequacy of the model was also evaluated by the residuals. The normal probability plot of the residuals, shown in Figure 4, revealed that all the points approximate a straight line proving no severe indication of non normality and a good fit of the model. This was also supported by the low value of the coefficient of variation ($\text{CV} = 1.84\%$). The significance of each term in the predictive model was evaluated by P values using 5% significance level. Independent variables of the quadratic model, N-F-TiO₂ concentration (x_1), Cr(VI)/BA ratio (x_2), pH (x_3), the second order effect of them, x_1^2 , x_2^2 , x_3^2 as well as the interaction between Cr(VI)/BA ratio (x_2) and pH (x_3) were highly significant parameters ($P < 0.001$). Moreover, the interaction between N-F-TiO₂ concentration (x_1) and Cr(VI)/BA ratio (x_2) was significant at $P < 0.05$. On the contrary, Cr(VI) removal was not significantly affected by the interaction between N-F-TiO₂ concentration (x_1) and pH (x_3) ($P = 0.1416$). The effects of the three independent variables and their interaction on the removal of Cr(VI) were graphically represented by three-dimensional response surface plots by means of response surface methodology. The interaction effect of N-F-TiO₂ concentration and Cr(VI)/BA ratio is shown in Figure 5(a). As can be seen there was an increase in the removal percentage of Cr(VI) with an increase of N-F-TiO₂ concentration and a decrease of Cr(VI)/BA

ratio. The removal percentage increased proportionally by the increase of N-F-TiO₂ dosage due to the increase of adsorption sites on the surface of catalyst as well as the generation of more electrons in the conduction band. An increase in the Cr (VI)/BA ratio by a consequently increase of initial Cr (VI) concentration led to a decreased removal. As initial Cr(VI) concentrations increased, more metal ions were adsorbed on the surface of the photocatalyst. Therefore, the photogenerated e⁻ required for the removal of Cr(VI) also increased and hence, the available electrons were inadequate for pollutant removal at higher concentrations. Moreover, with the increase in the Cr(VI) concentration, less photons reach the photocatalyst surface (light screening effect), resulting in slower production of the photogenerated pair hole/electron. Consequently, the photocatalytic activity was decreased, since fewer available e⁻ were available to reduce more metallic ions. Moreover, an increase in pH led to a decrease in the rate of Cr (VI) removal as illustrated in Figure 5(b). This can be attributed to the surface charge properties of the photocatalyst. Since, the point of zero charge of the NF-TiO₂ catalysts has been determined to be 5.7, the N-F-TiO₂ surface is negatively charged at pH > 5.7, whereas is positively charged in more acidic conditions (pH < 5.7). At pH values around 2.5 the predominant species of chromium are the negative charged HCrO₄⁻ and Cr₂O₇²⁻ ions and at pH values around 6.5 Cr(VI) exists mainly as HCrO₄⁻ and CrO₄²⁻ [24]. As the pH of the solutions increased, the negatively charged sites of the catalyst increased, thus, the absorption of Cr(VI) anions was prevented due to electrostatic repulsion and consequently their reduction on N-F-TiO₂ surface. The adsorbed percentage of Cr(VI) at pH = 10, Cr(VI)/BA ratio = 5, and [TNF] = 600 mg L⁻¹ was found to be 5%. Conversely, as pH decreased, the electrostatic attraction between the positively charged surface and anionic Cr(VI) was enhanced, leading to increased removal. The adsorption percentage (%) of Cr(VI) at pH = 4 and using the same Cr(VI)/BA ratio and catalyst concentration increased to about 21%. An increase in the Cr(VI) photocatalytic reduction with decreasing pH values has been also reported elsewhere [28, 29].

3.3. RSM Modeling and Optimization for Benzoic Acid Photocatalytic Degradation. The experimental design matrix and experimental results obtained for the BA photocatalytic degradation are given in Table 1. Similarly to % Cr(VI) removal, a quadratic model was suggested as the most appropriate to approximate the % photocatalytic degradation of BA. The model can be written in terms of coded variables as follows:

$$\begin{aligned} \% \text{Degr. Benzoic acid} = & +8.78 + 4.78x_1 + 4.16x_2 - 13.84x_3 \\ & + 1.06x_1x_2 - 3.07x_1x_3 - 1.14x_2x_3 \\ & + 0.40x_1^2 + 5.76x_2^2 + 5.82x_3^2 \end{aligned} \quad (4)$$

ANOVA results of the suggested quadratic model (Table 3) and the comparison of actual versus predicted values (Figure 6) indicated that the model could adequately

FIGURE 3: Plot of predicted versus actual values for % Cr(VI) removal.

FIGURE 4: The normal probability (%) plot of the experimental results for % Cr(VI) removal.

be used to describe the % benzoic acid degradation under the experimental range studied. The model *F* value of 426.95 and *P* value less than 0.0001 implied the high significance of the model. There was only a 0.01% chance that the “Model *F* value” could occur due to noise. Moreover, lack of fit was shown to be not significant relative to the pure error, indicating good response to the model. The high model regression coefficient (*R*²) of 0.9982 implied that 99.82% of the variability can be revealed by the model and only 0.18%

FIGURE 5: 3D response surface plots for % Cr(VI) removal; (a) as a function of N-F-TiO₂ concentration and Cr (VI)/BA ratio; (b) as a function of pH and N-F-TiO₂ concentration.

FIGURE 6: Plot of predicted versus actual values for % BA degradation.

FIGURE 7: The normal probability (%) plot of the experimental results for % BA degradation.

of residual variability remained. The R^2 of 0.9982 was in reasonable agreement with adjusted $R^2 = 0.9958$, indicating also good predictability of the model. A very high degree of precision and a good deal of reliability of the experimental values were indicated by the low value of the coefficient of variation ($CV = 5.48\%$). As can be observed from the residual plot in Figure 7 the data were normally distributed denoting too a good fit of the model. Using 5% significance

level, the independent variables of the quadratic model, N-F-TiO₂ concentration (x_1), Cr(VI)/BA ratio (x_2), pH (x_3), the second-order effects of Cr(VI)/BA ratio (x_2^2), and pH (x_3^2) as well as the interaction between ratio N-F-TiO₂ concentration (x_1) and pH (x_3) were highly significant parameters due to $P < 0.001$. Moreover the interactions between N-F-TiO₂ concentration (x_1) and Cr(VI)/BA ratio (x_2) and between Cr(VI)/BA ratio (x_2) and pH (x_3) were significant at $P <$

FIGURE 8: 3D response surface plots for the % BA degradation; (a) as a function of N-F-TiO₂ concentration and Cr(VI)/BA ratio; (b) as a function of pH and N-F-TiO₂ concentration.

TABLE 2: Analysis of variance (ANOVA) for % removal of Cr(VI).

Source	Sum of squares	df	Mean square	F value	P value Prob > F
Model	12510.88	9	1390.10	1841.56	<0.0001
x_1 -TiO ₂ mg L ⁻¹	2504.00	1	2504.00	3317.23	<0.0001
x_2 -Cr/BA ratio	4710.52	1	4710.52	6240.35	<0.0001
x_3 -pH	3593.50	1	3593.50	4760.57	<0.0001
$x_1 x_2$	21.35	1	21.35	28.29	0.0011
$x_1 x_3$	2.07	1	2.07	2.74	0.1416
$x_2 x_3$	276.95	1	267.95	366.89	<0.0001
x_1^2	22.49	1	22.49	29.79	0.0009
x_2^2	674.33	1	674.33	893.34	<0.0001
x_3^2	294.43	1	294.43	390.05	<0.0001
Residual	5.28	7	0.75		
Lack of fit	3.34	5	0.67	0.69	0.6829
Pure error	1.95	2	0.97		

TABLE 3: Analysis of variance (ANOVA) for % degradation of benzoic acid.

Source	Sum of squares	df	Mean square	F value	P value Prob > F
Model	3908.5	9	434.28	426.95	<0.0001
x_1 -TiO ₂ mg L ⁻¹	311.69	1	311.69	306.43	<0.0001
x_2 -Cr/BA ratio	236.80	1	236.80	232.80	<0.0001
x_3 -pH	2616.02	1	2616.02	2571.86	<0.0001
$x_1 x_2$	9.05	1	9.05	8.90	0.0204
$x_1 x_3$	75.34	1	75.34	74.07	<0.0001
$x_2 x_3$	10.33	1	10.33	10.15	0.0153
x_1^2	1.77	1	1.77	1.74	0.2284
x_2^2	374.00	1	374.00	367.69	<0.0001
x_3^2	382.08	1	382.08	375.63	<0.0001
Residual	7.12	7	1.02		
Lack of fit	6.24	5	1.25	2.84	0.2805
Pure error	0.88	2	0.44		

0.05. On the contrary, the second-order effect of N-F-TiO₂ concentration (x_1^2) was the only insignificant term (P value of 0.2284). Three-dimensional response surfaces computed for % BA degradation are depicted in Figure 8. As shown in Figures 8(a) and 8(b) the degradation percentage increased proportionally to N-F-TiO₂ concentration as expected, confirming the positive influence of the increased number of N-F-TiO₂ active sites/species (mainly holes and $\bullet$ OH) on the process kinetics. Several studies have indicated that photocatalytic degradation rate initially increased with catalyst loading and above a certain level of concentration, the reaction rate remains constant or even decreases and becomes independent of the catalyst concentration because of light scattering and screening effects as well as due to the

tendency towards agglomeration at high solids concentration [30, 31]. However, this study was based on the use of moderate catalyst concentrations, where this limit was still far away, and thereby the degradation rate increased with NF-TiO₂ concentration within the selected range. From the response surface in Figure 8(b), it was clear that the BA degradation percentage decreased as the pH values increased from acidic to alkaline region. This is related to the ionization state of the surface of catalyst according to the determined PZC (5.7) as well as to that of the parent compound. The pKa of benzoic acid is 4.2 [32] thus, at a pH greater than this value the molecule bears a negative charge. As mentioned above, N-F-TiO₂ surface will be positively charged at pH values

FIGURE 9: Kinetics of reduction of Cr(VI) and degradation of BA versus irradiation time under optimized conditions ($[N-F\ TiO_2]_0 = 600\ mg\ L^{-1}$, Cr(VI)/BA ratio = 5, pH = 4).

TABLE 4: Photocatalytic kinetic parameters (rate constants, half-lives, correlation coefficients) of Cr(VI) and BA under optimized conditions ($[N-F\ TiO_2]_0 = 600\ mg\ L^{-1}$, Cr/BA ratio = 5, pH = 4).

	$k\ (min^{-1})$	$t_{1/2}\ (min)$	R^2
Cr(VI)	0.0960	7.219	0.9929
BA	0.0109	63.578	0.9623

lower than 5.7 and negatively charged at higher ones. In consequence, as the pH increased from slightly acidic (5.7–6) to alkaline values, Columbic repulsion between the negative-charged surface of the catalysts and anionic form of BA was observed which led to decreased adsorption and consequently lower degradation. The adsorbed percentage of BA at pH = 10, Cr(VI)/BA ratio = 5, and $[TNF] = 600\ mg\ L^{-1}$ was found to be only 0.5%. An increase in the degradation rate of BA was also observed with an increase in the Cr(VI)/BA ratio (Figure 8(a)). As the Cr(VI) concentration increased, the recombination of the photo-induced hole/electron pairs was strongly inhibited, as the electrons were scavenged by Cr(VI), enhancing the BA degradation. The numerical optimization of the software using desirability approach was employed to find the specific points that maximize the % removal for both pollutants. Based on the models, the optimum conditions for simultaneous removal of Cr(VI) and BA were found as follows: N-F-TiO₂ concentration = $600\ mg\ L^{-1}$, Cr(VI)/BA ratio = 5, and pH = 4.

3.4. Model Validation and Confirmation—Evolution of Photocatalytic Reduction of Cr(VI) and Oxidation of Benzoic Acid under Optimized Conditions. To confirm the adequacy of the models for predicting the maximum simultaneous % removal Cr and % degradation of BA, verification experiments were conducted using the optimum conditions. The removal and degradation rates from the validation experiment are depicted in Figure 9. Under optimized conditions pseudo-first order kinetics were recorded for both the photocatalytic reduction of Cr(VI) and degradation of BA.

Table 4 lists the values of apparent rate constants, k_{app} , the correlation coefficients and the corresponding half-lives of Cr(VI) and BA. Half of Cr(VI) concentration was consumed within 7.22 min of irradiation under optimal conditions, while BA exhibited a much slower rate than the removal of Cr(VI). Complete Cr (VI) removal was achieved after 30 min of irradiation time. At the same time, the degradation of BA reached about 40%, and prolonged irradiation time was needed before complete degradation was achieved. As reported in the literature, the photocatalytic transformation products of BA using TiO₂ included salicylic acid, p-hydroxybenzoic acid, and 2,3- and/or 2,5-dihydroxybenzoic acid and phenol. The photocatalytic degradation pathway proceeds via $\cdot OH$ attack on the aromatic moiety on several positions to produce hydroxy and dihydroxy derivatives, via decarboxylation (photo-Kolbe) reaction resulting from the direct attack of the carboxylic group by $h\nu_{VB}^+$ and finally ring opening to produce aliphatic acids [15, 32, 33]. The formation of such by-products reacts also with $h\nu_{VB}^+ / \cdot OH$ resulting in a more prolonged time for the degradation of parent benzoic acid.

According to previous findings [26] N-F-codoping of TiO₂ enhances the oxidative power of the $h\nu_{VB}^+$ but lessens the reduction ability of e_{CB}^- . This unveils the use of such photocatalytic materials to control the photocatalytic reactions of the redox pair species, e_{CB}^- and $h\nu_{VB}^+$. Regarding the reduction process, the electrons of the N-F-TiO₂, at states below the CB of TiO₂, have weaker reduction ability, consequently they can reduce preferably strong oxidation agents such as Cr(VI) enhancing the target reduction reaction without the competence of other ineffective reactions for reduction, such as O₂ reduction. As far as the oxidation pathway, the enhancement in the oxidation power of the $h\nu_{VB}^+$ makes the oxidation of organic molecules and especially organic acids and water (for the $\cdot OH$ production) more favourable and consequently enables the reduction reaction to occur more efficiently.

4. Conclusions

The simultaneous photocatalytic reduction of Cr(VI) and oxidation of benzoic acid in the presence of N-F-codoped TiO₂ was investigated focusing on the influence of parameters such as catalyst concentration, Cr(VI)/BA ratio, and pH on the photocatalytic efficiency that was optimized and modeled by response surface methodology (RSM). A considerable enhancement of the photocatalytic efficiency was observed for the binary system than in the single component systems, indicating a promoting synergistic effect. Also, it was noted that the three parameters tested had significant effect on the total efficiency. Under optimized conditions the removal for both Cr(VI) and BA followed pseudo-first order kinetic model. The results provide an efficient treatment method to remove organic and inorganic pollutants simultaneously in complex systems which presents special significance to water pollution control and remediation. Moreover, this study proves that RSM constitutes a powerful tool for optimizing the operational conditions of the simultaneous reduction

of Cr (VI) and oxidation of benzoic acid by photocatalytic processes.

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