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Application of response surface methodology for optimization of operational variables in photodegradation of aqueous styrene under visible light

Narjes Keramati[a,*], Narges Fallah[b], Bahram Nasernejad[b]

[a]*Department of Nanotechnology, New Science and Technologies Paradise, Semnan University, Semnan 35131-19111, Iran, Tel. +98 2333383922; Fax: +98 2333654281; email: narjeskeramati@semnan.ac.ir*
[b]*Chemical Engineering Department, Amirkabir University of Technology, P.O. Box 15875-4413, Tehran, Iran, Tel. +98 2164543200; Fax: +98 2166405847; emails: nfallah2001@aut.ac.ir (N. Fallah), banana@aut.ac.ir (B. Nasernejad)*

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ABSTRACT

In this study, the center composite design in response surface methodology was firstly applied to optimize the photocatalytic degradation of aqueous styrene under visible light. Twenty experiments were done by adjusting three parameters (initial concentration of styrene, concentration of catalyst and initial pH of reaction mixture) at five levels by the method of multiple variable analyses. Based on the experimental design, an empirical expression was firstly established and subsequently applied to predict the photocatalytic degradation efficiency of aqueous styrene under visible light. The results showed that the experimental photocatalytic degradation efficiencies are in accordance with the theoretically predicted values very well with a high correlation. The strongest interaction between the parameters assessed was concentration of catalyst /initial pH of mixture. Optimal experimental conditions for arbitrary aqueous styrene concentration of 115 mg L^{-1} were found initial pH 6.8 and catalyst loading 2 g L^{-1}. The photocatalytic degradation efficiency of aqueous styrene under this condition reached to about 84%. Furthermore, the main degradation intermediate produced in this process was identified by GC/MS technique. The photocatalytic mineralization of styrene in aqueous solution has been studied by TOC.

Keywords: Aqueous styrene; Photocatalytic degradation; Visible light; Design of experiment

1. Introduction

Styrene is a volatile aromatic compound and widely used as petrifaction material for many industrial applications such as resin, plastic and medicine. However, styrene will damage human beings and the environment once it is released into the wastewater. According to the Clean Air Amendment of USEPA, styrene is listed among the 189 hazardous pollutants [1].

Elimination of toxic and bio resistant organic pollutants from industrial waste water by their transformation into nonhazardous species is a demanding area of research. Traditional waste water treatment methods have some limitations and disadvantages. Biochemical treatment is slow and requires control of proper pH and temperature along with the problem of disposal of activated sludge. Adsorption involves phase transfer of pollutants without decomposition, which induces another pollution problem [2,3].

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*Corresponding author.

Heterogeneous photocatalysis has been the subject of a vast amount of studies related to environmental abatement in both liquid and gas phase environments. This is essentially based in the excellent performance of titanium dioxide, the most prominent photocatalytic material, for the mineralization of typical pollutants, including refractory or non-biodegradable molecules, under mild conditions, e.g. room temperature and atmospheric pressure [4–6]. However, this wide band gap semiconductor has one key limitation. It is not activated by visible light in the pristine state and research into "visible sensitization" of TiO_2 has been intensive in recent years. It shows good activity in visible light after N-doping [7–10].

Some literatures attributed the photocatalytic degradation of styrene under UV irradiation [11–13] but it was not found in the open literature work that is specifically about photocatalytic degradation of styrene under visible light. Also, no statistical study about photocatalytic degradation of styrene under visible light by design of experiment has been related. The aim of this paper was to optimize the photocatalytic degradation of styrene under visible light using response surface methodology (RSM) based on the central composite design (CCD). RSM is nowadays, a promising as well as a powerful tool for multivariate optimization through sequential experimentation [14,15]. Other aspects of this work were (i) to identify the possible intermediate products by gas chromatography coupled to mass spectrometry, (ii) to investigate the total organic carbon (TOC) removal in order to explain the mineralization of aqueous styrene under visible light.

2. Experimental

2.1. Chemicals and reagents

N-TiO_2 as photocatalysis was prepared via impregnation method from TiO_2 and possibility of cyclic usage of it was investigated according to our previous work [16]. As was mentioned in our previous report [16], nitrogen atoms were successfully doped into the lattice of TiO_2, and N-doped TiO_2 exhibited strong absorption in the visible light range with a red shift in the band gap transition. The results of XPS spectra indicated that the chemical environments of doping nitrogen were N-Ti-O. Styrene with above 99.5% purity was obtained from Merck. All other reagents were of analytical grade, and all the water used was deionized.

2.2. Photocatalytic degradation procedures and analysis

A photochemical reactor was set up according to our previous work [16]. Styrene concentration in the liquid phase was estimated using the headspace method by gas chromatography system (Younglin). The oven temperature of the GC was maintained at 70°C for 1 min and raised to 140°C at the rate of 10°C min^{-1}. The temperatures of the injector and the detector were fixed at 200 and 240°C, respectively. This system was equipped with a helium ionization detector and a 50 m long capillary column. The analysis of intermediates formed along the reaction was carried out by gas chromatography coupled to a mass selective detector (Mass Model 5975 N/Agilent Technology GC 7890). Also, TOC was measured on filtered suspensions using a Shimadzu TOC-5000 analyzer.

2.3. Response surface methodology

Analysis of the experimental data was supported by the statistical graphics software system Design Expert® (Version 7.3.1). A RSM based on the CCD was used to determine the optimum conditions for photocatalytic degradation of aqueous styrene. It has been demonstrated by several authors that catalyst dosage, initial concentration of the target compound, light intensity, oxygen concentration, temperature, and pH for aqueous phase photoreactions were the main parameters affecting the degradation rate in the photocatalytic system [17]. However, it is quite difficult to carry out an experimental design including all these factors because of the large number of experiments and complex data analysis required. Therefore, in this study, the most important factors were chosen from preliminary experiments in which the three following factors namely pH, N-TiO_2 loading, concentration of styrene were retained. These parameters were investigated as well as the interactions between them. The determined values of them are presented in Table 1.

Twenty experiments were implemented on the base of CCD. Percent degradation efficiency of aqueous styrene achieved after 60 min of reaction was chosen as design response factor.

In addition, the relationship between the photocatalytic degradation efficiency of styrene and the above mentioned parameters was also discussed based on the experimental results. The complete experimental design matrix and the responses are shown in Table 2.

3. Results and discussion

3.1. Model establishment and analysis

Based on the experimental results listed in Table 2, an empirical expression in Eq. (1) which is consisted of 10 statistically significant coefficients is obtained in terms of coded factors and expressed as follows:

Table 1
Values and levels of chosen variables for CCD

Variable	Symbol	Coded levels				
		–α (–1.68)	−1	0	+1	+α (+1.68)
Styrene Concentration (mg L^{-1})	A	30.91	65	115	165	199.09
N-TiO_2 Concentration (g L^{-1})	B	0.12	0.6	1.3	2	2.48
Initial pH of mixture	C	1.64	3	5	7	8.36

Table 2
Experimental design matrix and the value of responses based on experiment runs

Run	Independent variables			Degradation efficiency after 60 min (%)
	A	*B*	*C*	
1	115	1.3	1.64	59.1
2	115	1.3	5	77.8
3	65	0.6	7	72
4	65	2	7	92.8
5	115	2.48	5	75.1
6	115	1.3	5	78.3
7	165	0.6	7	38.7
8	115	0.12	5	50.2
9	65	2	3	73.2
10	115	1.3	5	78.3
11	65	0.6	3	78
12	199.09	1.3	5	61
13	115	1.3	5	74.8
14	165	2	7	72.4
15	115	1.3	5	78
16	165	0.6	3	58.4
17	30.91	1.3	5	92.9
18	115	1.3	8.36	65
19	115	1.3	5	78.1
20	165	2	3	59.9

$$
\begin{aligned}
Y = 77.51 - 11.64A + 7.33B + 1.71C + 1.53AB \\
- 3.47AC + 8.10BC + 1.28A^2 - 5.01B^2 - 5.22C^2
\end{aligned}
\tag{1}
$$

where Y is the response variable of degradation efficiency of styrene and the variables A, B, and C represent three experimental factors, respectively. This model explains perfectly the experimental range studied, as can be seen from the comparison of the graphical representation of experimental vs. predicted values (Fig. 1).

Table 3 displays the analysis of variance of the quadratic model, which is also required to test the significance and adequacy of the model. It is indicating that the model is significant, as the F-value of it is 315.13 and the corresponding p-value is <0.0001. This means that, there is only a 0.01% chance of occurrence of model F-value because of noise. The lack of fit F-value of 0.53 is not significant as the p-value is 0.7649. For a model to be successfully used for prediction, the lack of fit should be not significant. Moreover, adjusted R^2 is very close to the corresponding R^2 value, which further confirms the adaptability of this model.

From these results, it can be concluded that the obtained model is adequate to descript the relationship between the degradation efficiency and three factors for degradation of aqueous styrene under visible light.

3.2. Response surface plots and optimal conditions

The three–dimensional response surface plots are constructed by using the statistical software to illustrate the interaction effects of selected factors on the

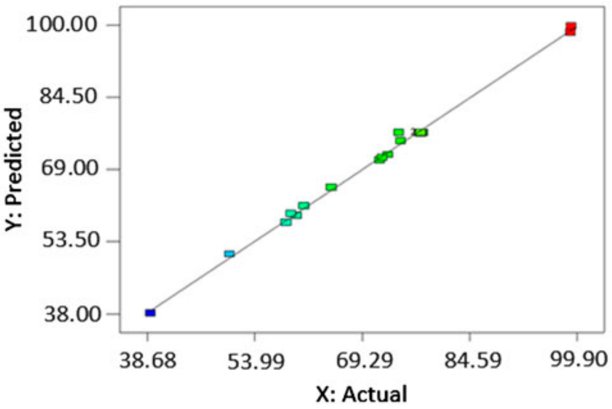

Fig. 1. Correlation between the predicted and experimental degradation efficiencies of styrene.

degradation efficiency and finally find out the optimal conditions. Each curve represents an infinite number of combinations of the two selected variables with the other maintained at its respective zero coded level.

In Fig. 2, the response surface plots of the degradation efficiency of styrene for the three pairs of factors are displayed under our experimental conditions: initial concentration of styrene vs. N-TiO_2 concentration, AB (Fig. 2(a)), N-TiO_2 concentration vs. initial pH of mixture, BC (Fig. 2(b)) and initial concentration of styrene vs. initial pH of mixture, AC (Fig. 2(c)).

Fig. 2(a) exhibits the interaction effect of initial concentration of styrene and N-TiO_2 concentration (initial pH of mixture = 5). The results revealed that the rate of degradation of styrene decreased with increase in concentration irrespective of the dose of catalyst. By increasing the initial concentration of styrene, higher amounts of reactant and reaction intermediates are adsorbed at the surface of the photocatalyst. Therefore, the requirement of reactive species ($^{\cdot}OH$ and $^{\cdot}O_2^-$) needed for the degradation of styrene also increases. However, the formation of $^{\cdot}OH$ and $^{\cdot}O_2^-$ on the catalyst surface remains constant for a given light intensity, catalyst amount and duration of irradiation. Hence, the available $^{\cdot}OH$ radicals are inadequate for the styrene degradation at higher concentrations. Consequently the degradation rate of styrene decreases as its concentration increases. Similar results were reported by others and usually attributed to the limited amount of active sites available for the adsorption of reactant at higher concentration [18–21].

Fig. 2(b) shows the interaction effects of the initial pH of reaction mixture and catalytic dose on the rate of degradation of styrene (styrene concentration = 115 mg L^{-1}). The saddle nature of the plots confirms that a significant interaction exists between these two factors (BC) [22]. According to our experiment, N-TiO_2 exhibits amphoteric behavior in aqueous media. The point of zero charge (pzc) of it was obtained about 6.2. This means that the surface of the catalyst is positively charged at $pH < pH_{pzc}$, negatively charged at $pH > pH_{pzc}$, and remains neutral at $pH = pH_{pzc}$. Such a behavior significantly affects not only the adsorption–desorption properties of N-TiO_2 surface, but also the changes of the pollutant structure at various pH values. Thus, adsorption of cationic and anionic styrene is favored at pH values above and below the PZC of catalyst, respectively. Meanwhile, in the alkaline solution there is repulsion between the negatively charged surface of photocatalyst and the hydroxide anions. This repulsion could prevent the formation of $^{\cdot}OH$ and thus decrease the rate of photo oxidation. At high acidic pH, the adsorption was relatively low. This effect is due to N-TiO_2 particle agglomeration that reduces styrene adsorption and photon absorption at low pH values.

It can be seen that the degradation efficiency increases with increasing catalyst dosage and then decreased. The enhancement in degradation rate as a result of photocatalyst loading is due to the ready availability of total surface area and active sites of the photocatalyst. Increased loading of the catalyst increases the generation rate of electron/hole pairs and thus, formation of $^{\cdot}OH$ radicals leading to the enhancement of photo degradation. A reduction in degradation rate was obviously observed at photocatalyst overdose

Table 3
ANOVA for the response surface quadratic model

Source	Sum of squares	Degree of freedom	Mean square	*F*-value	*p*-value
Model	4,023.06	9	447.01	315.13	<0.0001 significant
Residual	14.18	10	1.42		
Lack of fit	4.93	5	0.99	0.53	0.7649 not significant
Pure error	9.25	5	1.85		
Total	4,037.24	19			

Notes: $R^2 = 0.997$, Adjusted $R^2 = 0.993$.

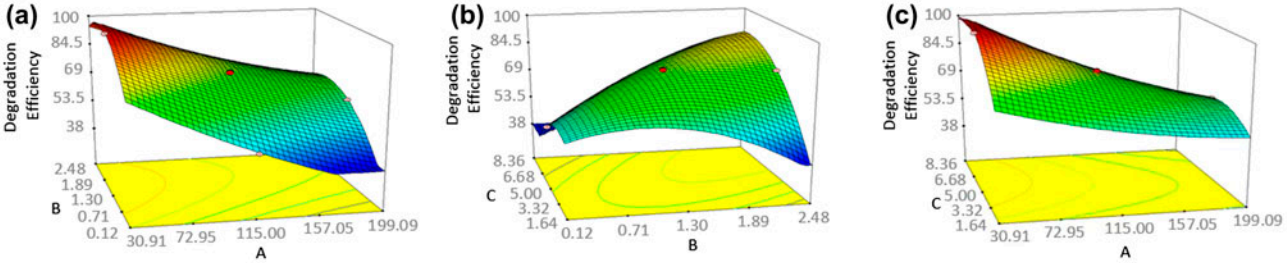

Fig. 2. The response surface plots of degradation efficiency of styrene by N-TiO$_2$: (a) styrene concentration vs. N-TiO$_2$ concentration, (b) N-TiO$_2$ concentration vs. pH, and (c) styrene concentration vs. pH.

due to the opacity caused by excess photocatalyst clusters. The presence of these clusters then reduces visible light penetration and increases the scattering effect. Results from extensive studies have demonstrated that the rates of photo degradation for pollutants are strongly affected by the number of active sites and the photo–absorption ability of the catalyst used [23–25].

The most suitable conditions to have a high degradation efficiency are mild acidic pH (5.0) and catalyst concentration comprised about 2 g L^{-1}.

The interaction effect of the initial pH of reaction mixture and the initial concentration of styrene on its degradation efficiency is shown in Fig. 2(c) (N-TiO$_2$ loading = 1.3 g L^{-1}). As can be seen from Fig. 2(c), the highest degradation efficiency is obtained when the styrene concentration is kept at its minimum. Furthermore, the degradation efficiency slightly increased with the increase in pH up to 5 and then slightly decreased. In the other word, in our experiments, the highest degradation was achieved at mild acidic pH (5.0).

At pH 5.0, most of the styrene remains undissociated, hence the maximum numbers of styrene molecules are adsorbed on the N-TiO$_2$ surface and consequently result in enhanced photodegradation. At high acidic pH (1.62), the adsorption was relatively low. This effect is due to N-TiO$_2$ particle agglomeration that reduces styrene adsorption and photon absorption at low pH values. On the other hand, in the alkaline solution there is repulsion between the negatively charged surface of photocatalyst and the

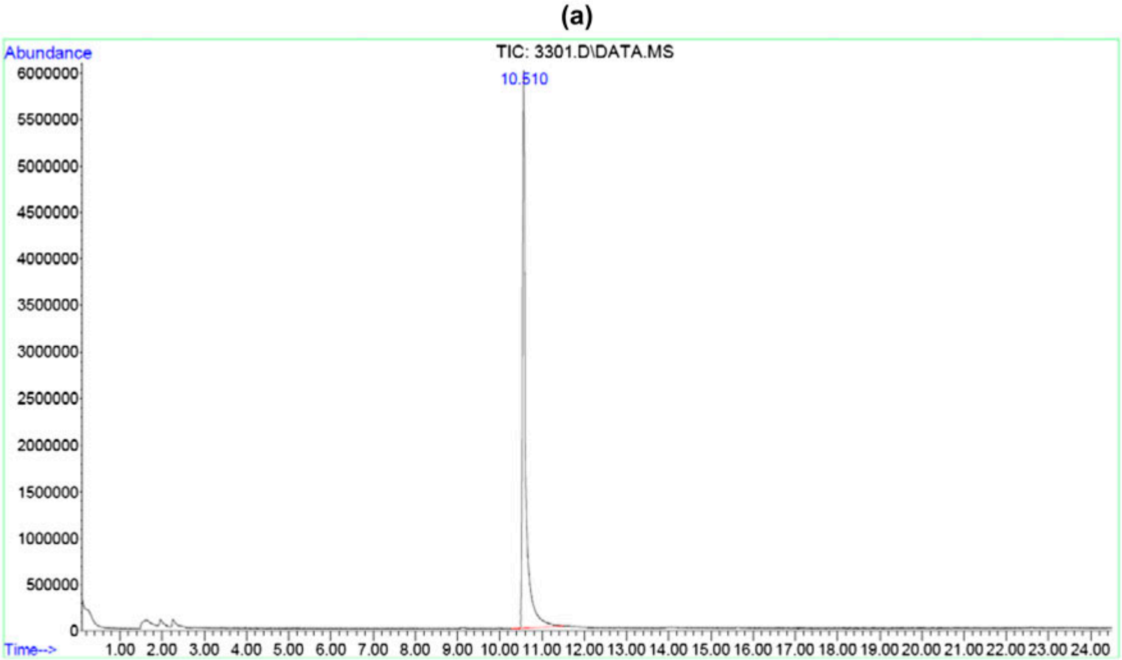

Fig. 3. Mass spectrometry profiles of styrene and its oxidative intermediates corresponding to the solutions after being degraded under visible light for different times: (a) Before irradiation, (b) after 90 min irradiation, and (c) after 240 min irradiation.

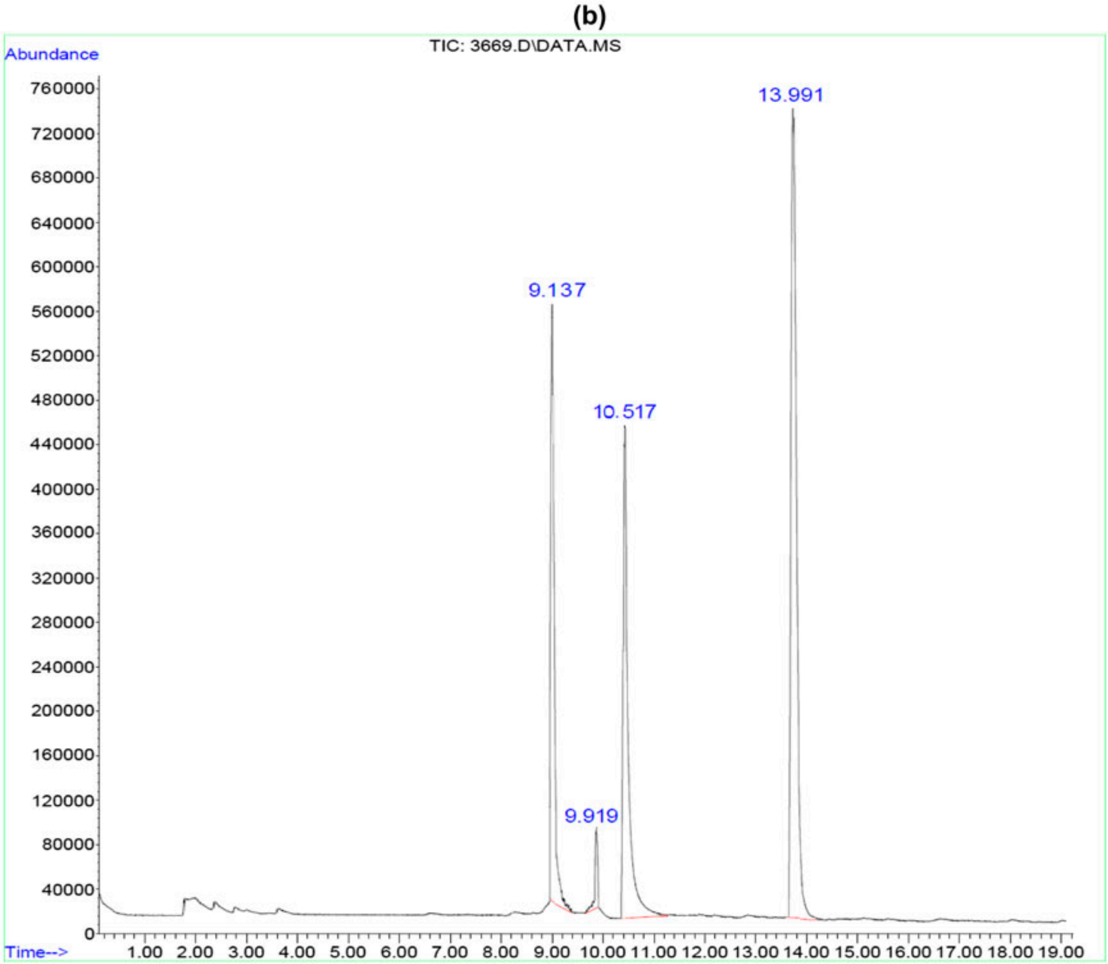

Fig. 3. (*Continued*).

hydroxide anions. This repulsion could prevent the formation of ·OH and thus decrease the rate of photo oxidation [18].

3.3. *Optimization of independent variables*

Overall, the main objective of this study is to effectively obtain the optimal conditions of parameters for the highest photocatalytic degradation efficiency of aqueous styrene under visible light based on the experimental results. Based on the design model, numerical optimization was carried out using Design Expert software and the optimal conditions for degradation of aqueous styrene at an arbitrary value of 115 g L^{-1} within the experimental ranges were 2 g L^{-1} N-TiO_2 and pH 6.8. The photocatalytic degradation efficiency of aqueous styrene using N-TiO_2 under optimal conditions reached about 84%.

3.4. *Model validation and confirmation*

Validation experiment was carried out at the optimal conditions to check the accuracy of the model. Styrene concentration was chosen at an arbitrary value of 115 mg L^{-1}, pH was set at a value of 6.8 and N-TiO_2 concentration was 2 g L^{-1}. The degradation efficiency was found out from the validation experiment to be 85%. It was in good agreement with the predicted result, which confirms the adequacy and validity of the model simulating the degradation of aqueous styrene under visible light.

In order to investigate main intermediates, mineralization of photocatalytic degradation of aqueous styrene under visible light/N-TiO_2 system, the obtained optimal conditions (N-TiO_2 2 g L^{-1}, initial pH of reaction mixture 6.8 and initial concentration of styrene 115 mg L^{-1}) were used to carry out photocatalysis experiments.

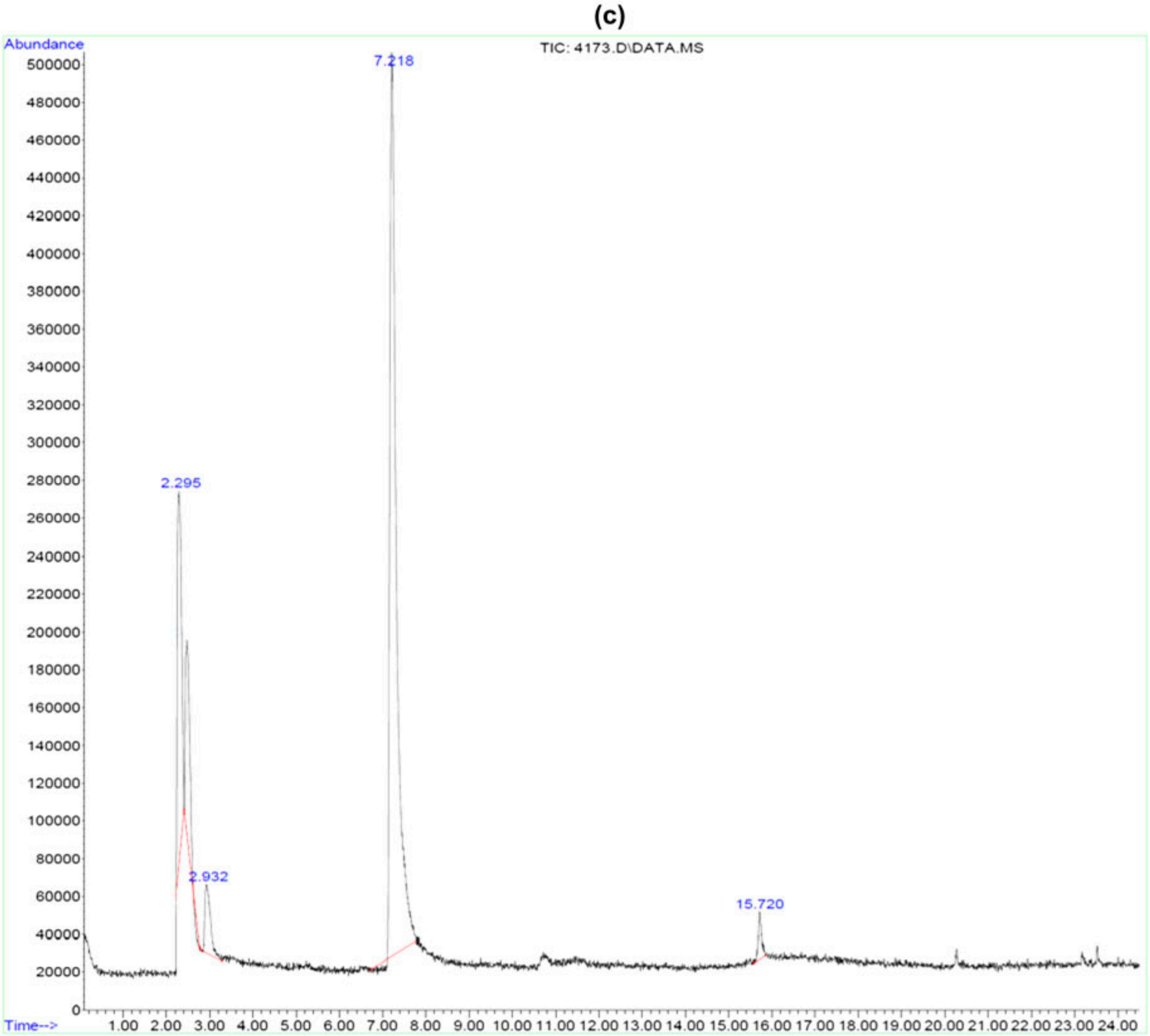

Fig. 3. (*Continued*).

3.4.1. The main intermediate of photocatalytic degradation at optimal conditions

Photocatalytic degradation processes proceed via radical–induced reactions through complex parallel consecutive pathway of intermediate products. The reactions involved either oxidation by the ·OH radical or reduction by conduction band electrons [26]. The possible intermediate was identified by GC/MS according to the m/z fragment distribution of chemical structure.

Fig. 3 reports the chromatogram of the solution before and after photocatalytic degradation for different times. Before visible light irradiation, it can be seen that there exists only one peak corresponding to the styrene at $m/z = 104$ and appeared at the retention time of 10.5 min in GC spectrum. After 90 min of visible light irradiation, the main absorption peak of styrene decreased a lot and three additional fragment peaks corresponding to new intermediate byproducts appeared of $m/z = 106$, 91, and 102. After 240 min visible irradiation, it is found that four new peaks are clear observed and peak of styrene was not detected.

The main intermediate of styrene photocatalytic degradation under visible light was benzaldehyde after 90 min and acetic acid after 240 min. Peak of styrene after 240 min was not detected. In other word, photocatalytic degradation of aqueous styrene under visible light was completed after 240 min. Further increasing the irradiation time, these compounds can decompose to lower molecular weight by-production by the attack of oxidative species (·OH and $\cdot O_2^-$). A previous study [19] on the intermediates generated

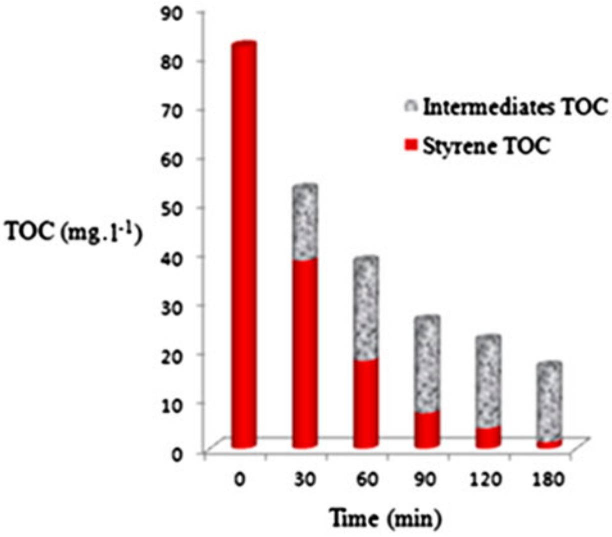

Fig. 4. Extent of mineralization by TOC.

in the photocatalytic oxidation of toluene (as a VOC) also identified benzaldehyde as one of the main intermediates.

3.4.2. Mineralization assessment at optimal conditions

TOC analysis provided valuable information about the efficiency of the photocatalytic process. The destruction of organic pollutants should be regarded as an overall degradation process that ultimately involves mineralization of both the parent substance and its intermediates. In this study, the mineralization of aqueous styrene under visible light was investigated using TOC analysis. The results are presented in Fig. 4 and revealed that concentrations of the main reaction intermediates rise initially and attain maximum values, but then decline and styrene degrades into small fragments as irradiation time increases [27].

According to the previous discussion, when styrene concentration is decreased, larger numbers of active sites and hydroxyl radicals become available to react with styrene and intermediates. The TOC removal was 80% at the end of 180 min of degradation. Indeed, the mineralization rate is rapid at the beginning but becomes much slower at longer time because carboxylic acids formed by oxidative ring opening reactions are less reactive toward hydroxyl radicals compared to the aromatics [28].

4. Conclusion

The photocatalytic degradation of styrene in an aqueous solution under visible light using an experimental design methodology was firstly studied. The initial pH of reaction mixture, N-TiO$_2$ loading and styrene concentration were systematically evaluated via the center composite design based on RSM. An empirical expression was proposed and successfully used to model the photocatalytic process with a high correlation, and an optimal experimental region was also obtained through the response surface plots.

From the quadratic models developed for degradation and subsequent ANOVA test using Design Expert software, the strongest interaction between the parameters assessed was concentration of N-TiO$_2$ /initial pH of mixture. The optimum values of the variables were found out as dose of N-TiO$_2$ 2 g L^{-1} and initial pH of reaction mixture 6.8 for initial arbitrary concentration of styrene 115 mg L^{-1}. Under the optimal conditions, the aqueous styrene degradation efficiency was predicted to be about 84% and the corresponding experimental value fitted well to the predicted value. Furthermore, the GC/MS results revealed after 90 min, benzaldehyde and after 240 min, acetic acid formation during styrene photocatalytic degradation under visible light as main intermediates. Results of TOC indicated that almost 80% mineralization of styrene is achieved in 180 min.

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