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Modelling and optimization of photocatalytic mineralization of acetaminophen using $ZnFe_2O_4$-TiO_2nanocomposite prepared via microwave assisted combustion method

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Abstract

Present work focuses on microwave assisted synthesis of $ZnFe_2O_4$-TiO_2 nanocomposite and its application for photocatalytic mineralization of acetaminophen (one of the most widely used analgesic drugs) in water under visible light illumination. The synthesized $ZnFe_2O_4$-$TiO_2$was characterized using x-ray diffractometry and scanning electron microscopy.The effects initial concentration of acetaminophen, $ZnFe_2O_4$-TiO_2dosage, and irradiation time on photocatalytic mineralization of acetaminophen were investigated using the central composite design. Photocatalytic mineralization of acetaminophen using $ZnFe_2O_4$-TiO_2 was described by a model quadratic equation with $R^2$of 0.993 and $R^2_{adj}$of 0.984. Under the optimized conditions (initial acetaminophen concentration of 11.2 mg/L, $ZnFe_2O_4$-TiO_2dosage of 1.0 g/L and irradiation time of 28.7 min), 95.9 % mineralization of acetaminophen was achieved. Experiments were conducted in order to validate the model. Under the predicted optimized conditions, the experimental percentage photocatalytic mineralization of acetaminophen was found to be 95.9 % which is very close to the predicted value of 96.3%.

1. Introduction

Occurrence of pharmaceutical products in water bodies poses serious threats to public health. Some of the adverse health effects caused by pharmaceutical products include: resistance development in pathogens, aquatic toxicity, genotoxicity, endocrine disruption,etc [1, 2]. Pharmaceutical products enter water bodies through direct disposal into water bodies, excretion by human beings and animals, and inadequate treatment of industrial effluents. Moreover, some pharmaceutical products are not biodegradable; therefore, they cannot be efficiently treated using conventional water treatment technologies. Acetaminophen is among the most frequently used analgesic drugs worldwide. However, about 58 to 68 % of acetaminophen is excreted from the human body after use [3].

Photocatalysis is an emerging technique for effective treatment of recalcitrant water pollutants and pathogens [4, 5]. Among various photocatalysts, TiO_2 has received the greatest attention because it has high photocatalytic activity under UV irradiation, chemical stability, non-toxicity, and relatively low cost. However, the large band gap (3.2 eV) of TiO_2 makes it inefficient for solar photocatalysis. To reduce the band gap and increase the photocatalytic activity of TiO_2, various strategies are being developed. The strategies include: coupling with other semiconductors, doping with metals and nonmetals, etc [6]. Moreover, it is very difficult to recover TiO_2 powders after photocatalytic treatment of water due to the high dispersive properties of TiO_2 powders [7]. Hence, there is the need to develop photocatalysts which can be easily separated after photocatalytic treatment of water [7, 8].$ZnFe_2O_4$ is a semiconductor with a bandgap of about 1.9 eV which exhibits good photochemical stability and magnetism [9]. However, $ZnFe_2O_4$alone is seldom used as a photocatalyst because it has low valence band potential [10]. $ZnFe_2O_4$has been coupled with other semiconductors such as TiO_2, to produce composite photocatalysts which can be readily activated by visible light and separated from treated water using magnets [10-13]. Thanks to the magnetic property of $ZnFe_2O_4$, $ZnFe_2O_4$-TiO_2 nanocomposite can be easily separated after photocatalytic treatment of water using an external magnet. Various techniques have been used to prepare $ZnFe_2O_4$-TiO_2nanocomposite [9,11,12, 14]. However, to the best of our knowledge, $ZnFe_2O_4$-TiO_2nanocomposite has never been prepared via microwave combustion method in spite of the several advantages of the microwave assisted method [15,16].

It shall be noted that photocatalysis involves chemical oxidation of the acetaminophen molecules, to generate several intermediates [17]. Hence, one of the best ways to assess the performance of a photocatalyst is by measuring the organic loading of the raw and treated water using lump parameters such as the Chemical Oxygen Demand (COD). Most of the published research works on photocatalytic treatment of acetaminophen monitor degradation of acetaminophen using either UV-Vis spectroscopy or high performance liquid chromatography [18-22]. Present work was aimed at microwave assisted synthesis of $ZnFe_2O_4$-TiO_2nanocomposite and its application for photocatalytic mineralization of acetaminophen in water under visible light illumination. Central composite design (CCD) based on the statistical Response Surface Methodology (RSM) was used to investigate the effects of three independent variables, namely, initial concentration of acetaminophen, $ZnFe_2O_4$-TiO_2dosage, and irradiation time on the photocatalytic process. The process variables were also optimized to maximize photocatalytic mineralization of acetaminophen using the synthesized of $ZnFe_2O_4$-TiO_2nanocomposite.

2. Material and Methods

2.1. Microwave assisted synthesis and characterization of $ZnFe_2O_4$-TiO_2nanocomposite

Analytical grade reagents were used in the work. The procedure reported by Feng et al., [16] for the synthesis of $ZnFe_2O_4$-ZnO nanocomposite was adopted and modified for the synthesis of $ZnFe_2O_4$-TiO_2nanocomposite. Briefly, 2.97 g of $Zn(NO_3)_2 \bullet 6H_2O$, 8.07 g of $Fe(NO_3)_3 \bullet 9H_2O$ and 0.94 g of polyethylene glycol, 3.6 g of TiO_2 were mixed with 18 mL of distilled water; 28 mL of sodium acetate solution (0.5 g/mL) was added into the solution. The solution was heated in a microwave oven for 5 min at 120 W, and then for 10 min at 700 W. The resulting solid product was washed with water and ethanol. $ZnFe_2O_4$-TiO_2powder was obtained after drying. The mole ratio of $ZnFe_2O_4$ to TiO_2 in the nanocomposite is 1:15. The XRD pattern of the synthesized $ZnFe_2O_4$-TiO_2 nanocomposite was recorded using a powder x-ray diffractometer (Shimadzu, model 6000) with Cu K radiation (40 kV, 40 mA) at Bragg angles ranging from 10◦to 80◦. The morphology of the $ZnFe_2O_4$-TiO_2nanocomposite was analysed using Phenom Pro-X desktop scanning electron microscope.

2.2. Photocatalytic experiments

The desired amount of the photocatalyst ($ZnFe_2O_4$-TiO_2nanocomposite) was added into 100 mL of the aqueous solution of acetaminophen of the desired concentration, and magnetically stirred for 60 minutes in the dark in order to reach adsorption-desorption equilibrium (We found that dark adsorption of acetaminophen onto $ZnFe_2O_4$-TiO_2nanocomposite reaches equilibrium within 50 minutes regardless of the initial concentration of acetaminophen). The suspension was then exposed to visible light supplied by a 500W halogen lamp for the desired period of irradiation time. Analytical samples were taken at various irradiation times. The samples were filtered and subjected to COD analyses using standard method [23]. Mineralization of acetaminophen was calculated using Equation 1.

$$Mineralization = \frac{(COD_0 - COD_t)}{COD_0} \times 100\% \qquad (1)$$

where COD_t is the COD of acetaminophen remaining in the solution after irradiation time, t, and COD_0 is the COD of acetaminophen solution before irradiation.

Two control experiments were performed: purely dark adsorption (in the presence of 1 g/L of $ZnFe_2O_4$-$TiO_2$and absence of light) and photolysis (under illumination by the 500W halogen lamp in the absence of $ZnFe_2O_4$-TiO_2). For the two control experiments, the initial concentration of acetaminophen was 10 mg/L. Photocatalytic experiment was carried out under similar conditions ($ZnFe_2O_4$-TiO_2dosage of 1g/L, initial concentration of acetaminophen of 10 mg/L, under illumination by 500W halogen lamp).

The effects of three independent variables, namely initial concentration of acetaminophen (A), $ZnFe_2O_4$-TiO_2dosage (B), and irradiation time (C) on the photocatalytic mineralization of acetaminophen were investigated using the central composite design (CCD) as implemented in the Design Expert version 6.0.6 software (Stat-Ease, USA). The dependent variable (response) of the process was chosen to be the photocatalytic mineralization as defined by Equation 1. The choice of CCD out of the numerous available designs was informed by it is popularity, reliability and its general acceptance as a standard second-order design [24]. **Table 1** shows the ranges of the studied independent variables for photocatalytic mineralization of acetaminophen solution in water using $ZnFe_2O_4$-TiO_2nanocomposite under visible light illumination. Twenty experimental runs were carried out.

Table1: Ranges of the actual values of the studied independent variables.

Independent variable (unit)	Abbreviation	Lower limit	Higher limit
Initial concentration of acetaminophen (mg/L)	A	4.8	18
$ZnFe_2O_4$-TiO_2 dosage (g/L)	B	0.1	1.0
Irradiation time (min)	C	15	60

3. Results and discussion

The XRD pattern of the synthesized $ZnFe_2O_4$-TiO_2composite is shown in **Figure 1**. The sharp XRD peaks of the anatase phase of TiO_2 were observed at Bragg angles of 24.9°, 3.8°, 48.0°, 53.9° and 57.4° (JCPDS card No 78 – 2486). The peaks at 18.3°, 29.8°, 35.3°, 42.8°, 53.1°, 56.7°, 62.5°, 70.6° and 74.6° correspond to $ZnFe_2O_4$ (JCPD card No 74-2397). The broadness of the XRD peaks can be attributed to the low crystallinity of the prepared composite [16]. The morphological characteristics of the synthesized $ZnFe_2O_4$-TiO_2nanocomposite were investigated by Scanning Electron Microscopic (SEM) analysis. The SEM image of $ZnFe_2O_4$-TiO_2nanocomposite displayed in **Figure 2** shows that the $ZnFe_2O_4$-TiO_2nanocomposite exhibits a compact arrangement of the particles. Most of the particles are aggregated which makes it difficult to determine the exact shape of the particles. **Figure 2** shows that the dimensions of the particles at some points are as little as 65.6 nm. Therefore, the synthesized $ZnFe_2O_4$-$TiO_2$is a nanocomposite [25].

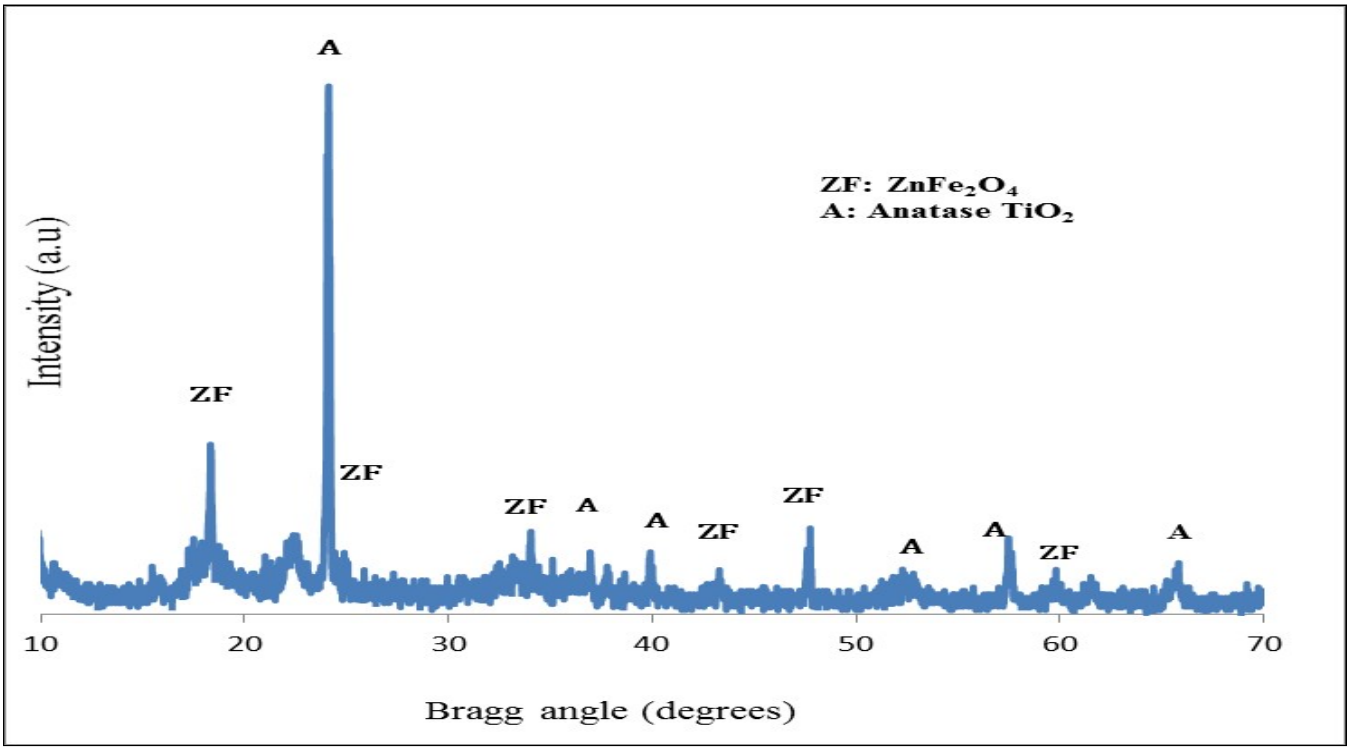


Figure 1: XRD pattern of the $ZnFe_2O_4$-TiO_2 nanocomposite

The results of the control experiments show that only 4% of acetaminophen was mineralized via photolysis (photochemical decomposition in the absence of any photocatalyst) under visible light illumination for 60 minutes. Hence, acetaminophen is fairly stable to visible light. Indeed, photolysis of acetaminophen is very low at wavelengths greater than 350 nm [22]. One hour of adsorption of acetaminophen onto $ZnFe_2O_4$-TiO_2 nanocomposite in the dark resulted in the removal of 35% of the initial amount of acetaminophen from its aqueous solution. This result implies that, under the experimental conditions employed, at equilibrium, only 35% of acetaminophen is adsorbed on the surface of $ZnFe_2O_4$-TiO_2because the adsorption-desorption equilibrium is established after 50 minutes.

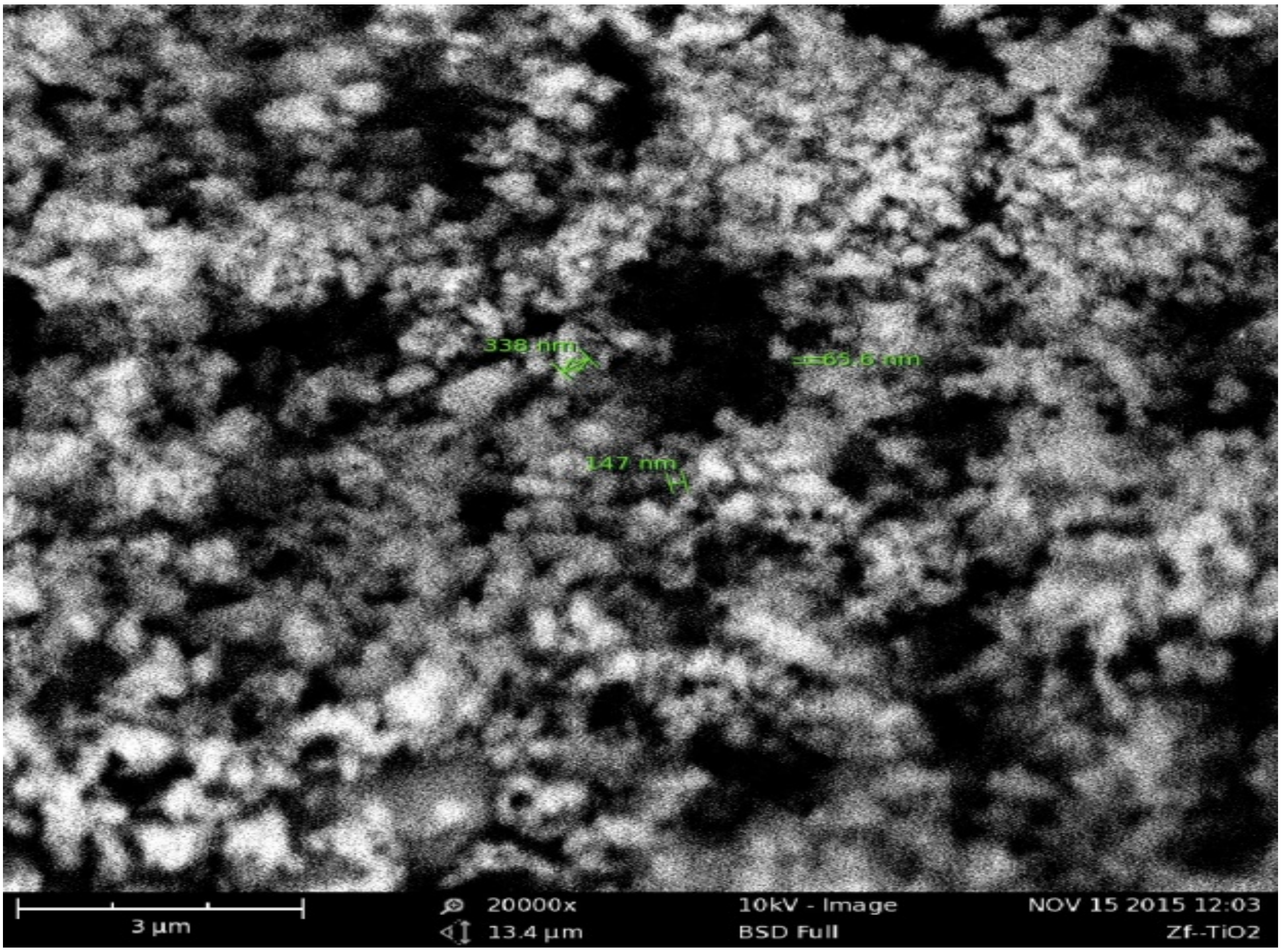


Figure 2: SEM image of the $ZnFe_2O_4$-TiO_2 nanocomposite

Table 2 shows the central composite design matrix and experimental values of the response that were used to determine the effects of the three independent variables (presented in **Table 1**) on photocatalytic mineralization of acetaminophen. By fitting the experimental data to various models (linear, two factorial, quadratic and cubic) and their analysis of variance (ANOVA) using the Desing Expert software, it was found that the photocatalytic mineralization process is best described by a quadratic model which is represented (in actual factors) by **Equation 2** :

$$Mineralization=-6.916+11.590*A+22.092*B+1.393*C-0.530*A^2-0.0687B^2-0.0153*C^2-0.395*AB+0.002*AC-0.175BC \qquad (2)$$

In order to determine the suitability of the quadratic model equation to describe the photocatalytic mineralization process, an analysis of variance (ANOVA) was conducted. The results of the ANOVA are presented in **Table 3**, from where it is seen that the model equation is significant with F-value of 99.80. A p-value of less than 0.05 indicates that a given model and/or model parameters are significant.

Here, the quadratic model equation is significant with p-value less than 0.0001; while the lack of fit is insignificant with p-value of 0.1640. Non significance of lack of fit indicates good predictability of the model [26]. The high values of the correlation coefficients ($R^2 = 0.993$, $R^2_{adj} = 0.984$) indicate that the experimental data fitted the quadratic model equation very well. The Adeq Precision ratio of 32.504 indicates good signal for the experiments since Adeq Precision ratio greater than 4 is desirable in experiments [27]. As apparent in **Table 3,** the significant model parameters (with p-values of less than 0.05) are A, B, C, A^2 and C^2. The interactions of variables (AB, BC and AC) are insignificant with p-values greater than 0.05.

Table 2: Central composite design matrix and experimental values of the response for photocatalytic mineralization of acetaminophen using $ZnFe_2O_4$-TiO_2 nanocomposite.

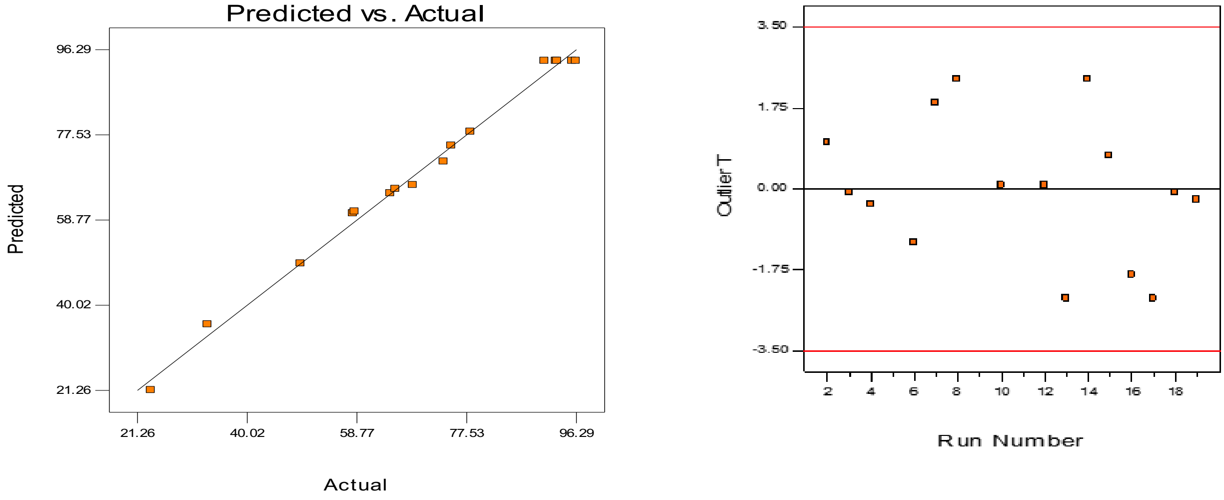
Run	Independent variables			Response
	A	B	C	Mineralization (%)
1	11.40	0.55	37.50	62.96
2	0.30	0.55	37.50	96.29
3	4.80	1.00	15.00	75.00
4	11.40	0.55	0.34	92.86
5	4.80	0.10	60.00	64.58
6	18.00	0.10	15.00	90.91
7	18.00	1.00	15.00	73.68
8	11.40	0.55	75.00	68.42
9	4.80	1.00	60.00	96.00
10	11.40	1.31	37.50	78.26
11	11.40	0.55	37.50	41.38
12	18.00	0.10	60.00	49.23
13	18.00	1.00	60.00	58.18
14	11.40	0.21	37.50	23.65
15	22.50	0.55	37.50	95.65
16	11.40	0.55	37.50	58.49
17	11.40	0.55	37.50	33.33
18	11.40	0.55	37.50	65.45
19	11.40	0.55	37.50	93.10
20	4.80	0.10	15.00	81.82

Table 3: Analysis of variance of the quadratic model for photocatalytic mineralization of acetaminophen using $ZnFe_2O_4$-TiO_2 nanocomposite.

Source	Sum of Squares	DF	Mean Square	F Value	Prob> F	Remark
Model	7150.15	9	794.46	99.8	< 0.0001	Significant
A	191.25	1	191.25	24.02	0.0027	Significant
B	125.92	1	125.92	15.82	0.0073	Significant
C	144.91	1	144.91	18.2	0.0053	Significant
A^2	6086.33	1	6086.33	764.54	< 0.0001	Significant
B^2	0.0006	1	0.0002	0.0001	0.9935	Insignificant
C^2	685.6	1	685.6	86.12	< 0.0001	Significant
AB	7.13	1	7.13	0.9	0.3804	Significant
AC	0.25	1	0.25	0.031	0.8662	Insignificant
BC	16.14	1	16.14	2.03	0.2043	Insignificant
Residual	47.76	6	7.96			
Lack of Fit	28.42	2	14.21	2.94	0.164	Insignificant
Pure Error	19.34	4	4.84			

$R^2 = 0.993$; $R^2_{adj} = 0.984$

The experimental photocatalytic mineralization of acetaminophen (actual values of the response) was plotted against the theoretical responses obtained from the quadratic model equation (predicted values of the response) in **Figure 3a**.



(a) **(b)**

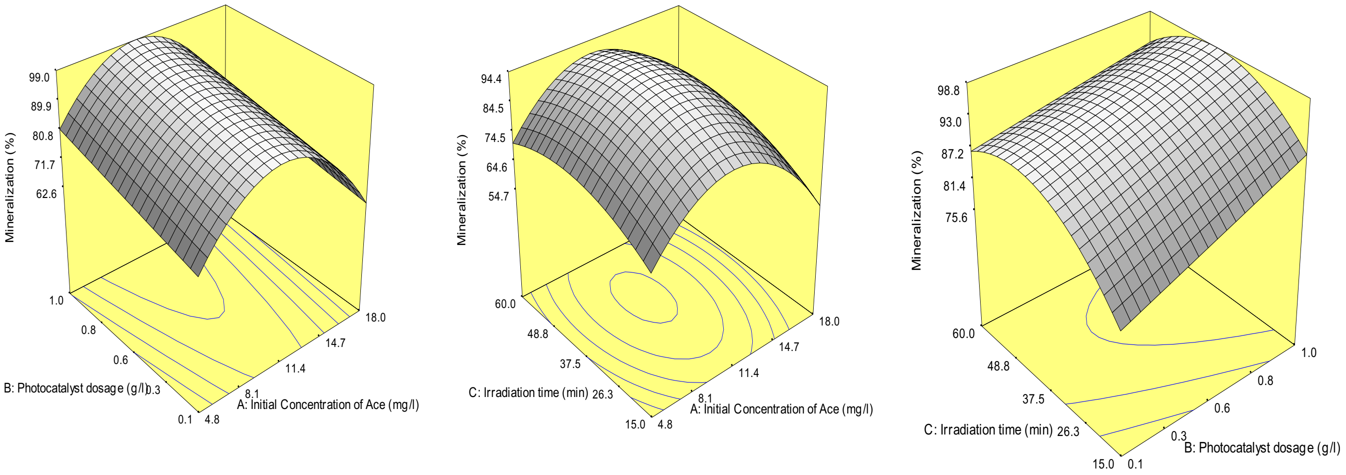
Figure 3: Diagnostic plots for photocatalytic mineralization of acetaminophen showing (a) actual vs. predicted values of photocatalytic mineralization of acetaminophen, and (b) internally outlier T points.

From where it is seen that there is a good agreement between the actual and the predicted values; this indicates reliability of the quadratic model equation. From the outlier plots depicted in **Figure 3b**, it can be seen that all the standardized residuals are in the range of -3.50 to +3.50. Hence, the quadratic model equation does not have significant data recording errors [27].

The three-dimensional response surface plots which show the relationship between the photocatalytic mineralization of acetaminophen and the three process variables are presented in **Figure 4**. **Figures 4a** and **4c** show that the percentage mineralization increases with increase in the photocatalyst dosage. The higher the amount of photocatalyst used, the more generation of the oxidizing species (hydroxyl radicals) for mineralization of the substrate [17]. If the photocatalyst dosage were too high, the excess amount of the photocatalyst will hinder light penetration into the suspension to activate the photocatalyst. This will lead to decrease in the amount of the active sites on the photocatalyst and subsequent decrease in the rate of the photocatalytic process [3, 22].

As shown in **Figures 4a** and **4b**, the percentage mineralization of acetaminophen increased as the initial concentration of acetaminophen was increased from 4.8 to 11.4 mg/L, and then decreased with further increase in the initial concentration. Under a fixed amount of photocatalyst, the probability of photochemical reaction between molecules of acetaminophen and hydroxyl radicals increases with increase in the initial concentration of acetaminophen. This leads to the observed increase in the percentage mineralization of acetaminophen when the initial concentration of acetaminophen was increased from 4.8 to 11.4 mg/L. Moreover, resistance to mass transfer at lower concentrations of acetaminophen (below 11.4 mg/L) may also contribute to the observed trend [28]. The efficiency of photocatalysis often decreases with increase in the initial concentration of a given substrate because high initial concentration of substrate makes it difficult for photons to penetrate the suspension and reach the photocatalyst surface to initiate a chemical reaction [28, 29]. Moreover, as the initial concentration of the substrate increases, the photocatalyst surface becomes saturated at a faster rate, thereby hindering adsorption of hydroxyl ions. This results in a decrease in generation of reactive hydroxyl radicals for subsequent photocatalytic mineralization. Thus, Zhou et al. [28] reported an increase in photocatalytic degradation of Orange G dye with increase in the initial concentration of the dye up to 10 mg/L; further increase in the in the initial concentration of the dye resulted in drastic decrease in photocatalytic degradation [28]. Similar observations were also made by Sohrabi and Akhlaghian[29].

The effect of irradiation time of acetaminophen on the mineralization process was studied by varying its irradiation time from 15 to 60 min. As apparent in **Figures 4b** and **4c**, photocatalytic mineralization of acetaminophen increases with increase in irradiation time up to about 40 minutes. Thereafter, the process becomes slower. This observation may be attributed to formation of various intermediates which occupy the surface of the photocatalyst at higher irradiation time, thereby competing with the molecules of acetaminophen in the photocatalytic process [30].



(a) (b) (c)

Figure 4: 3D response surface plot for photocatalytic mineralization of acetaminophen showing the simultaneous influence of (a) photocatalyst dosage and initial concetration of acetaminophen; (b) initial concetration of acetaminophen and irradiation time; (c) photocatalyst dosage and irradiation time.

Numerical optimization was performed in order to find the optimum values of the three process variables for the photocatalytic mineralization of acetaminophen. The process variables were assigned within the studied range reported in **Table 1**; while the percentage mineralization was to be maximized. Under the set constraints, the Design-Expert software found 96.3 % as the optimum percentage photocatalytic mineralization of acetaminophen. The optimized values of the process variables are: initial acetaminophen concentration of 11.2 mg/L, photocatalyst dosage of 1.0 g/L and irradiation time of 28.7 min. To validate the theoretical results, confirmatory experiments were conducted using the optimized values of the process variables. The experimental percentage photocatalytic mineralization of acetaminophen is 95.9 % which is very close to the predicted value of 96.3 %. This validates the developed model quadratic equation. Hence, the central composite design can be effectively used to model and optimize photocatalytic mineralization of acetaminophen using $ZnFe_2O_4$-TiO_2nanocomposite.

Conclusion

$ZnFe_2O_4$-TiO_2nanocomposite was synthesized via microwave assisted combustion method. Photocatalytic mineralization of acetaminophen using $ZnFe_2O_4$-TiO_2 is described by a model quadratic equation. Analysis of variance revealed significance of the developed model with $R^2 = 0.993$ and $R^2adj = 0.984$. Under the optimized conditions (initial acetaminophen concentration of 11.2 mg/L, photocatalyst dosage of 1.0g/L and irradiation time of 28.7min), 95.9 % photocatalytic mineralization of acetaminophen was achieved. Under the predicted optimized conditions, the experimental percentage photocatalytic mineralization of acetaminophen was found to be 95.9 % which is very close to the predicted value of 96.3%. Therefore, $ZnFe_2O_4$-TiO_2nanocomposite can be effectively used for photocatalytic mineralization of acetaminophen in water under visible light illumination.

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