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MODELING OF NITRATE REMOVAL FROM AQUEOUS SOLUTION BY Fe-DOPED TiO_2 UNDER UV AND SOLAR IRRADIATION USING RESPONSE SURFACE METHODOLOGY

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ABSTRACT

Nitrate is a common groundwater pollutant all over the world. In some regions of Iran, its levels are high enough to cause serious problems to human health and the environment. The objectives of this work were to evaluate the efficiency of Fe-doped TiO_2 nanoparticles at removing nitrate from aqueous solutions under UV and solar radiation and to model nitrate removal using response surface methodology techniques. In this study, a response surface methodology based on the Box–Behnken design matrix was used to describe the process of nitrate removal from an aqueous solution with four independent parameters, namely Fe-doped TiO_2 (dose 1-2 g l^{-1}), nitrate concentration (25-100 mg l^{-1}), contact time (10-120 min), and pH (4-9). The results indicated that the removal efficiency of nitrate in the presence of ultraviolet and solar radiation was 56.5 % and 21.8%, respectively. The removal efficiency of nitrate increased with time and initial concentration of nitrate. Analysis of variance (ANOVA) indicated that the proposed model was essentially in accordance with the experimental results with the correlation coefficient R^2 = 0.9237 and Adj-R^2 = 0.8347. Response surface methodology (RSM) proved to be a powerful statistical tool for investigating the operating conditions for nitrate removal under UV irradiation.

Keywords: Box–Behnken design, nitrate, response surface methodology, ultraviolet light, nano Fe-doped TiO_2

1. Introduction

Nitrate is a common pollutant in many areas of the world including Iran. Contamination of groundwater by nitrate has become more serious in recent years, possibly due to its high water solubility (Thompson, 2001, Mohseni-Bandpi *et al.*, 2013). Nitrogen fertilizers, animal manure, septic systems, industrial processes, agricultural and urban runoff, and atmospheric deposition from nitrogen oxide emissions generate high levels of nitrates (Xu *et al.*, 2012, Bhatnagar and Sillanpää, 2011). The mixing of nitrates in drinking water can cause serious threats to human health and the environment, including induction of blue-baby syndrome (Methemoglobinemia) in infants, eutrophication, and production of carcinogenic compounds (Huang *et al.*, 1998, Hwang *et al.*, 2011). According to the US Environmental Protection Agency (EPA) and European Union legislation (Council Directive 91/676/EEC) the maximum allowable levels of nitrates in drinking water are 10 mg l^{-1} of NO_3^-N and 50 mg l^{-1}, respectively (Kumar and Chakraborty, 2006; Rodríguez-Maroto *et al.*, 2009).

Several treatment technologies, such as ion exchange, reverse osmosis, biological denitrification and chemical reduction, are used for nitrate removal (Huang *et al.*, 1998; Kapoor, 1997). Among theses, ion exchange and reverse osmosis are the most common treatment methods. However, both of these methods are impractical due to secondary waste generation and requiring frequent regeneration of the media. Biological methods tend to produce excessive biomass sludge that requires further treatment. Moreover, microbial processes require continuous specialized maintenance (Huang *et al.*, 1998; Song and Carraway, 2008). In recent years, Nanoscale zero-valent iron (nZVI) for nitrate removal has attracted the attention of many scientists due to its high reduction capacity, high efficiency, abundance, low cost, and unique atomic, molecular, and chemical properties (Huang *et al.*, 1998; Huang *et al.*, 2003; Noubactep and Caré, 2010; Xiong *et al.*, 2007; Zazouli *et al.*, 2014a). TiO_2 has also recently emerged as a photocatalysis that can be used for the treatment of many contaminants.

TiO_2 is inexpensive and is useful in the treatment of contaminated water because of its chemical, optical and electronic properties (Karunakaran *et al.*, 2010). The main limitations to the use of nZVI are pH control, ammonium production, and degradation of efficiency as time and particle aggregation limit its efficiency (Noubactep and Caré, 2010; Lee, 2007; Huang *et al.*, 2007). Several studies have shown that addition of metals with TiO_2, including Fe^{2+} and Fe^{3+}, has considerable impact on TiO_2 efficiency (Huang *et al.*, 2007; Ranjit and Viswanathan, 1997). Researchers have reported photocatalytic reduction of nitrate ion into ammonia on metal-loaded TiO_2 catalyst systems; they observed that photocatalytic reduction of nitrate was dependent on various experimental factors such as irradiation time, the pH of the solution, the nature of the sacrificial agent, and the nature of the metal loaded on the semiconductor. There is an optimum metal content for TiO_2 activity, beyond which, its activity decreases. Fe-TiO_2 photocatalysis under irradiation caused hydrogenation of NO_3^- and NO_2^- ions to ammonia (Kobwittaya and Sirivithayapakorn, 2014; Gao *et al.*, 2004). To determine the optimal combination of these factors for nitrate removal, we propose a series of experiments examining the concentration of Fe-doped TiO_2, nitrate concentration, contact time, pH, effect of UV and solar irradiation.

There are several limitations to classical experimental methods. In a conventional method, typically only one variable can be examined at the time, which is time consuming and involves a lot of work. Moreover, the combined effect of several different variables cannot be determined (Myers, 2009; Montgomery, 2004). Response surface methodology (RSM) does not have the limitations of classical methods, and has many benefits such as the ability to design experiments with multiple variables at different levels while requiring the minimum number of experiments (Myers, 2009; Montgomery, 2004; Myers, 2002). In this study, a statistical model was used to design and analyze the experiments. The Box-Benkhen design (BBD) was selected over other methods such as the full factorial design (FFD) and Central Composite design (CCD) because the BBD technique is a second-order, spheroid design with other desirable features (Myers, 2002; Ray, 2009; Ray, 2006). Comparative studies with other available statistical design methods show that the Box–Behnken technique has many advantages such as its requirement for a low number of experiments, estimation of parameters for quadratic model, calculation of lack of fit, and its use of blocks that are more effective than the three-level full factorial designs (Mourabet *et al.*, 2012b, Kayan and Gözmen, 2012). Full factorial design is impractical because it requires a large number of runs to accurately predict the response (Ray, 2009). The aims of this research were to: (1) investigating the effects of an Fe-doped TiO_2 dose, initial concentration, contact time, and pH on the efficiency of nitrate reduction in water in the presence of UV and solar radiation; and (2) model the reduction process using BBD with Design Expert Version 16.2.4 (Stat Ease, USA).

2. Materials and Method

2.1. Fe-doped TiO_2 Synthesis

Fe-doped TiO_2 nanoparticles were synthesized using the sol-gel method without any pre-treatment. 4.128mL of titanium tetrachloride ($TiCl_4$) was dissolved in 70 mL of ethanol, followed by the addition of 5% molar of Fe $(NO_3).6H_2O$, which in turn was followed immediately by the addition of 2 ml of distilled water. Next, 17 ml propylene oxide was added slowly drop-wise at 50 ° C. A gel was formed after about 5 minutes. The resulting gel was aged for 48 h at room temperature and then dried for 12 h at 80 ° C. In order to form anatase, the dried gel was calcined for 2 h at 350° C (Chen *et al.*, 2006).

2.2. Preparation of Synthetic Solutions

The nitrate stock solution (1000 mg l^{-1}) was prepared by dissolving 0.7218-g KNO_3 (Merck, Germany) in deionized water. Solution pH was adjusted from 4 to 9 using 0.1-M NaOH or 0.1-M H_2SO_4 (Merck, Germany) in all experiments.

2.3. Experiments

2.3.1. Experiments in the presence of UV irradiation

Batch mode experiments were performed for the reduction process. All experiments for determining nitrate reduction were prepared by adding of Fe-doped TiO_2 nanoparticles (1-2 g l^{-1}) into a solution containing a certain amount of nitrate and the pH was adjusted to desired values (4-9). The solution was sonicated for six min to disperse any aggregations of nanoparticles and improve its stability during synthesis (Jiang *et al.*, 2011; Chen *et al.*, 2011), then irradiated by UV light of 254 to 265 nm wavelengths. The experiments were performed in a 2-L reactor, which was 14 cm in diameter and 18 cm in height. A quartz coated UV lamp with medium pressure (150 watt), 6.5 cm in length, and 1 cm in diameter was installed in the middle of the reactor lid, as schematically shown in Fig. 1. Following this, the solution was centrifuged. The final solution was filtered through a 0.45-µm pore membrane filter. Hereafter, this method is called the Fe-TiO2/UV process

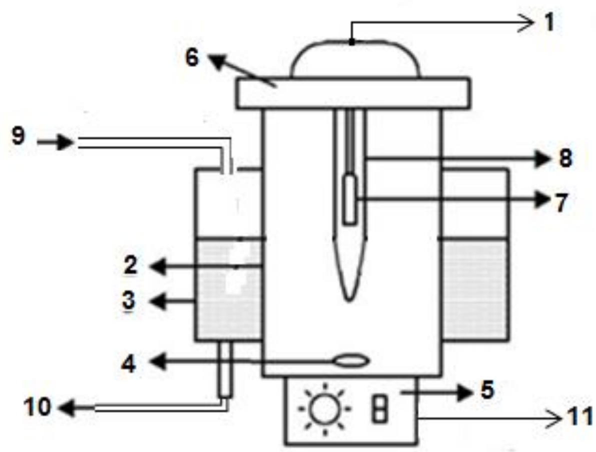


Figure 1. Schematic of the reactor used in the process
1-To power transformer, 2-glass reactor, 3-water condenser, 4-magnet, 5-magnetic stirrer, 6-reactor lid, 7- UV lamp, 8- quartz coat, 9-water in 10-water out 11-Electrical Wire

2.3.2. Experiments in the presence of solar radiation

Samples were prepared as described above and then placed outside for solar irradiation in the Mazandaran University campus (in northern Iran at longitude 48.17 °E and latitude 37.15° N) from10 am to 3 pm in 1 to 30 July 2013. Since in this area, solar radiation does not change substantially, photon flux was not measured. Temperature and humidity for all experiments were similar. According to Iran's Ministry of Energy, solar energy potential in northern Iran varies from 2.8 to 3.8 KWh m^{-2}. Hereafter, this method is called the Fe-TiO_2/Sun process.

2.4. Nitrate Analysis

After plotting the nitrate calibration curve, residual nitrate was measured by reading the ultraviolet absorption of the solution at 220 and 275 nm wavelengths. An absorbance reading two times the absorbance reading of the water sample at 275 nm was subtracted from the value of absorbance for that sample at 220 nm. This step provided a value for the experimental absorbance due to nitrate (APHA, 2005). All samples were diluted to the appropriate ratio and 1 ml of 1-M HCl was added to all diluted samples. Nitrate concentration was measured using a UV-Vis spectrophotometer (Perkin-Elmer model Lambda BZ 201) according to the 4500-NO_3^- B standard method (APHA *et al.*, 2005).

2.5. Box–Behnken experimental design

An RSM statistical model is used to investigate the relationship among independent variables and responses. BBD, one of the most powerful and efficient statistical tools, was used to design the experiments (Mourabet *et al.*, 2012b). Based on a literature review and results from prototype tests, a four-factor, three-level second-order model was developed (Zazouli *et al.*, 2013b, Zazouli *et al.*, 2013a). The four parameters included nitrate concentration (mg l^{-1}), Fe-doped TiO_2 dose (g l^{-1}), contact time (min), and pH, represented as X_1, X_2, X_3, and X_4, respectively. Nitrate removal (Y) was considered the response. Experimental range and the levels of the independent variables are presented in Table 1, where -1 corresponds to the minimum and +1 to the maximum value of each variable. The following equation represents a second-order model (Equation 1):

$$Y = \beta_0 + \beta_i + x_i + \Sigma\beta_{ii} + x_{ii}^2 + \Sigma\beta_{ij}\, x_i\, x_j + \varepsilon \tag{1}$$

In this equation, Y is the predicted response surface function, β_0 is a constant, β_i is the slope or linear effect of the input variable, x_{ii} is the quadratic effect of input variable x_i, and β_{ij} is the linear by linear interaction effect between the input variable x_i and variable x_j (Mourabet *et al.*, 2012a).

Table1. Experimental range and levels of independent variables.

Independent variables		Range & Level		
		+1	**0**	**−1**
X_1	Nitrate Con(mg l^{-1})	25	62.5	100
X_2	Catalyst dose (mg l^{-1})	0.2	0.6	1
X_3	Contact time (min)	10	65	120
X_4	pH	4	6.5	9

3. Results and discussion

3.1 Characteristics of synthesized Nano-Scale Fe-doped TiO_2

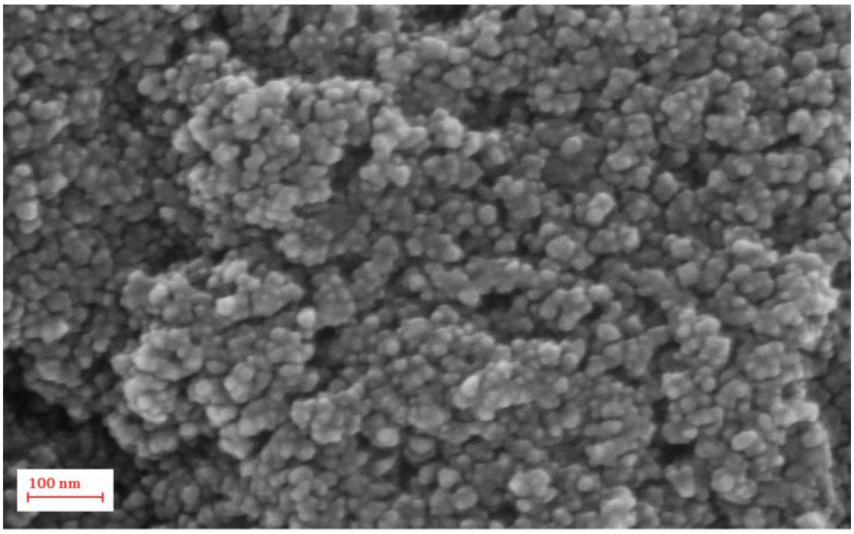
Figures 2(a) and (b) show a scanning electron micrograph (SEM) and the x-ray diffraction (XRD) pattern of the synthesized nano-scale Fe-doped TiO_2, respectively. The diameter of the nanoparticles was measured with Measurement software .

3.2. Experimental design, statistical analysis and regression model

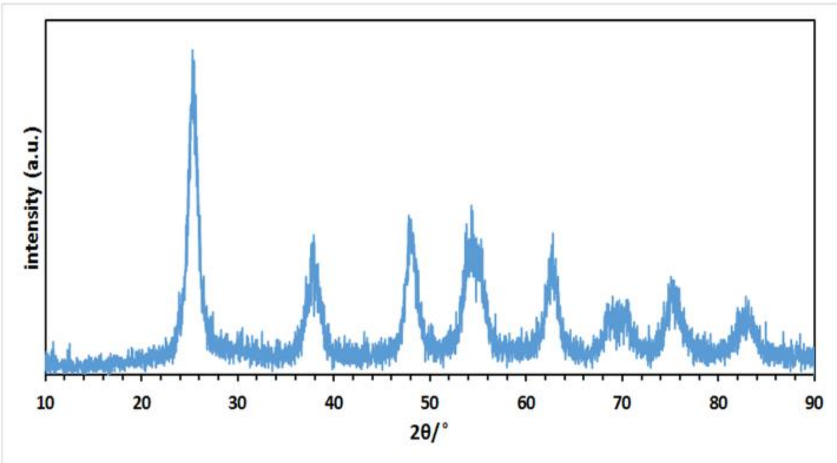
To evaluate the effects of various factors on nitrate removal efficiency, a total of 27 experiments were performed in the presence of UV radiation and 15 sets of experiments in the presence of solar radiation. The observed and predicted results for each experiment are given in Tables 2 and 3. Regression models were developed between nitrate removal efficiency and the experimental parameters using a quadratic and a linear equation, as shown in Eqs. (2) and (3).

$$Y_1 = 45.6333 + 16.2750X_1 + 9.4417\,X_3 - 9.5875(X_1)\,(X_1) - 7.1625(X_3)\,(X_3) - 8.1500\,(X_1)\,(X_4) \quad (1)$$

$$Y_2 = 11.100 + 6.374\,X_1 \quad (2)$$



A: SEM image



B: XRD image

Figure 2. Synthesized Fe-doped TiO_2 (A) SEM photographs and (B) XRD

Where X_1, X_2, X_3, and X_4 represent the four selected factors and Y_1 and Y_2 are the degrees of nitrate removal (%) in the presence of UV and solar radiation, respectively. Analysis of variance (ANOVA) was performed to test the significance and fit of the model. ANOVA results for the proposed models are shown in Table 4. Based on the ANOVA results, the coefficient of determination (R^2) and adjusted R^2 were 0.9237, 0.7432 and 0.8347, 0.2809 for UV and solar experiments, respectively. The value of R^2 and the adjusted R^2 are used to evaluate the fit of the model. High values (close to 1) of R^2 in experiments with UV irradiation indicated a stronger association between the experimental and predicted results, while lower values in experiments with sunlight indicated a poorer fit to the experimental data (Kayan and Gözmen, 2012; Sahoo and Gupta, 2012). The significance of the models was evaluated by the R^2, F-value, p-value and lack of fit. An F value of 10.38 indicated that the model is significant. Additionally, P-values less than 0.05 indicated that the quadratic and linear terms are also significant. An F-value of 2.70 confirmed that the lack of fit is not significant, as desired (Sharma *et al.*, 2009). In summary, the proposed model is suitable for the interpretation of nitrate removal processes and could be used in future studies.

Table 2. Box-Behnken design matrix with predicted and experimental results for nitrate removal using the Fe-TiO_2/Sun process.

Number	Experimental design			Y%	
	Nitrate con (mg l^{-1})	Catalyst dose (mg l^{-1})	pH	Observed	Predicted
1	1	1	0	16.09	17.5
2	0	0	0	4.10	11.1
3	-1	0	1	0.00	4.7
4	1	-1	0	14.70	17.5
5	0	1	1	21.80	11.1
6	-1	0	-1	0.00	4.7
7	0	-1	1	20.10	11.1
8	-1	1	0	0.00	4.7
9	0	-1	-1	16.30	11.1
10	1	0	1	13.20	17.5
11	-1	-1	0	10.80	4.7
12	1	0	-1	17.80	17.5
13	0	1	-1	7.77	11.1
14	0	0	0	9.20	11.1
15	0	0	0	20.00	11.1

Table 3. Box-Behnken design matrix with predicted and experimental results for nitrate removal using the Fe-TiO_2/UV process.

Number	Experimental design				Y%	
	Nitrate con (mg l^{-1})	Catalyst dose (mg l^{-1})	Contact time (min)	pH	Observed	Predicted
1	-1	1	0	0	27.1	19.7
2	0	-1	0	1	48.4	45.6
3	1	0	0	1	56.5	44.2
4	1	0	-1	0	30.3	35.7
5	0	0	0	0	49.1	45.6
6	0	0	1	-1	45.8	47.9
7	-1	0	1	0	21.6	22.1
8	0	-1	-1	0	29.7	29.0
9	0	1	0	1	42.6	45.6
10	1	0	0	-1	55.2	60.5
11	0	0	-1	-1	27.8	29.0
12	0	1	-1	0	29.7	29.0
13	1	0	1	0	51.7	54.6
14	0	0	1	1	50.3	47.9
15	1	1	0	0	53.2	52.3
16	-1	0	-1	0	11.2	3.2
17	-1	0	0	1	33.9	27.9
18	0	1	1	0	53.4	47.9
19	0	0	-1	1	25.3	29.0
20	0	1	0	-1	42.1	45.6
21	-1	-1	0	0	9.5	19.8
22	0	-1	1	0	44.5	47.9
23	-1	0	0	-1	0.0	11.6
24	0	0	0	0	41.3	45.6
25	0	0	0	0	46.5	45.6
26	1	-1	0	0	51.7	52.3
27	0	-1	0	-1	46.7	45.6

Table 4. Analysis of variance of the proposed model for nitrate removal.

Source	DF	Sum of square	Mean square	F value	Prob.> F
$Fe\text{-}TiO_2$/UV process					
Regression	14	5547.60	396.26	10.38	0.000
Linear	4	4403.43	1100.86	28.84	0.000
Square	4	751.02	187.76	4.92	0.014
Interaction	6	393.15	65.53	1.72	0.200
Residual error	12	458.06	38.17		
Lack-of-fit	10	426.51	42.65	2.70	0.300
Pure Error	2	31.55	15.77		
Total	26	6005.66			
$Fe\text{-}TiO_2$/Sun process					
Regression	9	609.711	67.746	1.61	0.312
Linear	3	379.844	126.615	3.00	0.134
Square	3	161.265	53.755	1.28	0.378
Interaction	3	68.602	22.867	0.54	0.674
Residual error	5	210.693	42.139		
Lack-of-fit	3	78.873	26.291	0.40	0.771
Pure Error	2	131.820	65.910		
Total	14	820.404			

3.3. Verification of the response surface model

The distributions of residuals were also analyzed to check the normality of the data, as shown in Fig. 3(a). Dot diagrams of these residuals illustrate that the distribution was normal, as the points are close to the line (Salahi *et al.*, 2013). A scatter plot of the experimental data, in Fig.3.(b), revealed no trends for high or low variance, and the assumption of constant variance was accepted (Salahi *et al.*, 2013). Fig. 3(c) is the outlier t plot for all experiments. To express the outlier, thresholds of three standard deviations were considered. An outlier outside of this threshold indicates an error (Salahi *et al.*, 2013). No outliers were observed beyond the standard, as shown in Fig. 3(c). All data were compatible with the model for experiments in the presence of UV irradiation.

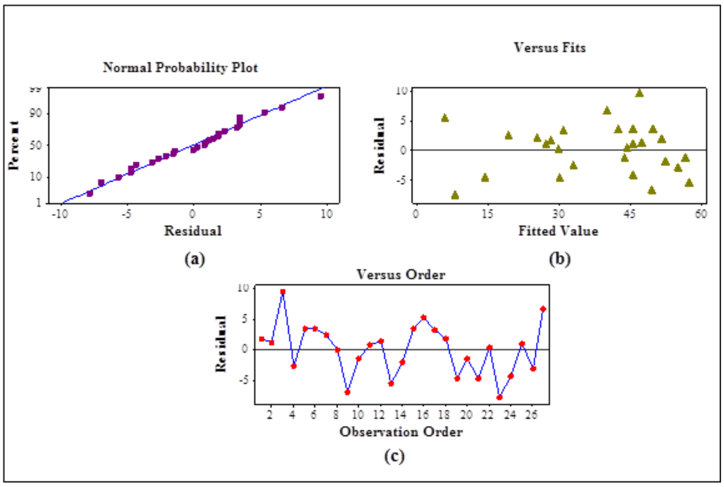


Figure 3. Residual plots for percentage of nitrate removal using the $Fe\text{-}TiO_2$/ UV process (a) normal probability plot (b) random scatter plot (c) outlier t plot.

3.4. Effect of contact time and nitrate concentration

The effects of the four variables and their interaction in terms of nitrate removal can be graphically illustrated by three-dimensional surface response plots. The combined effects of time and nitrate concentration are shown in Fig. 4. The removal of nitrate increases with contact time. These results are in accordance with previous studies such as Hwang *et al.* (2011), Yang and Lee (2005), Zazouli *et al.* (2014b) and Pan *et al.*, (2012). Such a phenomenon could be explained by the time required for activation of the Fe^0 surface and the amount of ferrous ions released from the Fe^0 surface such that the ferrous accumulation increased with time and, as a result, nitrate removal rate increased (Liao *et al.*, 2003, Anotai *et al.*, 2010). As presented in Fig. 4, high levels of initial nitrate concentration in water increased the efficiency of nitrate removal over time. Yang and Lee (2005) and Huang *et al.* (1998) also reported that at a high initial nitrate concentration, the removal increases.

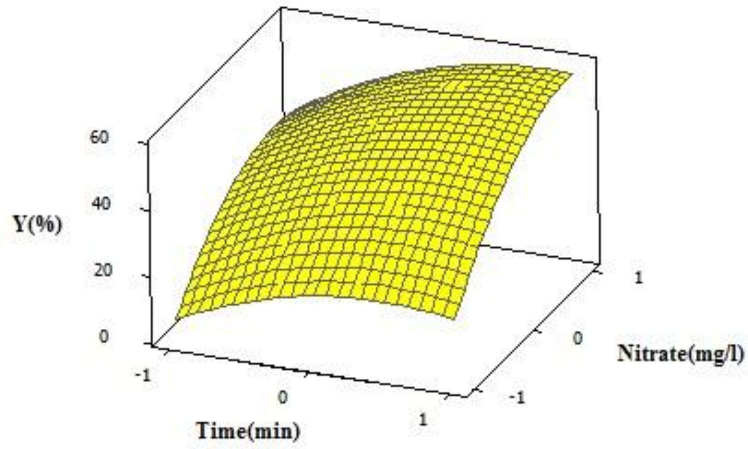


Figure 4. Three-dimensional surface response plot for the effect of nitrate concentration and time on nitrate removal efficiency

3.5. Mechanism of nitrate reduction by Fe-doped TiO₂

Adding Fe-doped TiO_2 to water containing nitrate and nitrite induces the production of Fe^{2+} and ammonia (NH^{4+}) or N_2 gas (reactions 1 and 2) (Li *et al.*, 2006).

1) $5\ Fe^0 + 2\ NO_3^- + 6\ H_2O \rightarrow 5\ Fe^{2+} + N_2 + 12\ OH^-$

2) $Fe^0 + NO_3^- + 7\ H_2O \rightarrow 4\ Fe^{2+} + NH_4^+ + 10\ OH^-$

Pan *et al.,* (2012) have reported that TiO_2 possesses both oxidative and reductive abilities when removing nitrate from aqueous systems. Without the presence of other materials to capture the electron, TiO2 is ineffective in terms of nitrate removal and assumes only a supplemental role in promoting the reaction (Pan *et al.*, 2012; Sá *et al.*, 2005). UV radiation causes Fe^0 surface activation and direct photolysis of nitrate itself; these are two advantages of the UV-irradiated system (Liao *et al.*, 2003).

4. Conclusions

In this study, response surface methodology was applied to investigate individual and combined effects of four process factors on nitrate removal in an aqueous media by Fe-doped TiO_2 under UV and solar radiation. From the statistical analysis of our results and quadratic models, contact time and nitrate concentration were observed to be the most influential parameters. RSM and BBD with a low number of experiments were considered suitable methods for interpreting experimental data obtained from nitrate removal processes in the presence of ultraviolet light. From the analysis of variance and the high values of the correlation coefficient (R^2 = 0.9237), we concluded that the experimental data were in good agreement with the predictions made by the model for nitrate removal efficiency.

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