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Response surface methodology for optimization of 4-nitrophenol degradation by a heterogeneous Fenton-like reaction on nano-zero-valent iron

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ABSTRACT

Heterogeneous Fenton-like reactions on nano-zero-valent iron (NZVI) were investigated for the degradation of 4-nitrophenol (4-NP). A three-factor central composite design coupled with response surface method (RSM) was applied to evaluate and optimize the important variables. A significant quadratic model ($p\text{-value} < 0.05$, $r^2_{(\text{adj})} = 0.9625$) was derived using analysis of variance, which was adequate to perform the optimization of the process variables. Optimum conditions were determined to be 0.66 g/L NZVI, 300 mM H_2O_2, pH 3.0, reaction time 50 min and 100–300 ppm 4-NP. More than 93% of 4-NP was experimentally degraded under the optimum conditions. The experimental results matched well with the predicted results which validated the RSM models with good correlation ($r^2 = 0.9680$).

Keywords: Fenton-like reaction; NZVI; 4-Nitrophenol; Response surface method

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1. Introduction

4-Nitrophenol (4-NP) is an important precursor that is being widely used for the preparation of herbicides, pesticides, insecticides, explosives, pharmaceuticals, and dyes [1]. The US Environmental Protection Agency has listed 4-nitrophenol as priority pollutants and recommended restricting their concentrations in natural waters to <10 ng/L [2]. 4-NP may enter the environment from industrial discharges, spills, and possibly as a breakdown product of certain pesticides containing 4-nitrophenol. Because of its stability and high solubility, 4-NP can persist a very long time in the soil and ground water and pose a significant environmental risk. Due to its low molecular weight and toxic nature, the conventional chemical coagulation method and the biological treatment become ineffective. Hence, the advanced oxidation processes, which generate strong oxidants of hydroxyl radicals ($^{\cdot}OH$), appear to be a promising alternative for the removal of such a material. The highly reactive and nonselective hydroxyl radicals can oxidize and mineralize most organic compounds, specially unsaturated organic compounds. Heterogeneous Fenton-like systems using iron-supported catalysts, for example, zero-valent iron (Fe^0) [3], Fe_3O_4 [4–6], and Fe^0/Fe_3O_4 [7], have recently been developed. Fenton-like process can effectively catalyze the oxidation of organic pollutants. Many

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processes have been developed for 4-nitrophenol removal. Experimental details of these reports are shown in Table 1. In the most of these works, one-at-a-time method was used for optimization of variables of 4-nitrophenol degradation. Sun and his coworker investigated heterogeneous Fenton-like reaction on nanomagnetite (Fe_3O_4) for the degradation of 4-NP. They applied a four-factor central composite design (CCD) coupled with response surface methodology (RSM) to optimize the important variables. They reported a significant quadratic model (p-value < 0.0001, $r^2 = 0.9442$) to perform the process variables optimization [6].

CCD coupled with RSM is a useful approach for optimizing the important variables in a process. CCD-RSM is very efficient, providing much information on experiment variable effects and overall experimental error in a minimum number of required runs. RSM is a collection of mathematical and statistical techniques based on the fit of a polynomial equation to the experimental data, which must describe the behavior of a data-set with statistical previsions. On the other hand, the CCD-RSM is a statistical technique for designing experiments, building models, evaluating the effects of several factors, and searching optimum conditions for desirable responses. With RSM, the interactions of possible influencing parameters with treatment efficiency can be evaluated with a limited number of planned experiments. Response surface methodology is widely used in various fields, for example, optimization of adsorption conditions of bovine serum albumin on thermosensitive magnetic composite particles [14], optimization of the extraction of flavonoids from fructus sophorae [15], influence of activated carbon characteristics on toluene and hexane adsorption [16], determination of indium by adsorptive stripping differential pulse voltammetry [17].

For the past 18 years, nano-zero-valent iron (NZVI) has been investigated as a new tool for the treatment of contaminated water and soil. NZVI was first tested for contaminated water treatment by Wang and Zhang [18]. Since then NZVI has been proven as highly effective for the removal/degradation of a wide range of chemical pollutants. NZVI is an electron donor, a strong reducing agent, and the spent agent, Fe^{2+} is environmentally innocuous. The main feature of this system is its ability to create *in situ* reactive oxygen species in aqueous phase employing less expensive and nontoxic reagents [19]. The NZVI technology has reached commercial status in many countries worldwide, however, is yet to gain universal acceptance [20].

Table 1
Experimental details of recently published reports on degradation of 4-nitrophenol

Method	Catalyst	Experimental parameters	Variable optimization	Removal efficiency	Ref.
Microwave-enhanced catalytic degradation	Nickel oxide	pH 3, 15 g/L ZVI, t: 40 min, 10,000 mg/L 4-NP	One at a time	Complete degradation	[8]
Heterogeneous Fenton-like	Acid-activated fly ash, AFA	166.5 mg L^{-1} H_2O_2, 10 g/L AFA, pH 2, t: 14 h, 100 mg/L 4-NP	One at a time	98%	[9]
Heterogeneous Fenton-like	Nanomagnetite (Fe_3O_4)	1.5 g/L Fe_3O_4, 620 mM H_2O_2, pH 7.0, t: 10 h, 25–45 mg/L 4-NP	CCD-RSM	90%	[6]
Adsorption	Lignin-based activated carbons (ACs)	0.1 g/L AC, pH 3, t: 120 min, 78.37 mg/L 4-NP	One at a time	4.4 mmol/g	[10]
BES-Fenton reaction	Limonite powder	2.24 g/L Limonite, t: 6 h, pH 2, external resistance of 20 Ω, 27.25 mg/L 4-NP	One at a time	96%	[11]
Ozonation	Nano-ZnO	300 mg/L ZnO, pH3, gas flow 1 L/min, 5.64 mg/L Ozone, t: 30 min, 16 mg/L 4-NP	One at a time	60.34% TOC removal	[12]
Electrochemical degradation	–	pH 2, 1 g/L Na_2SO_4, t: 300 min, 100 mg/L 4-NP	One at a time	92% 4-NP removal (40% TOC removal)	[13]
Heterogeneous Fenton-like	Nano-zero-valent iron	pH 3, 0.66 g/L NZVI, 300 mM H_2O_2, t: 50 min, 100–300 ppm 4-NP	CCD-RSM	93% COD removal	Present study

The degradation of 4-NP by heterogeneous Fenton-like reactions on NZVI has not yet been reported in the literature. Nanoparticles normally show higher catalytic activity due to their large specific surface area; hence, the use of nanoparticles as catalysts is more attractive than that of microparticles. Therefore, the aim of the present study was to investigate heterogeneous Fenton-like reactions on NZVI for 4-NP degradation in water. The degradation efficiency of pollutants by this process basically depends on catalyst concentration, the initial pH, hydrogen peroxide concentration, and the initial concentration of pollutants. The traditional method (one at a time) to determine the optimal conditions of these variables is to test a single factor at one time while keeping the other variables constant. This method does not include a study of interactions among variables, so this technique does not depict the complete effect of the parameters on response. The objective of this study was to evaluate and optimize the important variables for 4-NP degradation in the presence of NZVI using CCD-RSM, to quantify the contributions of reaction parameters on removal of 4-NP.

2. Materials and methods

2.1. Materials

4-Nitrophenol (4-NP), ferrous sulfate ($FeSO_4{\cdot}7H_2O$), sodium borohydride ($NaBH_4$, 96%), sulfuric acid (H_2SO_4), sodium hydroxide (NaOH), and hydrogen peroxide (30%, w/w) were purchased from Merck (Darmstadt, Germany). All chemicals were analytical-grade reagents and were used as received without further purification. Double-distilled water was used for the preparation of solutions. Stock solution of 1,000 ppm 4-NP was prepared, and other working solutions were obtained by successive dilution of stock solutions.

2.2. Preparation of NZVI

The NZVI particles were synthesized by the well-known wet reduction method [21]. Reagents were prepared using deoxygenated double-distilled water with N_2 gas for 30 min. 50 mL 0.4 M sodium borohydride (0.8075 g $NaBH_4$ in 50-mL volumetric flask) was dropped into the 100 mL 0.1 M $FeSO_4{\cdot}7H_2O$ (2.8111 g $FeSO_4{\cdot}7H_2O$) under vigorous mixing for 20 min on a shaker. Ferrous ion was reduced to elemental iron by borohydride according to the following equation:

$$Fe^{2+}_{(aq)} + 2BH_4^- + 6H_2O \longrightarrow Fe^0_{(s)} + 7H_{2(g)} + 2B(OH)_{3(aq)} \tag{1}$$

The solution was centrifuged at 3,400 rpm for 5 min and washed three times with 10 mL of deoxygenated double-distilled water to remove the residual reagents. The wet paste was suspended in 10^{-4} M deoxygenated hydrochloric acid. The size and shape of the NZVI particles were determined using a scanning electron microscopy. Characterization of synthesized nanoparticles has been published recently by author [22].

2.3. Experimental design with RSM

A CCD with three factors and three levels was used for the experimental design. Table 2 shows the experimental ranges, and coded and uncoded levels of the independent variables tested in the CCD. The 4-NP concentration (X_1), NZVI concentration (X_2), and the initial pH (X_3) were chosen as the independent input variables. The degradation efficiency of 4-NP in terms of %Removal (Y) was used as the dependent output variable. The response variable was fitted by a quadratic polynomial equation:

$$Y = \beta_0 + \sum_{i=1}^{n} \beta_i X_i + \sum_{i=1}^{n} \beta_{ii} X_i^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \beta_{ij} X_i X_j \tag{2}$$

where Y represents the predicted degradation efficiency of 4-NP, β_0 is the offset term, β_i are the linear coefficients, β_{ii} are the quadratic coefficients, β_{ij} are the interaction coefficients, and X_i and X_j are the independent variables.

All of the experiments were carried out in triplicates, and the experimental results were expressed as mean ± standard deviations. Statistical analysis was performed by using the Minitab 16 (Minitab Inc., State College, PA, USA) software and fitted to a second-order polynomial regression model containing the coefficient of linear, quadratic, and interaction terms. An analysis of variance (ANOVA) was then carried out for each response variable in order to test the

Table 2
Variable levels of CCD for the degradation of 4-NP by heterogeneous Fenton-like reactions on NZVI

		Actual values of the coded variables levels		
Process variables	Symbol	−1	0	+1
[4-NP] (ppm)	X_1	100	200	300
[NZVI] (g/L)	X_2	0.35	0.5	0.66
pH	X_3	3.0	5.0	7.0

model significance and suitability. The significances of all terms in the polynomial were statistically analyzed by computing the *F*-value at a probability (*p*) of 0.05.

2.4. Experimental procedures

Batch experiments were carried out in 50-mL flask. Typically, an appropriate concentration of 4-NP solution was prepared by diluting the stock solution of 4-nitrophenol. The pH of the 4-NP solution was adjusted to a desired value using 0.1 M sulfuric acid and 0.1 M sodium hydroxide. Following the pH adjustment, an appropriate concentration of NZVI was mixed with 20 mL 4-NP solution and the mixture was placed on a shaker. The Fenton-like reaction was started by the addition of the appropriate amount of hydrogen peroxide. All experiments were conducted at room temperature (22 ± 2˚C). During each experimental process, 3.0 mL sample was withdrawn at certain time intervals and immediately mixed with 0.1 mL 10% w/v sodium sulfite to quench ·OH. Before filtration, 0.05 mL NaOH solution 0.1 M (to get $\mathrm{pH} > 8.0$) and 0.1 g MnO_2 were added into the samples in order to remove the soluble iron, which can interfere with measurement of COD, and then, the mixture was centrifuged at 8,000 rpm for 5 min to separate particles. Finally, the supernatant liquid was collected for analysis. The 4-NP removal was monitored by the ratio of eliminated values to initial values of COD. COD was determined using closed reflux, colorimetric method (Standard method 5220D). For each experiment, corresponding blank solution was used. The 4-NP degradation or COD removal efficiency was calculated as:

$$(\%)\,\text{Removal} = \frac{C_0 - C_t}{C_0} \times 100 \tag{3}$$

where C_0 and C_t are initial and instantaneous COD (mg O_2/L).

The theoretical COD equivalent of 4-NP could be calculated according to the following reaction equation:

$$C_6H_5O_3N + 5O_2 \rightarrow 6CO_2 + H_2O + NH_3 \tag{4}$$

The COD can be estimated from the concentration of 4-NP in the sample, based on its stoichiometric reaction with oxygen, using the following formula:

$$\begin{aligned} \text{COD}\left(\frac{\text{mg}\,O_2}{\text{L}}\right) &= \left(\frac{1}{139.11}\right) \times 5 \times 32 \\ &= 1.15 \text{ for one ppm of 4-NP} \end{aligned} \tag{5}$$

Before the development of the response surface models, effects of hydrogen peroxide concentration and reaction time on degradation of 4-NP were investigated. Literature review of previous studies reports on 4-NP degradation show that in the most of them, measuring the absorbance of UV–vis spectrum of 4-NP is applied for the determination of the removal efficiency; hence, at the beginning of this study, degradation efficiency of 4-NP was monitored in two ways: (1) by measuring the absorbance at 317 nm at $\mathrm{pH} < 4$ by means of a UV–vis spectrophotometer (AvaSpec-2048, Avantes, the Netherlands), this response or removal rate was nominated as absorbance based and (2) by following the COD reduction, this response or removal rate was nominated as COD based.

3. Results and discussion

3.1. Effect of hydrogen peroxide concentration

The effect of H_2O_2 concentration on 4-NP degradation was investigated over the range of 50–300 mM at pH 5, initial 4-NP concentration 200 ppm, and NZVI dose 0.5 g/L. Fig. 1 shows that at low H_2O_2 concentrations of 50 mM, the removal efficiency of 4-NP degradation (COD reduction) was low because of the insufficient ·OH in aqueous solution. As the H_2O_2 concentration increased, the 4-NP degradation efficiency was enhanced, because more radicals (·OH) were produced. However, for a higher concentration (>300 mM), no significant additional improvement was observed due to the scavenging of hydroxyl radicals by excessive hydrogen peroxide [23]. Hence, the maximum H_2O_2 concentration of 300 mM was considered for the effective degradation of 4-NP.

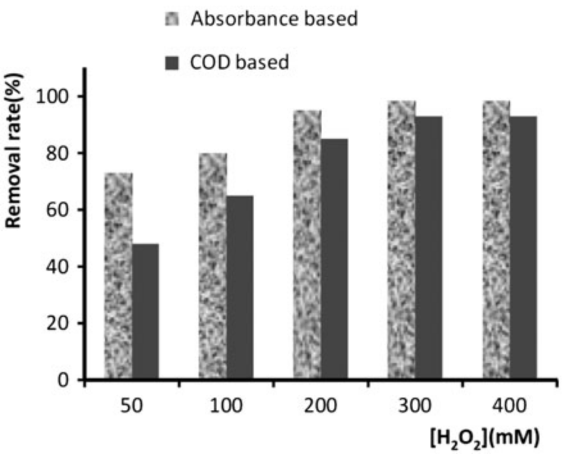

Fig. 1. Effect of H_2O_2 concentration on the degradation efficiency of 4-NP ([NZVI] = 0.5 g/L, [4-NP] = 200 ppm, and reaction time 50 min).

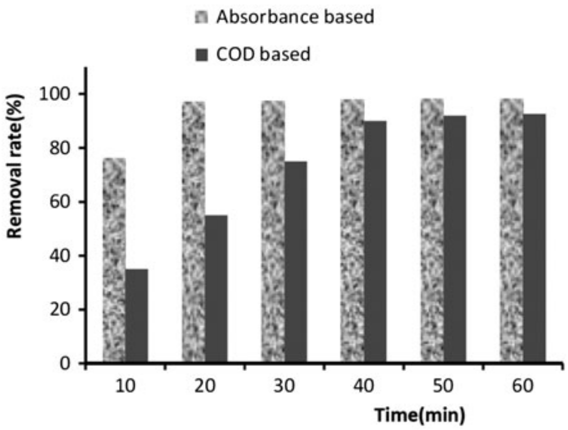

Fig. 2. Effect of time reaction on the degradation efficiency of 4-NP ([4-NP] = 200 ppm, $[H_2O_2]$ = 300 mM, and [NZVI] = 0.5 g/L).

3.2. Effect of reaction time

The effect of reaction time on 4-NP degradation was investigated over a range 10–60 min at pH 5, H_2O_2 concentration 300 mM, NZVI dose 0.5 g/L, and 4-NP concentration 200 ppm. Fig. 2 illustrates the effect of reaction time on both responses (% absorbance reduction and % COD removal). The results show that 97% absorbance is reduced after 20 min, while at this time, only 54% COD was removed. On the other hand, it takes 40 min till 90% COD reduced.

3.3. CCD results

A total of 16 batch experiments were carried out to develop the response surface model according to the experimental design, which were presented in Table 3. The ANOVA was used to estimate the statistical significance of the factors and interactions among them. The significance of each independent variable was evaluated according to its *p*-value (a *p*-value lower than 0.05 indicates that the term is significant at 95% confidence level). Regression coefficient and ANOVA of the second-order polynomial models are summarized in Table 4. As shown, the regression parameters of the surface response analysis of the models, the linear, quadratic, and interaction terms have significant effect ($p \leq 0.05$). The large values of the r^2 and r^2_{adj} reveal that the model adequately represents the experimental results. The absence of any lack of fit ($p > 0.05$) also strengthened the reliability of model. The second-order polynomial equation of the response surface is as follows:

$$\begin{aligned}(\%)\,\text{Removal} = {} & -74.53 - 0.14\,\text{NP} + 104.16\,\text{NZVI} \\ & + 1.05\,\text{pH} - 0.00056\,\text{NP}^2 + 0.58\,\text{NP} \\ & \times \text{NZVI} - 0.0074\,\text{NP} \times \text{pH} \\ & - 178.18\,\text{NZVI}^2 + 6.90\,\text{NZVI} \times \text{pH} \\ & - 0.59\,\text{pH}^2 \end{aligned} \tag{6}$$

Analysis of the experimental results showed that NZVI concentration had the greatest effect on removal

Table 3
CCD of three variables with their observed response

Exp.	Coded variables X_1	X_2	X_3	Uncoded variables 4-NP (mg/L)	NZVI (g/L)	pH	% Removal
1	1	1	1	300	0.66	7	82.00
2	0	0	0	200	0.50	5	90.01
3	1	−1	1	300	0.35	7	35.00
4	−1	−1	−1	100	0.35	3	91.80
5	0	−1	0	200	0.35	5	75.20
6	−1	1	1	100	0.66	7	89.00
7	1	−1	−1	300	0.35	3	55.00
8	0	0	−1	200	0.50	3	93.00
9	0	0	1	200	0.50	7	80.4
10	0	0	0	200	0.50	5	88.50
11	−1	1	−1	100	0.66	3	94.50
12	−1	0	0	100	0.50	5	93.00
13	0	1	0	200	0.66	5	95.17
14	1	0	0	300	0.50	5	74.05
15	−1	−1	1	100	0.35	7	80.20
16	1	1	−1	300	0.66	3	91.00

Table 4
Regression coefficients of predicted polynomial models for the investigated responses from the degradation of 4-NP

Source	Degree of freedom	Sum of square	Mean square	F-value	p-value
Regression	9	3,938.73	437.636	137.658	<0.0001
β_1:NP	1	31,242.11	24.273	7.635	0.03272
β_2:NZVI	1	1,288.81	14.84	4.663	0.04702
β_3:pH	1	344.54	0.389	0.122	0.03850
β_{11}	1	282.40	81.707	25.701	0.002289
β_{22}	1	74.41	48.198	15.161	0.008043
β_{33}	1	15.09	15.085	4.745	0.07222
β_{12}	1	636.97	639.97	200.359	<0.0001
β_{13}	1	17.70	17.70	5.568	0.05631
β_{23}	1	36.66	36.66	11.532	0.01456
Error	6	19.07	3.179		
Lack of fit	5	17.79	3.559	2.780	0.4251
Pure error	1	1.28	1.28		
Total	15	3,957.80			

Notes: $r^2 = 0.9847$, adjusted $r^2 = 0.9625$.

percent. On the other hand, concentration of NZVI exerted a pronounced influence on response in linear and quadratic manner. The initial pH of the solution and interaction effect of NZVI and pH had significant effect on the 4-NP degradation, too.

3.4. Response surface optimization

The illustration of the predicted model equation has been shown by the response surface plot. This graphical representation is a two dimensional surface in the three-dimensional space. Fig. 3(A)–(C) illustrate response surfaces for dependent variables (pH, NP, and NZVI) in function of two factors when the third factor was kept constant at center point (Table 2). These surfaces were drawn by MATLAB R2012b (Math Works, Inc., Natick, Massachusetts, USA) software.

The effect of initial pH on the degradation of 4-NP on NZVI catalyst has been shown in Fig. 3(A). The initial pH value ranging from 3 to 7 were investigated in the present study. As shown in Fig. 3(A), a negative effect of increasing the initial pH on the degradation of 4-NP was observed. This effect can be explained by the fact that the low pH may remove the passive layers from the NZVI core, rendering them free to react to generate hydroxyl radicals effectively. On the other hand at high pH, the ferrous and ferric ions dissolved from the surface of NZVI are able to collide with hydroxyl ions in the neutral and alkaline solution to produce oxides and hydroxides of Fe(III) or Fe(II). These compounds precipitate on the NZVI surface and occupy the reactive sites, hindering the degradation reaction [22]. In addition, the oxidation potential of the $^{\bullet}$OH at neutral and basic solution is smaller than that at acidic conditions (E^0 at acidic condition = 2.7/2.38 V, E^0 at basic conditions = 1.8 V). The optimal pH for heterogeneous Fenton-like reactions is generally reported to be around 3 (Table 1).

Fig. 3(B) shows the response surface modeling of the effect of NZVI concentration on the degradation of 4-NP by heterogeneous Fenton-like reaction. As shown, by increasing the catalyst concentration, higher reaction rate and performance are obtained. Since higher concentration of NZVI increases $^{\bullet}$OH production, the reaction efficiency enhances. However, impact of increasing NZVI concentration on the degradation efficiency of 4-NP at a low level of 4-NP concentration is moderate, while at a high level of 4-NP concentration, the degradation efficiency of 4-NP was significantly improved by increasing NZVI concentration. The results suggest that 0.66 g/L NZVI is sufficient to obtain a good degradation efficiency of 4-NP for the contaminated water with each level of pollutant (4-NP) concentration over range 100–300 ppm.

The interaction effect of NZVI concentration and initial pH on the degradation of 4-NP is presented in Fig. 3(C). The results show that the impact of increasing NZVI concentration on the degradation efficiency of 4-NP at pH of 7 is more significant than that at pH 3. On the other hand in acidic solution with lower concentration of catalyst, good removal efficiency is obtained, while in neutral solution, a higher concentration of NZVI is required to get the same removal efficiency.

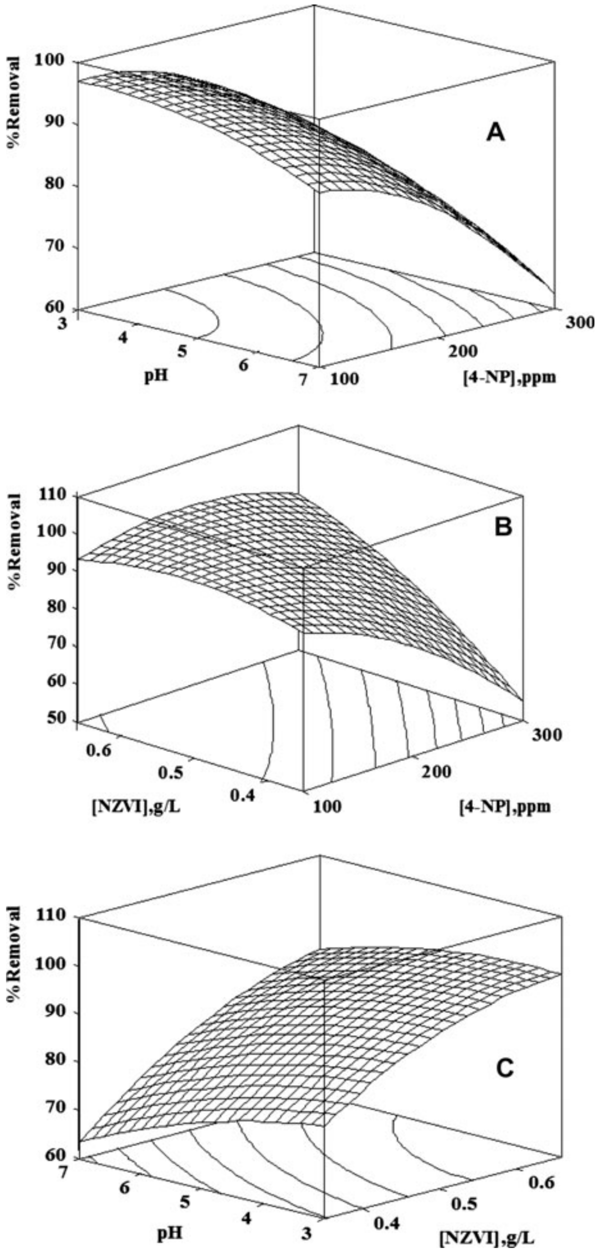

Fig. 3. Response surface plot and contour plot of the degradation efficiency of 4-NP as a function of (A) initial pH and concentration of 4-NP ([NZVI] = 0.5 g/L, $[H_2O_2]$ = 300 mM, and reaction time 50 min). (B) NZ+VI concentration and concentration of 4-NP (pH 5, $[H_2O_2]$ = 300 mM, and reaction time 50 min). (C) Initial pH and concentration of NZVI ([4-NP] = 200 ppm, $[H_2O_2]$ = 300 mM, and reaction time 50 min).

3.5. Optimal conditions

Based on the model prediction as obtained by CCD-RSM, the optimum conditions for the degradation of 4-NP by heterogeneous Fenton-like reaction on NZVI were determined to be 0.66 g/L NZVI, 300 mM H_2O_2, pH 3.0, reaction time 50 min, and 100–300 ppm 4-NP. The experimental removal efficiencies of 4-NP were greater than 93% under the optimum conditions. The experimental results matched well with the predicted results which validated the RSM models with good correlations (Fig. 4, $r^2 = 0.9680$). As shown in Fig. 4, the triangles represent the experimental data for the model development and the squares represent the additional experimental data for the model validation. It can be seen, the predicted removal efficiencies of 4-NP agree well with the experimental values.

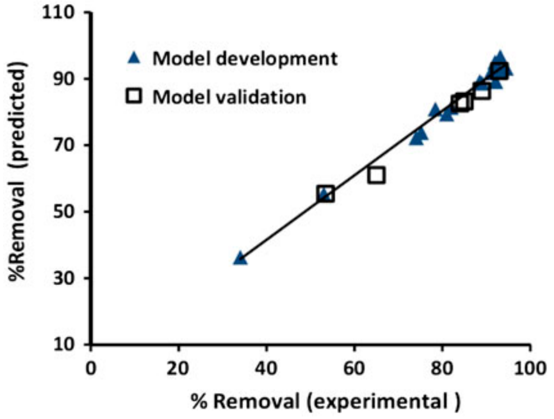

Fig. 4. Comparison of the experimental values and the model prediction degradation efficiency.

3.6. Analysis of real samples

To investigate the applicability of the proposed method for the removal of 4-NP, the method was employed for synthetic effluent treatment. The synthetic effluent has been made by spiking 100, 200, and 300 ppm of 4-NP into the well water with the following chemical composition: Ca^{2+} 110 mg/L, Mg^{2+} 17.6 mg/L, Na^+ 20.7 mg/L, Cl^- 17.8 mg/L, K^+ 1.1 mg/L. All conditions for effluent treatment were adjusted according to the optimized parameters which were already defined (0.66 g/L NZVI, 300 mM H_2O_2, pH 3.0, and reaction time 50 min). The obtained results of removal rate of 4-NP in real samples were 94, 92, and 91% according to COD based for 100, 200, and 300 ppm of 4-NP, respectively. The results obtained by the proposed method reveal the capability of the method for removal of 4-NP in real samples.

4. Conclusion

The successful and rapid degradation of 4-NP in water solution was achieved by the heterogeneous

Fenton-like reaction on NZVI catalyst. Experimental details of previous studies on 4-NP degradation are summarized in Table 1. Comparison of results of these reports and present study shows that (i) In most of them, the effect and the interaction of the experimental variables have not simultaneously evaluated. (ii) The present study develop an effective and rapid method for the degradation of 4-NP with the experimental conditions which are reasonable in point of utility. The results show that CCD coupled with RSM is a useful technique to optimize the important parameters of 4-NP degradation reaction.

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