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Removal of Nitrate by Bimetallic Copper-Nanoscale Zero-Valent Iron (Cu-nZVI): Using 2^k Full Factorial Design

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Abstract

Enhanced nitrate reduction of nanoscale zero valent iron (nZVI) by Cu prepared by impregnation method was studied in this work. Using a full factorial design, the performance of nZVI with and without Cu on surface in acidic and neutral conditions was investigated. Static batch reactor was selected in this study to investigate the effects of the independent variables such as catalysts (nZVI with and without Cu), initial pH of solutions (3, 7), and reaction times (10, 30 min). The results found that nitrate removal over Cu-nZVI was greater than that of nZVI by about 37% and 36% at pH 3 and pH 7 for 30 min, respectively. Both catalysts were effective in removing nitrate under acidic conditions (pH 3). Thus, this study concludes that nZVI can enhance the performance by Cu in nitrate removal. Moreover, acidic conditions were more effective than neutral conditions in removing nitrate.

Keywords: Cu; nZVI; bimetallic; nitrate reduction; acidic condition; Full Factorial Design (FFD)

Introduction

Urea fertilizer ($CO(NH_2)_2$) is widely used as a source of nitrogen in the agricultural industry in Thailand. Over-use is a major cause of high rates of leaching of nitrate in both surface and groundwater [1, 2]. Increased nitrates in the environment increase the risks of harmful from algal bloom (HABs) and dead zones in water bodies. Moreover, high nitrate concentration in drinking water is the main cause of methemoglobinemia disease. Nitrate can transform to nitrite in the blood and react the hemoglobin to become methemoglobin which is unable to bind and transport oxygen to body tissues through the bloodstream [2]. At high methemoglobin levels above 50-60% blood, a person can lose consciousness, enter a coma or even die. In infants from 0-3 months, methemoglobin causes a blue skin coloration [3]. Moreover, nitrate can affect the course of other diseases such as cancers, brain tumor, leukemia and nasopharyngeal [3, 4]. Thus, the U.S. Environment Protection Agency (US-EPA) has set maximum permitted levels for nitrate and nitrite in drinking water at 10 ppm and 1 ppm, respectively [3].

In view of the major health and environmental implications of high nitrate levels in water, techniques for removal of nitrate from water have been sought by many researchers, who have tested technologies such as biological denitrification, catalytic denitrification, chemical denitrification, electrodialysis, reverse osmosis, and ion exchange [2, 5-10]. However, technologies such as electrodialysis, reverse osmosis and ion exchange are expensive and impractical for large volumes of inorganic wastewater. For these reasons, chemical denitrification using nanoscale zero-valent iron (nZVI), known as the nitrate reduction process, has attracted the interest of many investigators as a more practical, lower cost solution. Although, nZVI is known to be highly effective in nitrate removal, the pH of the reaction is an important limitation [2-5, 11-12] since the possible reaction mechanisms between nZVI (Fe^0) and nitrite (NO_2^-) can produce the main products ammonium (NH_4^+) and nitrogen (N_2) under acidic conditions, following Equations (1) – (3) for direct reduction and Equations (4) – (5) for indirect reduction [2]. Yang and Lee reported nitrate reduction mechanism as shown in Equations (6) – (7) [2] to produce ammonium (NH_4^+) and nitrogen (N_2) on acidic conditions, as well.

Many researchers are interested in exploiting the nZVI reaction pathway from nitrate to gaseous nitrogen (Equations (2), (4) and (7)). By coating nzVI with novel metal catalysts such as Pt, Pd, and Cu [5, 13], called “bimetallic”, is a simple method to enhance the performance of nZVI because of the effect of increased surface area in bimetals in increasing nitrate adsorption on nZVI [14]. Liou et al. [5] found that Cu-nZVI shows higher efficiency than Pt and Pd loading because Cu can extract oxygen from nitrate and highly adsorb hydro-gen with both adsorbed species reacting continuously. Other researches such as Hwang et al. [11] have reported that bimetallic particles (nZVI/Cu 5% mol/mol) can increase the efficiency of nitrate removal from 50% to 98% compared with nZVI alone at initial concentrations of about 100 ppm and 180 minutes of reaction time. Mossa Hosseini et al. [14] also reported that about 2.5% w/w of Cu loaded on nZVI surface gave the highest performance in reducing nitrate through a packed sand column over 300 minutes. This finding was confirmed by Liou et al. [15]

Furthermore, nitrate reduction depended on the initial pH of the solution, as explained by Huang and Zhang [12] and Yang and Lee [2] because in conditions with pH > 4, nZVI cannot release electrons to reduce nitrate and nitrite to NH_4^+ and N_2. Thus, nZVI loaded with Cu was examined with the effect of initial pH of solutions in terms of main and interaction effects. Based on our existing knowledge, Design of Experiment (DOE) was not used to compare nZVI and Cu-nZVI and their interaction effects with the initial pH of solution. Instead, Full Factorial Design (FFD) was applied to elaborate these effects. The value of FFD for simulation and experimental analysis is widely acknowledged by researchers [16]. FFD offers a valuable tool for interpreting main effects and their interactions, and also for determining the optimal conditions using a mathematical model

$$3Fe^0 \rightarrow 3Fe^{2+} + 6e^- \quad (1)$$

$$2NO_2^- + 8H^+ + 6e^- \rightarrow N_2 + 4H_2O \quad (2)$$

$$2NO_2^- + 8H^+ + 6e^- \rightarrow NH_4^+ + 4H_2O \quad (3)$$

$$3H_2 + 2NO_2^- + 2H^+ \rightarrow 4H_2O + N_2 \quad (4)$$

$$3H_2 + 2NO_2^- + 2H^+ \rightarrow 4H_2O + NH_4^+ \quad (5)$$

$$NO_3^- + 4Fe^0 + 10H^+ \rightarrow 4Fe^{2+} + NH_4^+ + 3H_2O \quad (6)$$

$$2NO_3^- + 5Fe^0 + 12H^+ \rightarrow 5Fe^{2+} + N_2 + 6H_2O \quad (7)$$

$$\mathrm{Fe(H_2O)_6^{+3} + 3BH_4^- + 3H_2O \rightarrow Fe^0 + 3B(OH)_3 + 10.5H_2} \quad (8)$$

$$\mathrm{Fe^0 + Cu^{2+} \rightarrow Fe^{2+} + Cu^0} \quad (9)$$

$$\mathrm{Y} = \frac{\mathrm{C_0 - C_t}}{\mathrm{C_0}} \times 100 \quad (10)$$

The aim of this work was to synthesize nZVI and bimetallic Cu-nZVI and investigate their performance in nitrate removal. The experimental conditions were designed by 2^k FFD in terms of catalyst types (nZVI with and without Cu), initial pH of solutions (3, 7), and reaction times (10, 30 min) at 10 ppm of initial nitrate concentration. The experiments were done by following designed conditions and using a nitrate removal for response value.

Materials and methods

The chemicals used in this work were ferric chloride 6-hydrate (>97%, $FeCl_3 \cdot 6H_2O$, Panreac Química S.L.U.), sodium borohydride (>98%, $NaBH_4$, RFCL Limited), ethanol (>99%, C_2H_5OH, Merck & Co., Inc.), and copper (II) chloride (>99.9%, $CuCl_2$, Ajax Finechem Pty Ltd.). Nitrate stocks were prepared from potassium nitrate. Adjustments to the initial pH of solutions were done by 1 M hydrochloric and 1 M sodium hydroxide solutions. All solutions were prepared using deionized water (DIW).

The nZVI synthesis was applied from the procedure of Glavee et al. [17]. About 0.25 M of $NaBH_4$ solution was slowly dropped into 0.045 M of $FeCl_3 \cdot 6H_2O$ solution under continuous stirring and then nZVI was separated from the solution by magnetic technique. The fresh nZVI was washed with DIW two times. The reaction for ferric iron was reduced by borohydride to nZVI (Fe^0) as seen in Equation (8). The bimetallic Cu-nZVI was applied from Zhang et al. [18] and Mossa Hosseini et al. [14]. The fresh nZVI samples were washed with DIW and ethanol two times, respectively. Then, the samples were impregnated by 1 g Cu/L of $CuCl_2$ solution, about 2.5 mL on 0.1 g of nZVI as about 2.5% Cu on nZVI, to nZVI, with vigorous stirring in ambient temperature. The redox reaction between Cu and nZVI (Fe^0) is shown in Equation (9) [14].

The independent variables were catalyst types (A), initial pH of solutions (B) and reaction times (C) as shown in Table 1. The response values were the percent nitrate removal (%Y). The formula used to calculate the percentage of nitrate removal (%Y) is displayed in Equation (10) where Y is the percentage of nitrate removal (%), and C_0 and C_t are initial nitrate concentration (ppm) and residual nitrate concentration (ppm), respectively.

The 8 sets of static batch experiments selected to give the different efficiencies of catalysts were generated using 2^k FFD (using MiniTab 16) as shown in Table 2. The experiments were done using 250 mL of initial nitrate concentration (10 ppm) prepared from potassium nitrate, and the initial pH of solutions was adjusted using 1 M HCl and 1 M NaOH. The samples were collected and filtered through a 0.45 µm membrane filter. The remaining nitrate concentrations were deter-mined by UV-VIS spectroscopy according to standard method (ASTM 3867) [19].

Table 1 Investigated variables for nitrate removal

Variables	Levels	
	-1	+1
Catalyst (A)	nZVI	Cu-nZVI
Initial pH of solutions (B)	3	7
Reaction times (C)	10 min	30 min

Table 2 Static batch experiments generated using 2^k FFD

Runs	Catalyst	pH	Reaction Time (min)	Y (%)
1	nZVI	3	10	10.163
2	Cu-nZVI	3	10	46.856
3	nZVI	3	30	14.264
4	Cu-nZVI	3	30	49.962
5	nZVI	7	10	7.702
6	Cu-nZVI	7	10	34.620
7	nZVI	7	30	10.774
8	Cu-nZVI	7	30	41.894

Results and discussion

The static batch experiments studied three parameters: catalysts (A), initial pH of solution (B) and reaction times (C) following FFD designation. The percentage of nitrate removal results (%Y) are shown in Table 2. The effects and coefficients were calculated by least square of error technique as illustrated in Table 3.

Table 3 shows that the catalyst type (32.607) displayed the highest effect on nitrate removal compared with the other types tested (as also shown in Figure 1 and Figure 2). The finding implies that nitrate removal could be enormously enhanced by Cu loaded on nZVI surface. Initial pH of solutions had negative effect values for both catalysts, with and without Cu on the surface nZVI. Nitrate removal by nZVI varies by 3-4% for pH 3 and pH 7. The author claimed that it was similar efficiency (F-value = 1.30). However, for Cu-nZVI, percent of nitrate removal has very different values (F-value = 5.80) tested by analysis of variance (ANOVA). In this case it was about 10-12%. The percentage of nitrate removal (%Y) shown in Table 2 can be plotted to present the relationships of nitrate removal for both catalysts with the initial pH of solution and reaction times as illustrated in Figure 1.

The results indicate that Cu-nZVI reduced nitrate to greater effect than nZVI with 36.7% and 35.7% for pH 3 of solutions, and 26.9% and 31.1% for pH 7 of solutions in 10 and 30 min of reaction times, respectively. Accordingly, Liou et al. [13] found that Cu/Fe has k_{obs} value more than nZVI, about 3 times from 0.0214±0.0011 min^{-1} to 0.0664 ±0.0036 min^{-1}. The reduction mechanism of nitrate on Cu-nZVI can be explained by high adsorption of nitrate and hydrogen on Cu surfaces [5, 14].

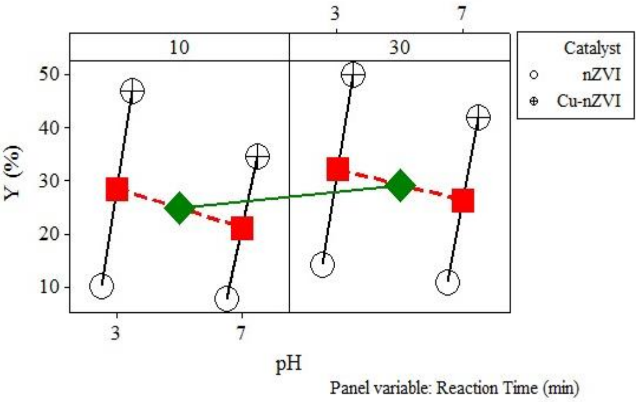

Figure 1 The relationship between percentage of nitrate removal (%Y) and reaction times of nitrate removal for nZVI with and without Cu^{2+} on the initial pH of solutions (3, 7).

Table 3 Effects and coefficients of nitrate removal

Factors	Effects	Coefficients
Constant		27.029
Catalyst (A)	32.607	16.304
Initial pH of solutions (B)	-6.564	-3.282
Reaction times (C)	4.388	2.194
Catalyst (A)* Initial pH of solutions (B)	-3.588	-1.794
Catalyst (A)* Reaction times (C)	0.802	0.401
Initial pH of solutions (B)* Reaction times (C)	0.785	0.392
Catalyst (A)* Initial pH of solutions (B)* Reaction times (C)	1.299	0.650

The data summarized in Table 2 also shows that at different solution pH (3 and 7), the percentage of nitrate removal over nZVI have similar efficiencies of about 3-4% while the percentage of nitrate removal over Cu-nZVI have very different values. The differences in nitrate removal efficiency with Cu at pH 3 were higher than at pH 7, about 12% and 8% at 10 and 30 min, respectively.

Figure 2 shows the Pareto chart of the effect values of all the variables. The data indicate that catalyst type has more effect than the initial pH of solutions, reaction time and their interactions of the variables for this experiment.

The main effects and the interactions of the variables are shown in Figure 3. In Figure 3(a), it was found that the Cu coating and increasing reaction times increased the percentage of nitrate removal while the initial pH of solutions showed the opposite. At high initial pH of solutions, the rate of reaction is lower than that at low initial solution pH. In addition, not all factors show interaction effects between the independent variables (Figure 3(b)). Under acidic conditions, Cu-nZVI shows high level of hydrogen adsorption (H_{ads}) on the surface, confirming the results of previous studies [11, 12]. Moreover, the high amounts of H_{ads} on the surface of nZVI continuously reacted with nitrate to form NH_4^+, as shown in Equation (6). Additionally, under neutral conditions, nZVI alone cannot reduce nitrate to products because it cannot release electrons as explained elsewhere [2]. Another reason for the observed effectiveness under acidic conditions is explained by the zeta potential of nitrate, which has a positive charge. Thus, under acidic conditions, nZVI totally exposes surface electrons for easy adsorption and chemical reduction of nitrate [2].

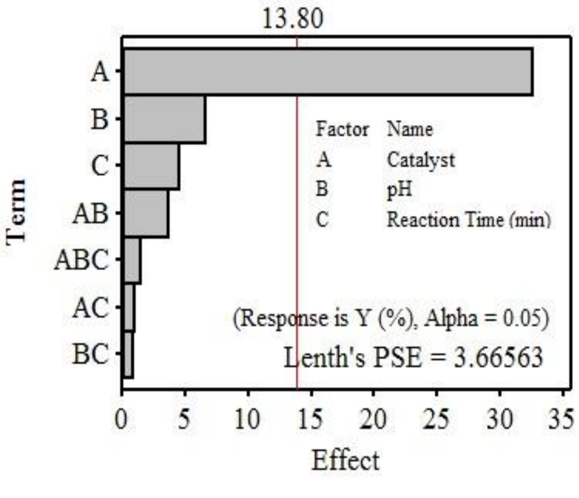

Figure 2 Pareto chart of effects of each factors.

The possible mechanisms of bimetallic Cu-nZVI for nitrate removal are illustrated in Figure 4, which shows that Cu-nZVI has about three main products for nitrate removal more than that of nZVI alone as nitrite and nitrogen gases. Therefore, coating Cu can enhance nitrate removal performance since Cu is reduced by nZVI to Cu^0 on the nZVI surface. Significantly, Cu can effectively adsorb hydrogen produced from the reaction between nZVI and water (Equations (11) and (12), which can then react with nitrate to produce nitrite (Equation (14)) and continuously react to form nitrogen gas and NH_4^+, as shown in Equations (2), (4) and (7) for nitrogen gas and Equations (3), (5), (6) and (15) for NH_4^+ ions. Under equilibrium conditions, nitrate can be adsorbed on Cu surfaces and then react with adsorbed hydrogen as shown in Equation (13), as explained elsewhere [5] to proposed possible reaction mechanisms in two pathways (Equations (11) – (15)). Liou et al. [15] also confirmed that the nitrite products can be produced by the bimetallic Fe^0 couple with Cu, while it cannot be produced by nZVI on nitrate removal. The coefficient values shown in Table 3 can be used to predict the percentage of nitrate removal as displayed in Equation (16), where Y is the percentage of nitrate removal (%), A is coded catalysts, B is coded initial pH of solutions, and C is coded reaction times. The interaction effects between with and without Cu loading on nZVI and initial pH of solutions are shown in Figure 5.

Figure 5 shows the contour plots of the percentage of nitrate removal as calculated from Equation (16). The results confirmed that the initial pH of solutions had an effect to reduce nitrate in which acidic conditions have more activity than neutral conditions on both catalysts. Huang and Zhang [12] reported that nitrate could be rapidly and completely reduced to ammonia because the H^+ ion directly affects the redox reaction of nitrate with its absorption onto reactive sites. Huang et al. [1] also indicated that nitrate greatly enhanced the rate and extent of its reduction on acidic solutions. Liou et al. [5] studied the loading Pd/Cu on nZVI surface with pH variables between 5.0-8.5 found that with the increase in pH, the k_{obs} (min^{-1}) will be decreased for nitrate reduction. Moreover, the Cu-nZVI can be used in higher initial pH of solutions than nZVI. Figure 5(b) shows the percentage of nitrate removal are more than 40-47.5% within pH 3–5 at 10 min while with nZVI, the values were lower at the same times (Figure 5(a)). Therefore, the co-process between Cu and nZVI surface can increase nitrate removal performance.

Anodic reaction:

$$Fe^0 \rightarrow Fe^{2+} + 2e^- \tag{11}$$

Cathodic reaction:

$$H_2O + Cu + e^- \rightarrow Cu - H_{ads} + OH^- \tag{12}$$

$$NO_3^- ads + Cu \leftrightarrow Cu - NO_3^- \ (at\ equilibrium) \tag{13}$$

$$Cu - NO_3^- + Cu - H_{ads} + 2e^- \rightarrow NO_2^- + OH^- + 2Cu \tag{14}$$

and then

$$NO_2^- + 3Fe^0 + 8H^+ \rightarrow 3Fe^{2+} + NH_4^+ + 2H_2O \tag{15}$$

$$\mathrm{Y} = 27.029 + 16.304\mathrm{A} - 3.282\mathrm{B} + 2.194\mathrm{C} - 1.794\mathrm{AB} + 0.401\mathrm{AC} + 0.392\mathrm{BC} + 0.650\mathrm{ABC} \tag{16}$$

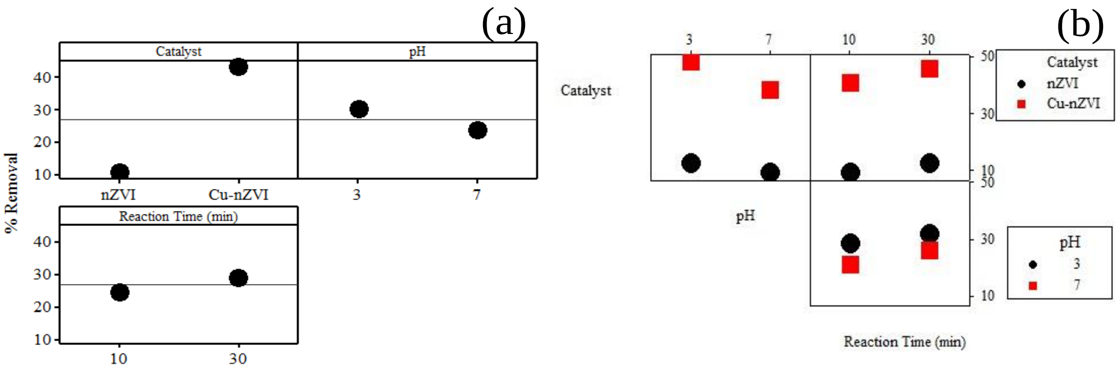

Figure 3 Main effects (a) and interactions effects (b) of variables.

Liou et al. [5] reported the effect of initial pH of solutions on nitrogen selectivity, which increased from about 4 to 30% with increasing initial pH of solutions from 5 to 8. Thus, Cu-nZVI in neutral conditions has shown an efficiency of about 35% and 42% at 10 min and 30 min, respectively, which would produce high nitrogen selectivity. Comparisons of nitrate removal performance are shown in a cube plot (Figure 6).

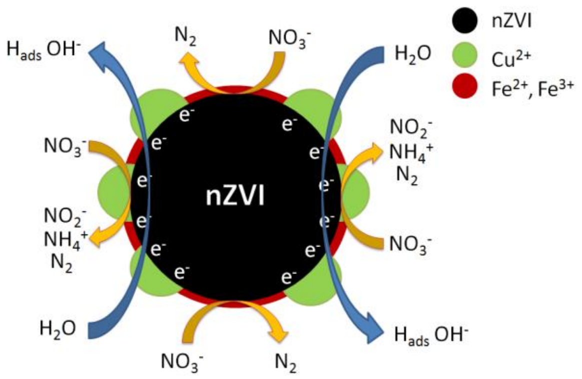

Figure 4 The mechanism of bimetallic Cu-nZVI for nitrate removal.

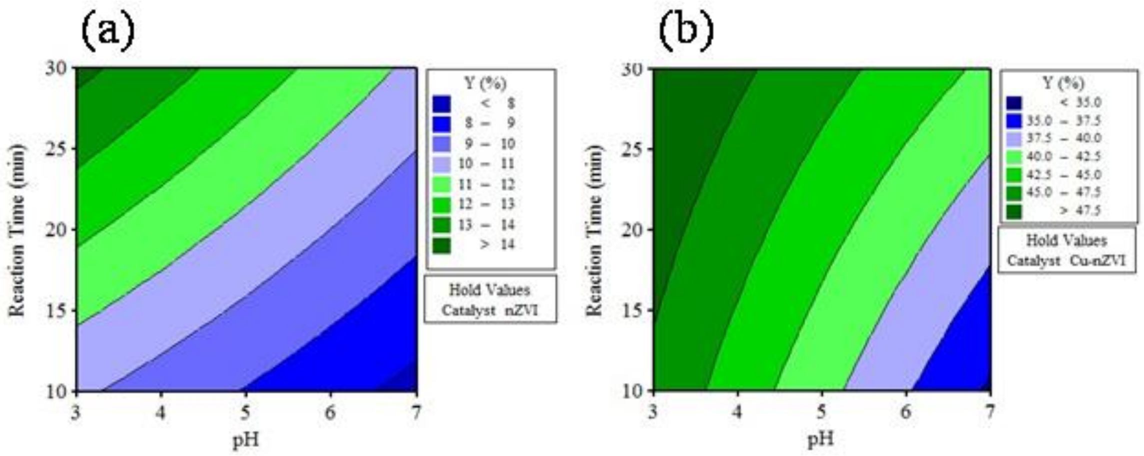

Figure 5 Contour plots between the percentage of nitrate removal vs. reaction times (min) and pH conditions of (a) nZVI and (b) Cu-nZVI.

Figure 6 demonstrates that the maximum condition for nitrate removal on Cu-nVZI at pH 3 and 30 min of reaction time was about 50%, while at pH 3 and 10 min of reaction time, it was about 47%. Referring to Equation (16), the percentage of nitrate removal can be calculated as the predicted values of nitrate removal. Comparison of experimental and predicted values for nitrate removal is shown in Figure 7 to check the accuracy of the Equation (16).

Figure 7 shows that Equation (16) was reliable because of its R^2, which is equal to 100%. We can conclude that the equation can be used to predict the percentage of nitrate removal in the variable ranges of our study.

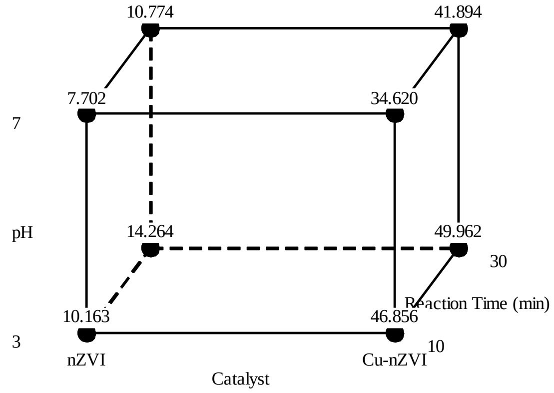

Figure 6 The cube plot of performance for nitrate removal.

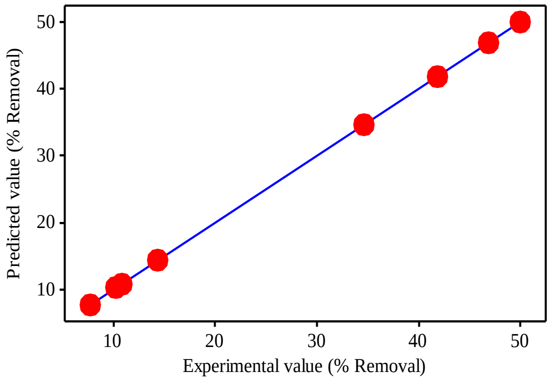

Figure 7 The relationship between experimental and predicted values of nitrate removal.

Conclusions

The performance of nZVI on nitrate removal can be enhances by coating Cu on its surface. Effect value of Cu-nZVI as shown the highest effect on nitrate removal was about 32.6 compared with nZVI alone. Cu-nZVI has shown higher effects on the nitrate reduction reaction than initial pH of solutions and reaction times as about 5 and 7.5 times, respectively. Nitrate can be reduced under acidic conditions more effectively than under neutral conditions. The interaction effects of each variable were insignificant. Moreover, Cu-nZVI in pH 3 and 30 min of reaction time was the optimum condition for nitrate removal as shown in this research, whilst Cu-nZVI can also be used under neutral conditions.

Acknowledgements

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