

Article

A Clean Method for Vanadium (V) Reduction with Oxalic Acid

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Abstract: Water pollution deteriorates ecosystems and is a great threat to the environment. The environmental benefits of wastewater treatment are extremely important to minimize pollutants. Here, the oxalic acid used as reductant was used to treat the wastewater which contained high concentration of vanadium (V). Nearly 100% of vanadium was efficiently reduced at selected reaction conditions. The optimization results simulated by response surface methodology (RSM) analysis indicated the parameters all had significant effects on the reduction process, and followed the order: dosage of oxalic acid > reaction temperature > reaction time > initial pH of vanadium-containing wastewater. The reduction behavior analysis indicated that the pseudo first-order kinetics model could describe well the reduction process with $E_a = 42.14$ kJ/mol, and was described by the equation as followed: $-\ln C = K_0 \cdot [pH]^{0.1016} \cdot [n(O)/n(V)]^{2.4569} \cdot [T]^{2.2588} \cdot \exp(-42.14/T) \cdot t$.

Keywords: vanadium; response surface methodology; reduction; oxalic acid



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1. Introduction

The environmental pollution caused by the smelting activities and intensive mining had brought serious threats to the living environment. Among them, vanadium pollution was a typical one [1–3]. In China, vanadium often existed in the vanadium-titanomagnetite, black shale and stone coal [4–8]. Large amounts of wastewater containing vanadium were produced during the vanadium production process by processing these vanadium-sources; some of them might distribute to the soil or groundwater [9–13]. For example, the wastewater collected from the vanadium plant in Chengde, China, contained a concentration of vanadium varying from 0.05 g/L to 0.2 g/L [2,14,15], and 0.076–0.208 mg/L in Panzhihua, China [15,16], which was far more than the regulation standard (50 µg/L) [1,2,17–22]. Vanadium belongs to the list of environmentally hazardous elements commented by the United Nations Environment Program (UNEP) and the minimum level was set as 0.2 µg/L [23]. Vanadium has existed in multiple valences, including −3, −1, 0, +2, +3, +4, and +5 in the environment, among which vanadium in +4 and +5 were stable and common [24–27]. The low concentration of vanadium was beneficial for growing plants, whereas a high concentration increased the risk of functional lesions in spleen, bones, liver, kidneys and nervous system by food chain [28]. Hence, the vanadium-containing wastewater needs to be treated before discharging.

Many methods have been developed for vanadium removal. Biological remediation came into view due to its low cost and potential applications for in situ remediation [13,29–35], but knowledge was limited on their interaction during the process, as well as their biogeochemical cycling in groundwater. Another low-cost and easy-operation technology is adsorption, which had been widely applied [36–40]. Additionally, many materials were evaluated, such as zeolite, chitosan, biochar, and orange peel [41–46]. However,

adsorption was limited to large-scale and industrial application, and the low concentration of vanadium in the vanadium-containing water streams.

Commonly, reduction in high-valence vanadium to low-valence was recognized as a reasonable route to detoxify them in groundwater as the low valence vanadium had less toxic and mobile [22,23]. Oxalic acid as a reductant had been widely used to treat wastewater containing oxidative metal ions due to low cost and its environmentally friendly nature [47–49]. It had been successfully applied in the reduction in chromium-containing wastewater and showed efficient performance [50–54]. This paper focused on the reduction process of vanadium (V) with oxalic acid. The experimental parameters including the initial pH of vanadium-containing wastewater, the dosage of oxalic acid, reaction time and reaction temperature on the reduction process were investigated. The optimal reaction conditions were improved by response surface methodology (RSM), which was an efficient method offering a large amount of information from a relatively small number of experiments, allowing the observation of both the effect of the independent variables on the response, as well as their possible interactions. Moreover, it had been extensively applied for optimization studies of test parameters and obtained response surfaces. The results obtaining in this work will provide a theoretical basis and technological support for the treatment of real wastewater.

2. Experimental Procedure

2.1. Materials

Sodium vanadate, sulfuric acid and oxalic acid were purchased from Kelong Co., Ltd., Chengdu, China. All the chemicals were analytical grade, and the solution was prepared with distilled water [10,55–57].

2.2. Experimental Procedure

The detailed experimental procedure could be seen in our previous works [56,57]. For the batch experiments, 0.05 M sodium vanadate solution (prepared by dissolving amount of sodium vanadate in the distilled water) was added into the 300 mL beaker placed in a water bath, the initial pH of the vanadium solution was adjusted by adding sulfuric acid. After the temperature was heated to the determined, the oxalic acid was added and then stirred at 500 rpm. During the reaction process, the samples were collected every 5 min and the concentration of vanadium (V) was measured by ICP-OES [56–58], and the reduction efficiency (η) of vanadium (V) was calculated by following Equation (1):

$$\eta = \frac{C_{t-1} - C_t}{C_{t-1}} \times 100\% \quad (1)$$

where, C_t , C_{t-1} , are the concentration of vanadium (V) at reaction time of t and the last time, mg/L.

2.3. Response Surface Methodology

The response surface methodology (RSM) was applied to optimize the experimental process and order the significance of experimental parameters as the single factor ignore the interactions between the parameters [57,59,60]. In this paper, the experimental parameters were selected as A (initial pH of vanadium solution), B (Reaction temperature), C (dosage of oxalic acid ($n(O)/n(V)$)), and D (Reaction time). Reduction efficiency was selected as the response. The actual values for them were confirmed through the single-factor experimental results and displayed in Table 1.

Table 1. Parameters and level values.

Parameters	Unit	Level		
		−1	0	1
A: initial pH of vanadium solution	–	1.5	5.0	8.5
B: Reaction temperature	°C	30	50	70
C: dosage of oxalic acid (n(O)/n(V))		2	6	10
D: Reaction time	min	10	55	100

3. Results and Discussion

It was well known that the potential of oxalic acid ($E^0(\text{C}_2\text{O}_4^{2-}/\text{CO}_2) = 0.49 \text{ V}$) was significantly lower than vanadium ($E^0(\text{VO}_2^+/\text{VO}^{2+}) = 1.35 \text{ V}$), the oxalic acid was a potential reductant for the reduction in vanadium (V) [61]. The E-pH diagram of vanadium and oxalic acid measured by HSC Chemistry 6.0 was shown in Figure 1a, it was clear that vanadium (V) was above than oxalate, which indicated that oxalic acid could reduce V(V) into V(IV) in theory. The ΔG of main reactions during the reduction process were calculated at 30 °C [59,62,63]. Figure 1b showed that the ΔG of all reactions were negative, which indicated that all the reactions were thermodynamically spontaneous.

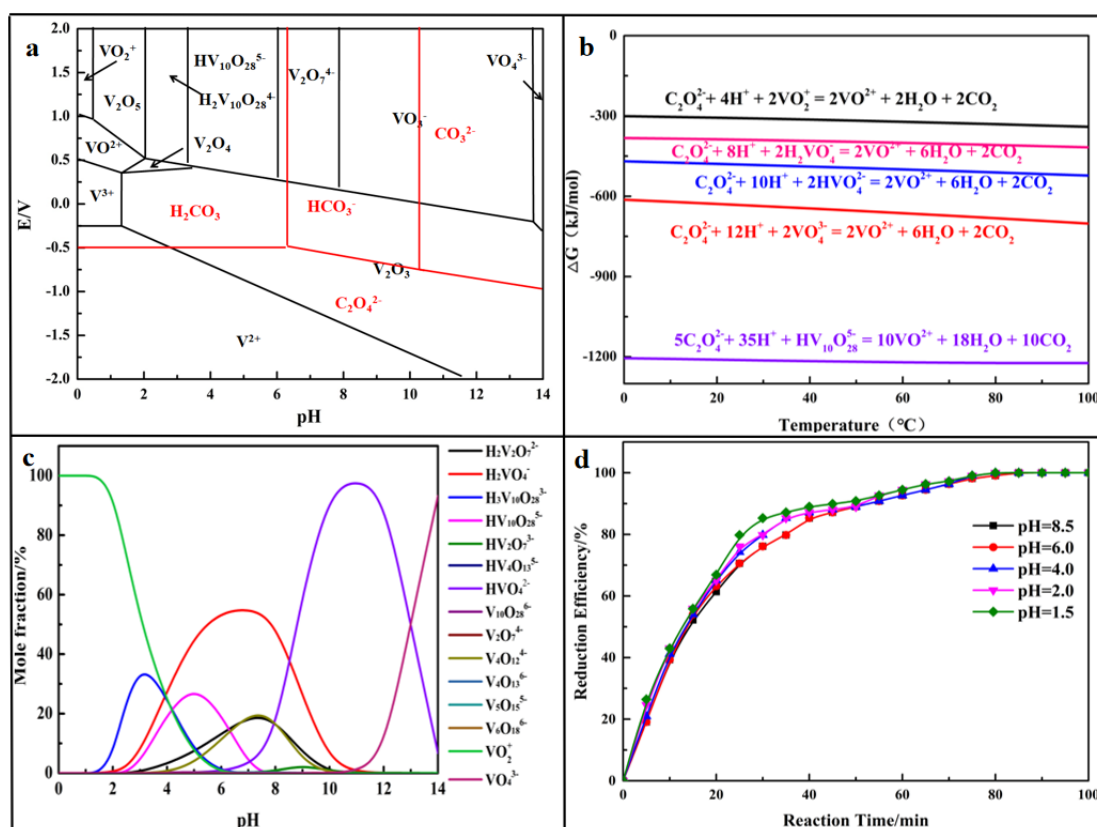


Figure 1. (a) E-pH diagram of vanadium (V) and oxalic acid at 30 °C; (b) relationship of ΔG -T; (c) The V-species in V-H₂O system at 30 °C (0.05 M); (d) effect of pH on the reduction efficiency of vanadium (V) at 30 °C and n(O)/n(V) = 10.

3.1. pH

Figure 1c summarized the mole distribution of vanadium species [64,65] indicated that the vanadium (V) existed in the form of VO_2^+ , HVO_4^{2-} , H_2VO_4^- , $\text{V}_2\text{O}_7^{4-}$, $\text{HV}_2\text{O}_7^{3-}$, $\text{H}_2\text{V}_2\text{O}_7^{2-}$, $\text{V}_4\text{O}_{12}^{4-}$, $\text{V}_4\text{O}_{13}^{6-}$, $\text{HV}_4\text{O}_{13}^{5-}$, $\text{V}_5\text{O}_{15}^{5-}$, $\text{V}_6\text{O}_{18}^{6-}$, $\text{V}_{10}\text{O}_{28}^{6-}$, $\text{HV}_{10}\text{O}_{28}^{5-}$, $\text{H}_2\text{V}_{10}\text{O}_{28}^{4-}$, $\text{H}_3\text{V}_{10}\text{O}_{28}^{3-}$. And the existence form was transformed along the pH of the vanadium-containing wastewater. The existing form of vanadium was varied with the

pH and concentration. The effect of initial pH of vanadium-containing wastewater was investigated at 30 °C and dosage of oxalic acid at $n(\text{O})/n(\text{V}) = 10$ with a continuous stirring of 500 rpm. Figure 1d displayed that the initial pH of vanadium solution had no obvious effect on the reduction efficiency of vanadium. The reduction efficiency was increased linearly at the beginning and then smoothly along the reaction time, and went to stabilize at last. On the other hand, the pH of the vanadium-containing wastewater was changed with the addition of oxalic acid, and along with the reaction time, the existing form of vanadium changed at the same time as the change in pH and concentration of $\text{V}(\text{V})$. The similarity of the reduction efficiency at various initial pH indicated that the reduction in vanadium was just affected by the vanadium valence, not the existing form.

3.2. Oxalic Acid

Figure 2 displayed the effect of dosage of oxalic acid ($n(\text{O})/n(\text{V})$) on the reduction efficiency at various reaction temperatures. When the $n(\text{O})/n(\text{V}) = 2$, the reduction efficiency was almost the same at 30 °C and 45 °C which were below 8.0%, and it was below 25.0% even the reaction temperature increased to 70 °C. It was indicated that low dosage of oxalic acid was not suitable for reduction even at high reaction temperature. Though the $n(\text{O})/n(\text{V}) = 2$ was far more than the theoretical dosage ($n(\text{O})/n(\text{V}) = 0.5$), the reduction efficiency was relatively low at all reaction temperatures, because the oxalic acid was not enough to reduce all the vanadium. During the reduction process, not all the oxalic acid was reacted, because some oxalate was formed soluble complex compounds with the reducing products (VO^{2+}). The reduction efficiency was increased from 8.0% to 100% as $n(\text{O})/n(\text{V}) = 2$ to $n(\text{O})/n(\text{V}) = 10$ at 30 °C confirmed that the dosage of oxalic acid accelerated the reduction process. The vanadium was easy to reduce at low dosage of oxalic acid within the increase in reaction temperature, which meant that the reaction temperature had an important influence on the reduction efficiency; thus, the effect of reaction temperature needs to be investigated.

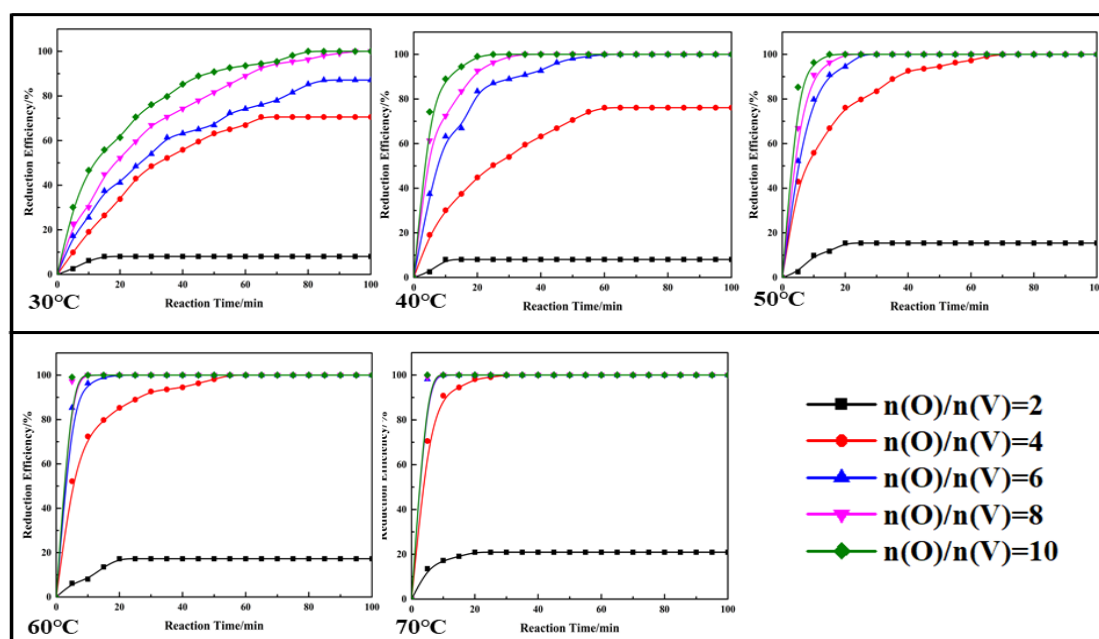


Figure 2. Effect of dosage of oxalic acid on the reduction efficiency of vanadium.

3.3. Reaction Temperature

It could be seen that the reduction process was enhanced at high temperature and high reduction efficiency was easily achieved at high reaction temperature from Figure 3. Near 100% of vanadium was reduced at high dosage of oxalic acid. Higher temperature was not beneficial for the stable complex of vanadium (IV) and oxalate, also could enforce

the reduction reaction between vanadium (V) and oxalate [56,57,65]; thus, almost all high-valence vanadium could be reduced to low-valence at higher reaction temperature. With the increase in reaction temperature and dosage of oxalic acid, the reduction efficiency was easy to achieve 100% at short time, which indicated that the reaction temperature and the dosage of oxalic acid played a synergy relationship on the reduction process, whereas whoever had the most important role was needed to be researched further.

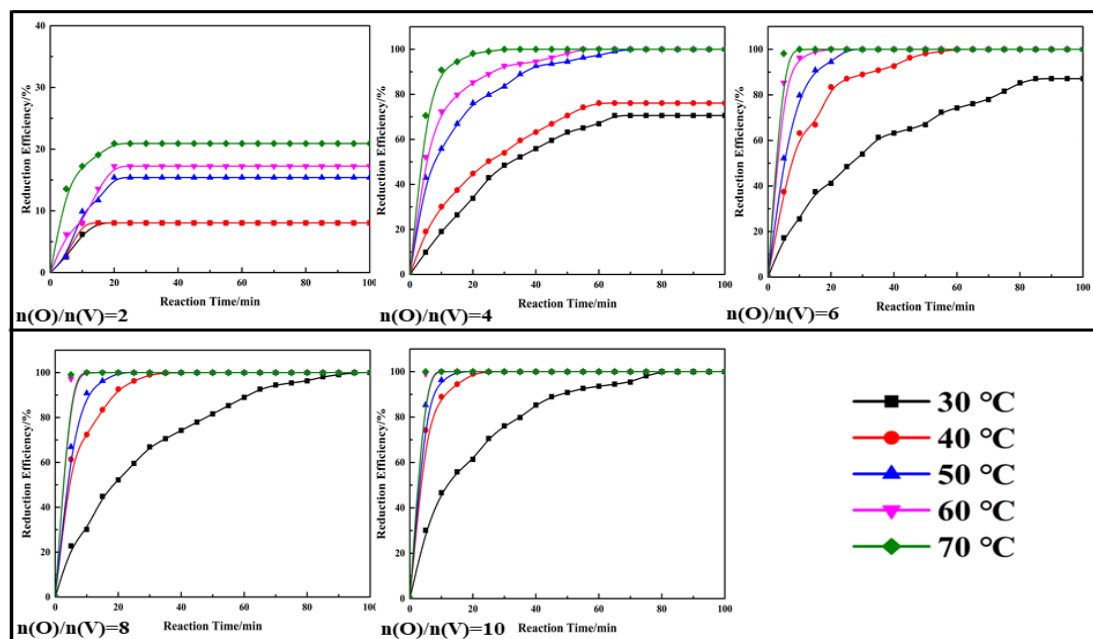


Figure 3. Effect of reaction temperature on the reduction efficiency of vanadium.

3.4. Response Surface Methodology

From the results analyzed above, the parameters including reaction time, reaction temperature, initial pH of vanadium-containing wastewater and dosage of oxalic acid all had influences on the reduction process, but was hard to distinguish the important for all. Thus, the response surface methodology was applied.

3.4.1. Model Fitting

The natural log was used to describe the relationship between reduction efficiency and experimental parameters, the simulated result was displayed in Equation (2):

$$\begin{aligned} \ln(\eta) = & 4.61 - 0.00003346 \times A + 0.26 \times B + 0.99 \times C + 0.18 \times D + 0.00006904 \\ & \times AB + 0.00003134 \times AD - 0.22 \times BC - 0.31 \times BD + 0.10 \times CD + 0.008452 \times A^2 \quad (2) \\ & - 0.17 \times B^2 - 0.90 \times C^2 - 0.16 \times D^2 \end{aligned}$$

The coefficients of the experimental parameters were -3.346×10^{-5} , 0.26, 0.99 and 0.18 according to Equation (2), and the positive coefficients corresponding to the positive effect (the coefficient of A was relatively small, which could be ignored). The order of the parameters affected the reduction efficiency was $C > B > D > A$ (showed in Figure 4). Above all, the dosage of oxalic acid and reaction temperature had the greatest influence on the reduction process.

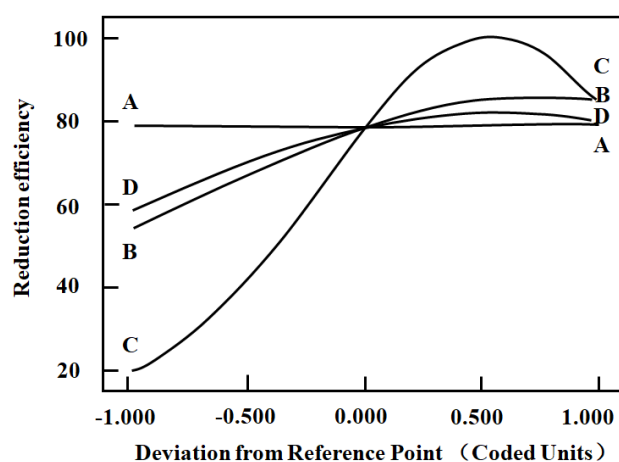


Figure 4. Perturbation plot for the precipitation efficiency of vanadium (initial pH of vanadium solution (A), reaction temperature (B), $n(\text{O})/n(\text{V})$ (C) and reaction time (D)).

3.4.2. Interaction Effects of Parameters

The reduction process of vanadium using oxalic acid through various variables could be investigated through these model equations. Different parameters R^2 , p values, F values and adjusted R^2 values were measured as standard that were helpful to determine the accuracy of every coefficient in order to appraise the significance of predicated model. The ANOVA results (seen in Table 2) confirmed that model F values of 80.96 showed that the predicated model was substantial. There was only 0.01% chance that an F values, which could occur owing to noise. The model p values less than 0.050 confirmed significant model terms. In this optimization case, several model terms such as B, C, D, BC, CD, B^2 , C^2 and D^2 were in significant form due to their less p values. The values larger than 0.10 means insignificant model terms. In this case, A, AB, AC, AD, BD and A^2 were insignificant model terms. The R^2 value exhibited a measure of how much variability in the observed response values could be expressed by the experimental factors as well as their interactions by establishing a relationship between predicated and experimental consequences. R^2 close to one revealed good fitting of experimental data into the predicated model equation. The regression model produced higher R^2 up to 0.9878 signifying excellent fitting between model as well as experimental data values. The R^2 up to 0.9297 was in reasonable agreement with an adjusted- R^2 of 0.9756. The Adequate-precision was helpful to evaluate the signal-to-noise ratio. A ratio greater than 4 was desirable. Here, higher adequate precision of 28.532 revealed an adequate signal. This regression model could be applied to navigate the design space. The relationship between actual and predicated data values was shown in Figure 5b. It could be analyzed that maximum data values fall over the straight line without passing any residual through variance, which confirmed the applicability of proposed model for adsorption processes. The association between normal plot of residuals and normal probability in the RSM method for the reduction of vanadium were shown in Figure 5a. From this plot, the data points were also close to the straight region, confirming ideal and normal distributions and independent of the residuals. Figure 5c described the residuals plotted on the run number. It also helpful to examine the accuracy of regression model for predication purposes. Similarly, the plot between leverage and run number was shown in Figure 5d, which was employed to standardize the residuals.

Table 2. ANOVA results.

Source	Sum of Squares	Z	Mean Square	F Value	p Value Prob > F
Model	19.12	14	1.37	80.96	<0.0001
A	1.343×10^{-8}	1	3.60	7.966×10^{-7}	0.9993
B	0.84	1	1.76	49.78	<0.0001
C	11.78	1	11.78	698.64	<0.0001
D	0.39	1	3.31	23.08	0.0003
AB	1.907×10^{-8}	1	0.12	1.131×10^{-6}	0.9992
AC	0	1	0.19	0	1.0000
AD	3.928×10^{-8}	1	0.24	2.329×10^{-7}	0.9996
BC	0.19	1	2.54×10^{-3}	11.28	0.0047
BD	0.38	1	0.26	22.35	0.1400
CD	0.041	1	0.16	2.45	0.0003
A ²	4.634×10^{-4}	1	5.787×10^{-3}	0.027	0.8707
B ²	0.20	1	0.41	11.72	0.0041
C ²	5.27	1	2.533×10^{-3}	312.59	<0.0001
D ²	0.16	1	0.60	9.72	0.0076
Residual	0.24	14	0.017	-	-
Lack-of-fit	0.24	10	0.024	-	-

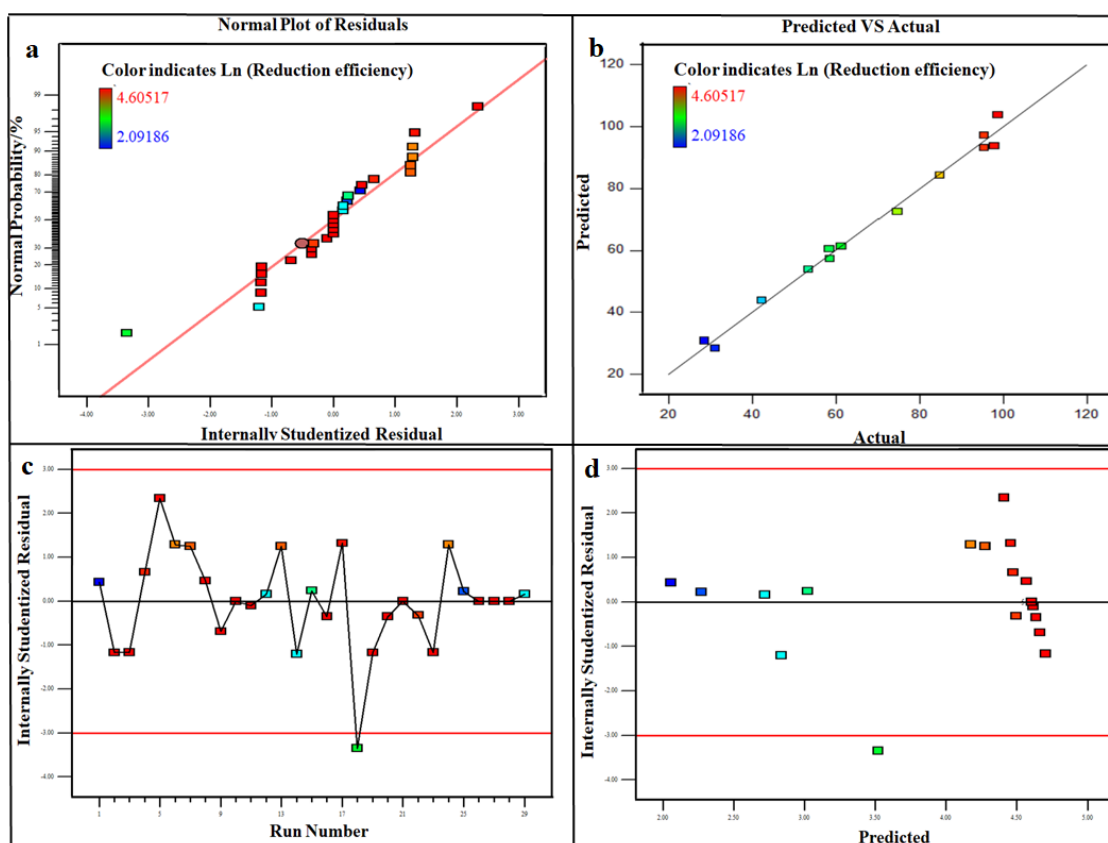


Figure 5. Diagnostic plots of the quadratic model. (a) Internally studentized residual, (b) actual, (c) run number, (d) predicted.

The possible inspiration of variables over maximum reduction efficiency for vanadium using oxalic acid was explained through response surface plots. These response surface plots were helpful for the determination of cooperative association between specific parameter and response for the maximum reduction efficiency. Figures 6–11 described 2D counter plots of combined influence of four experimental parameters over the reduction efficiency for vanadium using oxalic acid. The counter plots were providing the mutual interactions

among the independent parameters. It could be analyzed that all selected parameters had direct effect over the reduction in vanadium. These response surface plots confirmed the perfect and strong interactions among the selected independent experimental parameters.

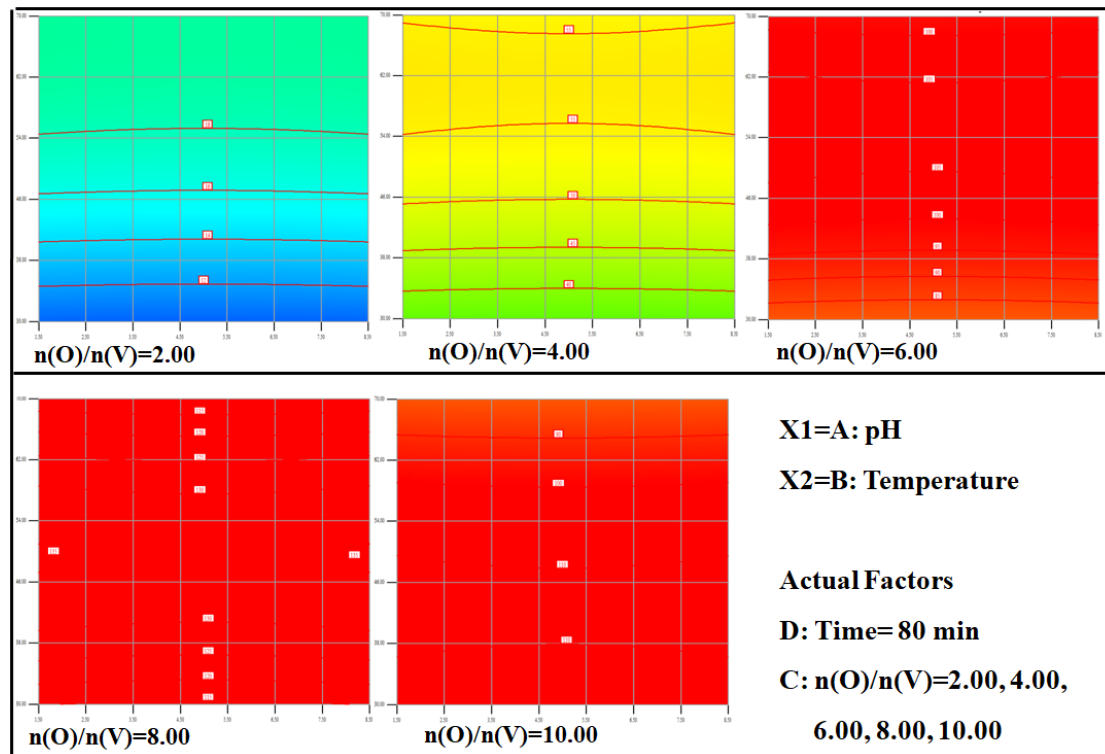


Figure 6. Response surface plots for factors (A to B).

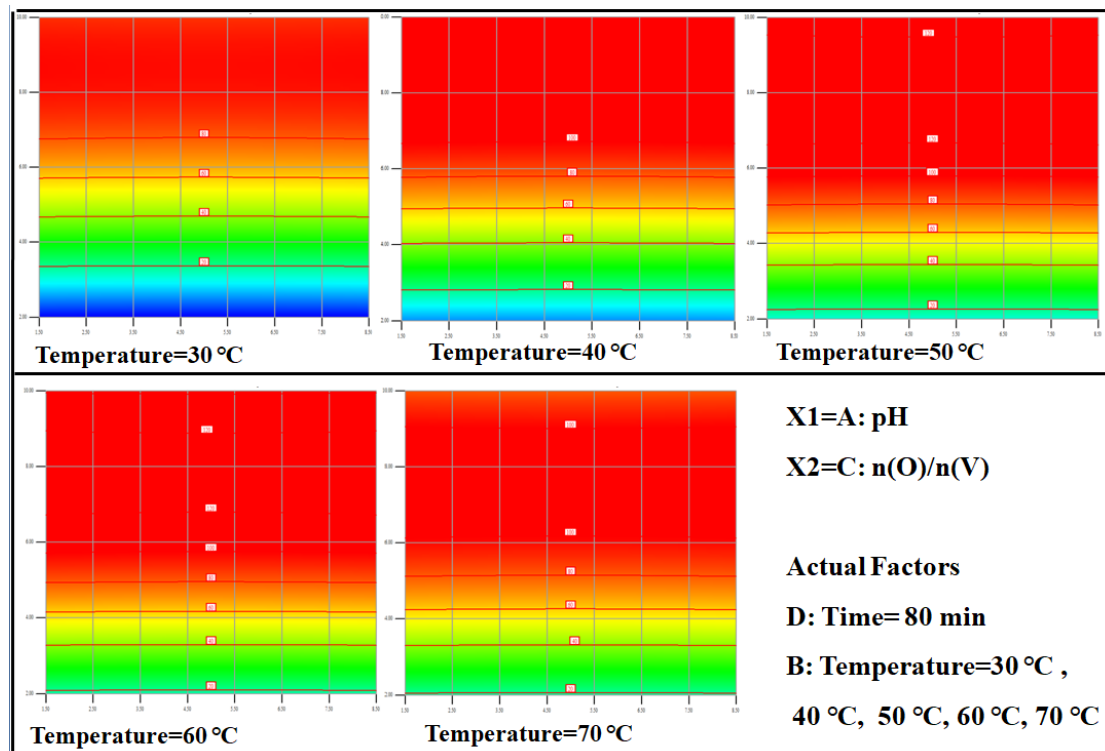


Figure 7. Response surface plots for factors (A to C).

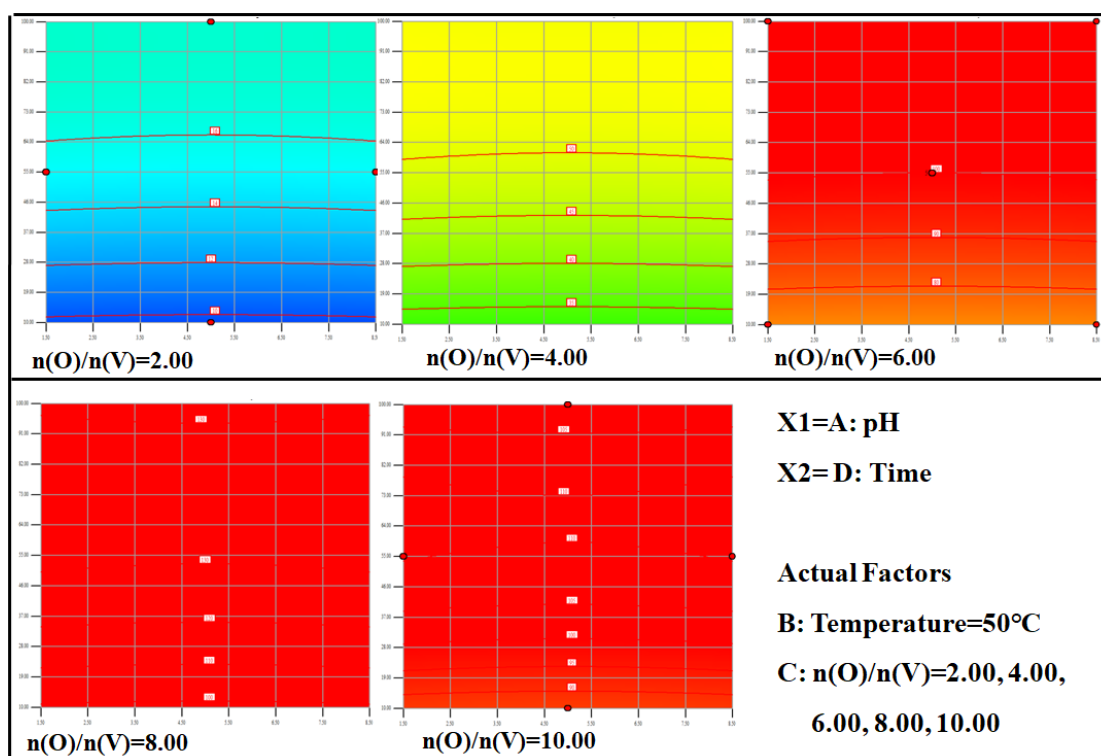


Figure 8. Response surface plots for factors (A to D).

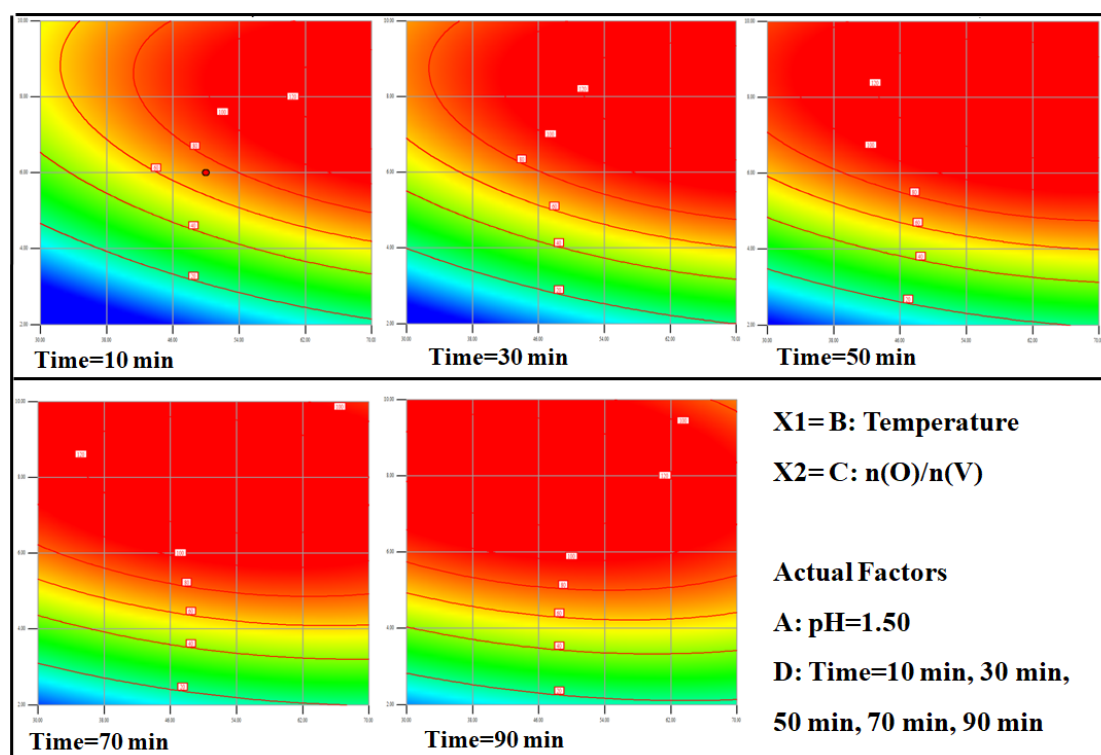


Figure 9. Response surface plots for factors (B to C).

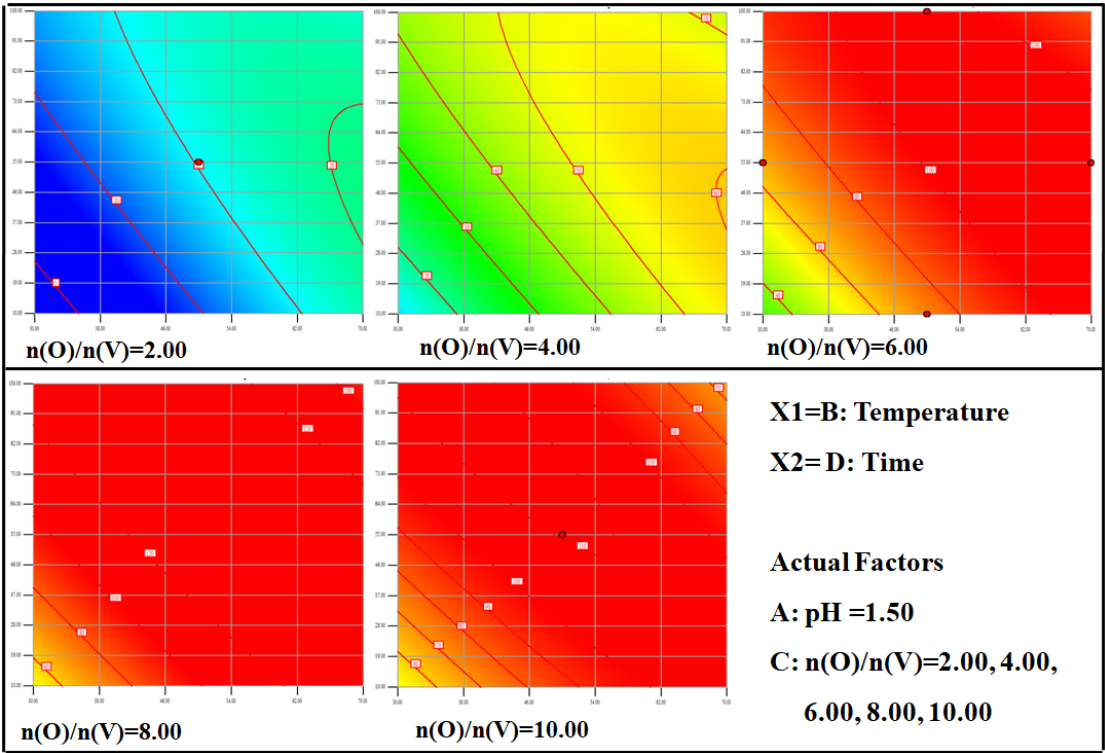


Figure 10. Response surface plots for factors (B to D).

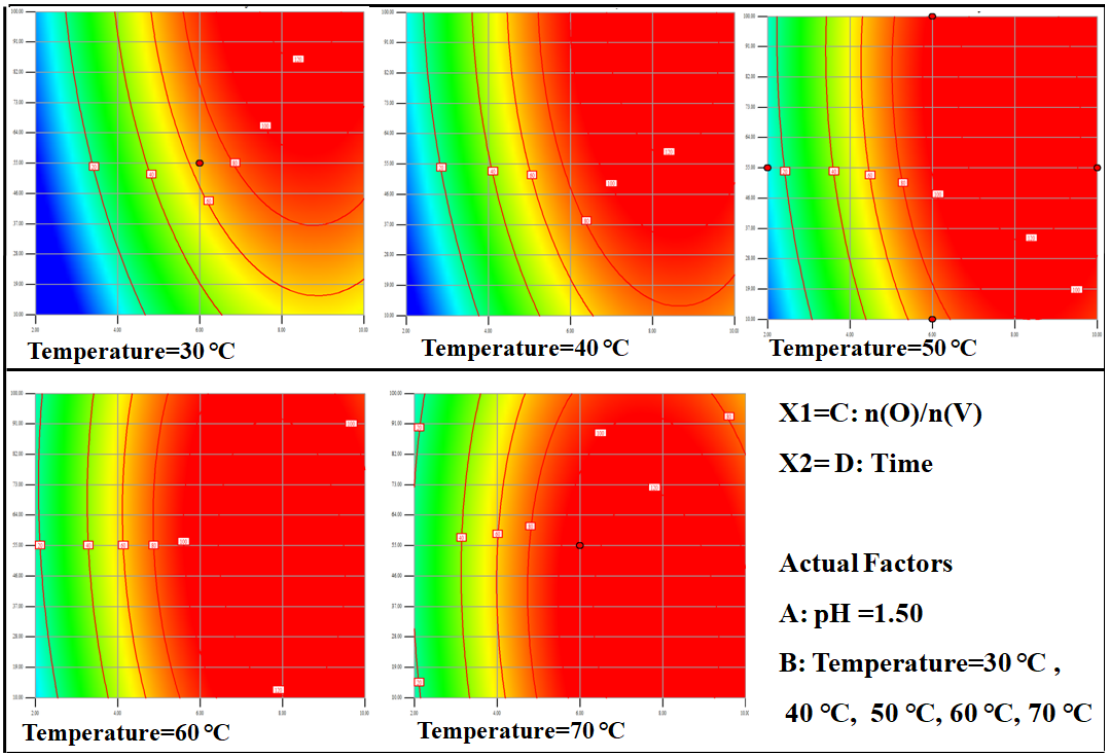


Figure 11. Response surface plots for factors (C to D).

3.5. Reduction Kinetics Analysis

Based on the references, the reduction behavior kinetics of vanadium (V) with oxalic acid was simulated by the pseudo first-order model (Equation (3) [66–68]).

$$v = \frac{dC}{dt} = -KC \quad (3)$$

Integrate.

$$-\ln C = Kt - \ln C_0 \quad (4)$$

Table 3 showed the apparent rate constants K correlation coefficients fitted with Equation (4); it was indicated that the selected model could describe the reduction behavior kinetics well (all the R^2 were closely to 1). The E_a of reduction of vanadium (V) was calculated as 42.14 kJ/mol following Equation (5) (Figure 12a).

$$\ln K = \ln A - E_a/RT \quad (5)$$

The reduction process was significantly affected by dosage of oxalic acid, reaction temperature and the initial pH of vanadium-containing wastewater according to the results analyzed above. Equation (6) described the relationship between the reaction rate constant and the reaction parameters, and it could be determined as fitting plot of $-\ln C$ versus time for different initial pH of vanadium-containing wastewater [pH], dosage of oxalic acid $[n(O)/n(V)]$ and reaction temperature $[T]$. The results were showed in Table 4 and Figure 12b–d.

$$K = K_0 \cdot [\text{pH}]^a \cdot [n(O)/n(V)]^b \cdot [T]^c \cdot \exp(-E_a/RT) \cdot t \quad (6)$$

After the transformation of above equations, the Equation (7) was obtained:

$$-\ln C = K_0 \cdot [\text{pH}]^a \cdot [n(O)/n(V)]^b \cdot [T]^c \cdot \exp(-E_a/RT) \cdot t \quad (7)$$

A $\ln K$ versus $\ln [\text{pH}]$, $\ln [n(O)/n(V)]$ and $\ln [T]$ plot (Figure 12b–d) were conducted to confirm the order of dependency with respect to pH, mole ratio of oxalic acid on vanadium and reaction temperature. The orders were calculated as 0.1016, 2.4569 and 2.2588, respectively. Therefore, the reduction kinetics equation was described as followed:

$$-\ln C = K_0 \cdot [\text{pH}]^{0.1016} \cdot [n(O)/n(V)]^{2.4569} \cdot [T]^{2.2588} \cdot \exp(-42.14/T) \cdot t \quad (8)$$

Table 3. Apparent rate constants K correlation coefficients.

Temperature	K	R^2
30	0.01874	0.9839
40	0.02274	0.9667
50	0.04118	0.9701
60	0.06918	0.9926
70	0.12442	0.9902

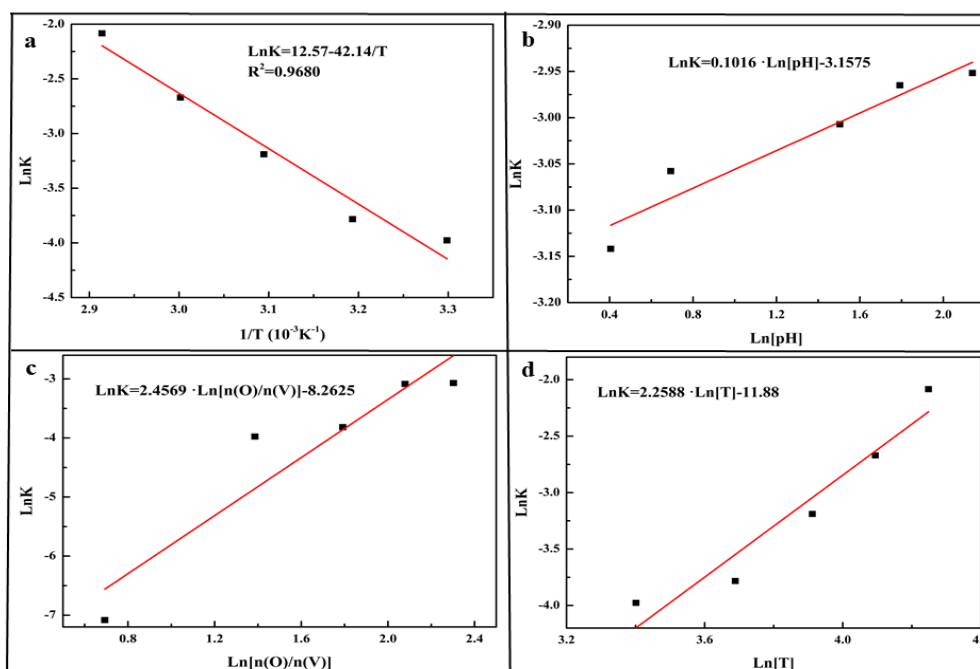


Figure 12. Kinetics plots: (a) Natural logarithm of reduction reaction constant vs. reciprocal temperature; (b) plot of K as a function of pH; (c) plot of K as a function of n(O)/n(V); (d) plot of K as a function of temperature.

Table 4. Apparent rate constants and correlation coefficients for experimental parameters.

Parameters	K	R ²
pH		
30	0.05225	0.9555
40	0.05156	0.9572
50	0.04943	0.9286
60	0.04699	0.9792
70	0.0472	0.9798
n(O)/n(V)		
2	0.00084	0.9654
4	0.01874	0.9902
6	0.02197	0.9878
8	0.04570	0.487
10	0.04637	0.9806
Temperature		
30	0.01874	0.9839
40	0.02274	0.9667
50	0.04118	0.9701
60	0.06918	0.9926
70	0.12442	0.9902

4. Conclusions

In this paper, the oxalic acid used as reductant was used to reduce vanadium from the aqueous solution. The following conclusions could be obtained:

- (1) The vanadium could be reduced efficiently by oxalic acid. Reaction temperature and oxalic acid played a synergy relationship on the reduction process. High dosages of oxalic acid and higher reaction temperature were beneficial for the reduction process.
- (2) Several independent experimental parameters named initial pH of vanadium-containing wastewater, reaction time, dosage of oxalic acid and reaction temperature were optimized through RSM as statistical techniques. The influence of each parameter on the

reduction efficiency followed the order: dosage of oxalic acid > reaction temperature > reaction time > initial pH of vanadium-containing wastewater.

- (3) Pseudo first-order kinetics model was good fitted with the experimental data and the E_a for the reduction in vanadium was calculated to 42.14 kJ/mol. The reduction process was significantly affected by the parameters including pH, dosage of oxalic acid, reaction time and reaction temperature, the reduction kinetics equation was described as followed: $-\ln C = K_0 \cdot [\text{pH}]^{0.1016} \cdot [\text{n(O)}/\text{n(V)}]^{2.4569} \cdot [\text{T}]^{2.2588} \cdot \exp(-42.14/\text{T}) \cdot t$.

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