

# Recovery of Vanadium by ammonium chloride precipitation method using response surface methodology

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## ABSTRACT

In this study, vanadium recovers from an alkaline solution based on the precipitation process and response surface methodology. A white salt ammonium metavanadate was obtained using the ammonium chloride precipitation method. Ammonium chloride was added directly to the alkaline liquor solution and the pH was adjusted approximately between 5 and 7 to form the white salt. The parameters affecting the recovery of vanadium, including the ammonium chloride concentration, the pH and the vanadium concentration in the caustic solution, were examined. The precipitation time had no significant influence on the vanadium recovery. The concentration of vanadium in the caustic solution and the concentration of ammonium chloride used for the precipitation were inversely related. It was found that a high recovery (over 90%) can be achieved with ammonium chloride and vanadium with concentrations over 4% (w/v) or 1000 mg L<sup>-1</sup> (in the lye solution). It has also been observed that working in the pH range of 5 to 7 results in over 90% recovery. The influence of the parameters mentioned on the recovery of impurities was examined and the optimal values determined. Ultimately, the maximum vanadium recovery (97.29%) was achieved at the optimal point obtained from the reaction surface methodology.

## 1. Introduction

Vanadium is of industrial and strategic importance due to its particular use. The main application of this element is in the steel industry. The highest production of vanadium in the world is in the form of vanadium pentoxide. Vanadium and its compounds are widely employed in the metallurgical, petrochemical, defense, electronics and paint and coating industries due to their excellent mechanical, catalytic, magnetic and other

physicochemical properties. The primary sources of vanadium compounds are ore feedstocks, concentrates, metallurgical slags, and petroleum residues [1,2]. Different methods have been applied for vanadium precipitation depending on leach solution (acidic, alkaline, or aqueous solutions). The followings are the studies and methods used to precipitate vanadium from these three leach solutions. Vanadium can be recovered from a leach solution by adjusting the pH with sulfuric acid or hydrochloric acid and adding an ammonium salt at temperatures between 22 and 28 °C [3]. Sodium hexavanadate Na<sub>4</sub>V<sub>6</sub>O<sub>17</sub> (red cake) can be

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precipitated by adding sulfuric acid with a pH of 2-3, and the precipitate is dissolved in an aqueous sodium carbonate solution. The red cake is cleaned and some impurities such as iron, aluminum, and silicon are separated from the solution by pH adjustment and precipitation. Then, ammonium chloride is added to the ammonium metavanadate precipitate. The calcination step is carried out, and vanadium pentoxide ( $V_2O_5$ ) is finally obtained with a purity of 99.8% [4]. There is a relationship between the temperature of ammonium addition and the Precipitation Rate (PR), with the PR being 99.5% from 30 to 65°C while the PR decreases at temperatures below 35°C because the solubility of ammonium sulfate is not the same at different temperatures and dissolves faster at high temperatures. The presence of pollutants also affects the precipitation process. The sodium concentration influences the precipitation process, as sodium ions replace  $NH_4^+$  ions. High sodium contents prevent the replacement of  $Na^+$  by  $NH_4^+$ . Therefore the amount should be controlled and below 25 g L<sup>-1</sup>. The silicon concentration should be below 1.5 g L<sup>-1</sup>. A high aluminum concentration prevents the formation of ammonium polyvanadate crystals, so the concentration should be below 0.1 g L<sup>-1</sup> [5]. In another study, the technology for extracting vanadium from coal was investigated. Scholars were able to precipitate ammonium metavanadate by leaching (with water) and adding acid (sulfuric acid or hydrochloric acid) to form polyvanadate. The precipitate was dissolved with sodium hydroxide, and ammonium salt was added. Then, calcination process was performed at 550 °C. Finally, vanadium pentoxide was obtained [6, 7]. Based on research by Wang et al., they worked on an alkaline sodium hydroxide leach solution containing 84.45 gL<sup>-1</sup> vanadium pentoxide.

Ammonium metavanadate was precipitated by adjusting the pH with hydrochloric acid in the range of 8 to 8.5. Ammonium chloride was added at 40 - 45 °C. Then, vanadium pentoxide was obtained with a purity of 99.12% by calcination at 550 °C for one hour [8]. Iron and nickel do not enter the solution in alkaline leaching with sodium hydroxide, but

aluminum and silicon enter the solution with vanadium. During acid leaching, sulfuric acid, iron, nickel, aluminum, and silicon enter the solution with vanadium. In leaching with sodium carbonate, only aluminum is introduced, and other metals do not get into the solution with vanadium. In the alkaline leaching process, sodium hydroxide was precipitated by adjusting the pH to 8 with sulfuric acid in the absence of ammonium chloride, aluminum, and silicon, while vanadium was in the solution. The addition of 1-2 M ammonium chloride solution and adjustment of the pH to 5 was resulted in the formation of a vanadium precipitate [9]. The technology of vanadium extraction from coal was also developed in another study. The focus was on cleaning the alkaline leach solution to remove silicon and aluminum. This purification took place in two stages. In the first stage, most of the sulfuric acid impurities were removed by adjusting the pH in the range of 8 to 9. In the second stage, the remaining silicon, aluminum, and other impurities such as phosphorus were removed by chemical precipitation. The chemical precipitation was obtained by adding 8 g L<sup>-1</sup> magnesium nitrate and 10 ml L<sup>-1</sup> ammonia at 60°C for 1 hour in a shaker with a speed of 500 rpm. The vanadium recovery in this process was 94.25% [10]. In another study, the focus was on vanadium recovery from consumer catalysts. Acid leaching and precipitation were performed by adjusting the pH to 6 – 7 with 1 M sodium carbonate solution. It was found that precipitation at pH levels above 7 should be avoided as this will lead to the precipitation of nickel and other metals [11]. The precipitation of vanadium can be achieved by adding ammonium chloride and an alkali such as sodium hydroxide to an acidic leach solution to adjust the pH. The solubility of sodium metavanadate increases with the pH value of the alkaline solution and temperature. Vanadium pentoxide was obtained with a purity of 99% [12]. In the recovery of vanadium from the acidic leach solution of charcoal, scholars could obtain vanadium pentoxide with a purity of 99%. Ammonium chloride was added to a solution at a pH of about 2, and the precipitate of ammonium

vanadate was taken out. The precipitate was roasted at 520 °C for 2 hours, and vanadium pentoxide was obtained with a purity of 99% [13]. The recovery of molybdenum and vanadium from consumable catalysts was investigated. Ammonium chloride is widely used for vanadium precipitation in the industry because of its economic cost. An excessive amount of ammonium chloride is required because excess ammonium chloride causes vanadium precipitation and ammonium solubility. As a result, the solubility of ammonium vanadate in the solution decreases as the ammonium chloride concentration increases. More than 99% of vanadium precipitates if the concentration of vanadium pentoxide in the solution is 25 g L<sup>-1</sup>, and the concentration of ammonium chloride is more than 40 g L<sup>-1</sup>. It was found that the concentrations of vanadium pentoxide in the leach solution and ammonium chloride are heavily involved in the vanadium precipitation process and are interdependent. It is also stated that the precipitation reaction takes place at pH range of 8 to 9 [14,15]. Based on studies carried out and considering that the Saghand ore is of the titanium magnetite type and the amount of vanadium in the ore is about 5000 mg L<sup>-1</sup>, the suitable method for vanadium recovery from this ore type is salt roasting with sodium carbonate and leaching with hot water. The leach solution used in our study has been prepared under the same conditions, ie salt roasting and leaching with hot water, and the precipitation process has been performed in the alkaline solution obtained by leaching with hot water. The reason for choosing the precipitation method is its low cost and simplicity of the process. Therefore, such a process is of great importance for large-scale use due to industrial needs and constraints. A thorough review of similar studies revealed that complete and accurate information about the optimal conditions for vanadium precipitation is not available. In this study, preliminary experiments were performed to determine the optimal precipitation conditions. The important parameters including ammonium chloride concentration, pH, precipitation time and vanadium concentration in the leach solution were investigated and their optimal values were specified

## 2. Experimental

### 2.1. Materials and analytical instruments

All materials and reagents including FeCl<sub>3</sub> (99%), NaVO<sub>3</sub> (98.5%), Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (95%), Ca(NO<sub>3</sub>)<sub>2</sub> (100%), Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (99%), Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O (99.5%), K<sub>3</sub>PO<sub>4</sub>·3H<sub>2</sub>O (99%), SiO<sub>2</sub> (99%), NH<sub>4</sub>Cl (99.5%), HCl (37%), H<sub>2</sub>SO<sub>4</sub> (98%) and (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> (99.9%) were provided by Merck (Germany) in analytical grade. All solutions were made with deionized water. Concentration of the ions in the solutions was determined using inductively coupled plasma (ICP) (Varian liberty 150 XL). Inductively coupled plasma spectroscopy is a method of emission spectroscopy in which the atomization takes place with the aid of plasma that is generated by an inert gas, mainly argon. This method is used for elemental analysis (mainly cations) of most elements.

### 2.2. Precipitation process

First of all, the Saghand ore was roasted with 50% by weight sodium carbonate at 900 °C for two hours. Then, leaching was carried out with hot water at 90 °C for three hours with a liquid to solid ratio of 1 to 3. Impurities in the leach solution were identified by ICP analysis (Table 1). According to the exact amount of impurities, a simulation solution was prepared. The Saghand ore leach solution is in an alkaline media (pH about 10) and the simulation solution was made under the same condition. The salts listed in Table 2. and Table 3. Were used to prepare the alkaline leach solution. Vanadium precipitation from alkaline leach solutions can be carried out in two methods. In first method, by adjusting the pH value (pH = 2), the red precipitate of ammonium polyvanadate is formed together with some impurities. The red precipitate is dissolved in dilute sodium carbonate solution and impurities are removed by setting the pH value. Then ammonium chloride is added and the ammonium metavanadate precipitate is formed. In second method. Ammonium chloride is added directly to the alkaline leach solution and the pH value is set in the range of 5 to 7 to form the white salt called ammonium metavanadate. If the

**Table 1.** Chemical composition of the vanadium-associated impurities in the leaching solution

Composition	Al	Ca	Fe	Mg	Mo	P	Ti	Na	Si
Concentration, mg L <sup>-1</sup>	10.583	3.6	0.455	1.81	32.283	0.56	0.036	1383.33	72.916

**Table 2.** The precipitates of sodium vanadate salts

No.	pH	Vanadium Recovery (%)	Sodium (%) in precipitation
1	1.028	17.50	0.660
2	1.368	80.83	1.486
3	1.544	90.65	1.134
4	1.876	97.64	0.451
5	2.045	94.43	0.515
6	4.566	73.47	2.619
7	5.023	46.98	2.619
8	5.540	95.17	2.579
9	5.850	90.11	2.714
10	6.024	95.53	2.013
11	6.040	94.52	1.371
12	6.734	98.84	0.224

**Table 3.** Influence of the concentrations of vanadium in sodium vanadate salts in the presence of NH<sub>4</sub>Cl and pH value of 5

Vanadium concentration, mg L <sup>-1</sup>	Ammonium chloride concentration (% w/v)								
	10				2.5				
	100	200	500	800	500	800	1000	2000	3000
Vanadium recovery (%)	91.125	95.396	95.833	97.948	66.433	94.406	98.125	99.125	99.288

amount of impurities in the leach solution is low, the second is recommended and there is no need for a separate step to remove impurities. Therefore, we employed the second method because the amount of impurities in the alkaline leach solution used in our study is low. In this study, the concentrated ammonium chloride was added to an alkaline leach solution. The pH was adjusted in the range of 5 – 7 with 0.5 M HCl. A white precipitate was formed, which corresponds to the ammonium metavanadate. The resulting precipitate was then washed with 2.5% ammonium chloride solution (w/v). Finally, the resulting precipitate dried at room temperature.

### 3. Results and discussion

#### 3.1. Effect of pH

Preliminary tests were carried out to determine the optimal pH range for the vanadium precipitation on sodium vanadate salt. Sodium metavanadate ( $\text{NaVO}_3$ ) with a purity of 98.5% and  $\text{NH}_4\text{Cl}$  with a purity of 99.8% were used in these experiments. Besides, 0.5 M HCl (with a purity of 32% and a density of  $1.16 \text{ kg L}^{-1}$ ) was used to adjust the pH. In this case, 2.085 g of  $\text{NaVO}_3$  was dissolved in 252 mL of distilled water. Then, 28 mL of 25% ammonium chloride (w/v) was added so that its amount in water was 2.5% (w/v). Finally, the pH was adjusted with 0.5 M HCl. Based on the experiments' results (Table 2), the highest vanadium recovery occurred at pH values close to 2 to and close to 7. Vanadium has polyvanadate and metavanadate structures at pH 2 and 7, respectively. For the rest of the experiments, the pH value was considered to be 7 for high vanadium recovery and minimum recovery of sodium.

#### 3.2. Effect of ammonium chloride and vanadium concentrations

In order to investigate the influence of ammonium chloride concentration in sodium vanadate solution on the vanadium recovery, a solution containing sodium vanadate with different concentrations in the range of 100 to  $3000 \text{ mg L}^{-1}$  was tested by adding ammonium chloride salt at a pH of about 5.5. The corresponding results are shown in Table 3.

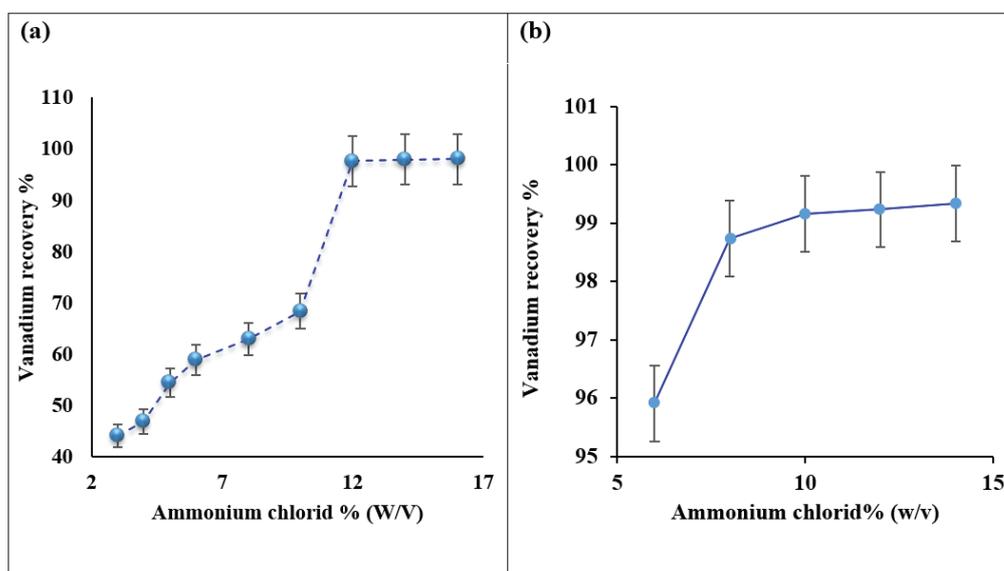
We find from the results in Table 3. that a vanadium recovery of 98% with a vanadium concentration of  $1000 \text{ mg L}^{-1}$  can be achieved in the presence of 2.5% ammonium chloride. At low vanadium concentrations, 10% ammonium chloride (which is a very high concentration) is required for a vanadium recovery of more than 95%. Similar experiments were carried out in simulation solution to examine the effect of ammonium chloride concentration. Finally, the concentration range of ammonium chloride was determined. The experiments were carried out under  $\text{pH} = 5.5$ , a precipitation time of 2 hours, and a  $1000 \text{ mg L}^{-1}$  vanadium concentration. Figure 1a shows how an increase in the ammonium chloride concentration affects the recovery of vanadium. With regard to the vanadium concentration ( $1000 \text{ mg L}^{-1}$ ), it is observed that an ammonium chloride with concentration of about 12% (w/v) must be used to achieve a recovery of over 90%, which is economically and industrially unprofitable. These tests show that the amount of ammonium chloride used depends on the vanadium concentration in the leach solution. The experiments were carried out under  $\text{pH} = 6.35$ , a precipitation time of 16 hours, and a vanadium concentration of  $2100 \text{ mg L}^{-1}$ . In Figure 1b, the effect of increasing the ammonium chloride concentration on the vanadium recovery can be observed. Ammonium chloride was added in the range of 6 to 14 % (w/v) to the solution containing  $2100 \text{ mg L}^{-1}$  of vanadium. The recovery rate of vanadium was over 95%. Increasing the concentration of ammonium chloride leads to increased vanadium recovery. Since Saghand ores contain about  $5400 \text{ mg L}^{-1}$  of vanadium, a range between 2 to 8% for the concentration of ammonium chloride and a range between 1400 and  $2700 \text{ mg L}^{-1}$  for vanadium concentration were considered for the remaining tests.

#### 3.3. Effect of precipitation time

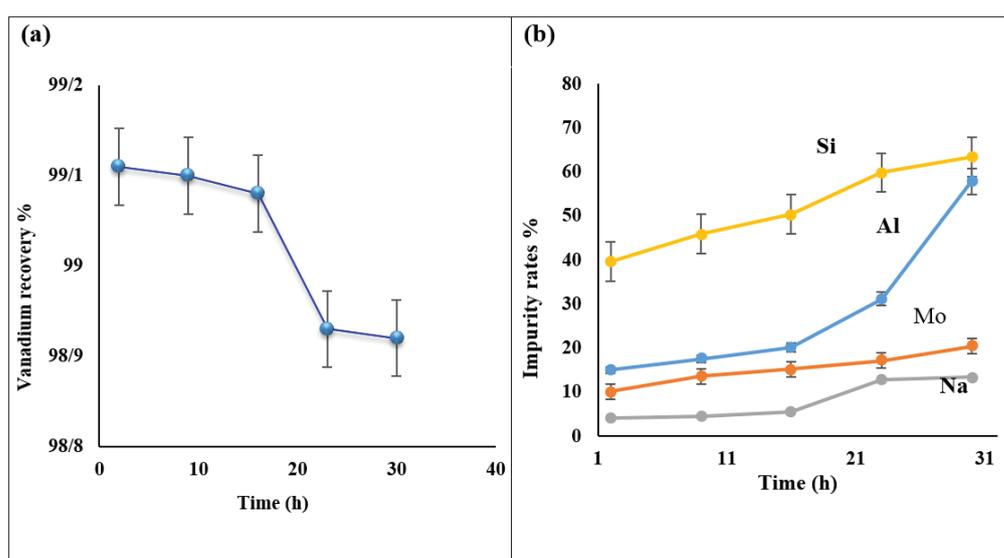
The result of time evaluation is shown in Figure 2a. These tests were carried out under  $\text{pH} = 6.35$ , 10% (w/v) ammonium chloride, different times, and vanadium concentration of  $2100 \text{ mg L}^{-1}$ .

The results showed that the increase in time did not significantly affect vanadium recovery. The difference in recovery rates related to precipitation data is less than 1% with a maximum and minimum time of 30 and 2 hours, respectively. So, it is better to choose the shortest time for precipitation to achieve the maximum recovery of vanadium. According to empirical observations, by increasing precipitation time, the amount of impurities in vanadium rises significantly. To prove this claim, the effect of time on the recovery of impurities, including aluminum,

molybdenum, sodium, and silicon was investigated. Over time, as shown in Figure 2b, this can lead to an increase in the amount of contaminants on ammonium metavanadate precipitate. In the case of elements such as silicon and aluminum, the passage of time, in contrast to molybdenum and sodium, significantly influenced the increase in ion precipitation. Our goal is to minimize the pollution caused by ammonium metavanadate precipitation. As described above, two hours was considered optimal for the precipitation process.



**Fig. 1.** Influence of the ammonium chloride concentration on the vanadium recovery for a solution with vanadium concentration of 1000 mg L<sup>-1</sup> (a) and 2100 mg L<sup>-1</sup> (b).



**Fig. 2.** a) Effect of time on vanadium recovery, b) Influence of time on the precipitation of various ions on ammonium metavanadate

### 3.4. The simultaneous effect of important parameters using design expert software

#### 3.4.1. Design of experiments

The DOE (Design of Experiment) method is one of the new statistical methods that can be used to identify important variables that affect the product's quality. By Using DOE techniques, we can first identify the variables that will have the greatest impact on the output. Second, the effective input variables are determined to bring the response values closer to their nominal value, reduce their variability, and minimize the influence of uncontrollable factors on the response variable. One technique that is widely used to optimize the input variables is response surface methodology (RSM). Central composite designs, abbreviated as CCD or Box-Wilson, are common methods for response surface design. The CCD method is used to design experiments. In the CCD method, each factor has five different levels (including three points within limits specified for each factor and two points outside

the limits specified for each factor). CCD design is usually done in five stages, including  $-\alpha$ ,  $-1$ ,  $0$ ,  $+1$ ,  $+\alpha$ . About the mentioned stages,  $-1$  and  $+1$  are the upper and lower levels, and  $-\alpha$  and  $+\alpha$  are the new limits of the factors. Zero is also at the heart of the design. In this experiment, the CCD experiment design was performed using the design-expert software to obtain the relationship between the three process variables. For the three variables pH ( $X_1=A$ ), weight-volume percentage of the ammonium chloride concentration ( $X_2=B$ ), and vanadium concentration in the leaching solution ( $X_3=C$ ), 20 experiments were carried out to determine the interaction of the parameters. Each time the parameter is designed and executed by the software by determining the optimal point. The specifications of each Central Composite Design (CCD) test and their results are shown in Table 4. The experiment design was carried out with three factors in mind. The order and the range of the factors are given in Table 4. And the precipitation time was considered to be 2 hours.

**Table 4.** Design of the experiments

Std.	Run	Block	A: pH	B: NH <sub>4</sub> Cl % w/v	C: V <sub>2</sub> O <sub>5</sub> mg L <sup>-1</sup>
11	1	1	6.15	2.98	2100
5	2	1	5.6	4	2500
3	3	1	5.6	7	1700
6	4	1	6.7	4	2500
19	5	1	6.15	5.5	2100
12	6	1	6.15	8.02	2100
17	7	1	6.15	5.5	2100
1	8	1	5.6	4	1700
7	9	1	5.6	7	2500
4	10	1	6.7	7	1700
13	11	1	6.15	5.5	1427.28
18	12	1	6.15	5.5	2100
15	13	1	6.15	5.5	2100
10	14	1	70.7	5.5	2100
20	15	1	6.15	5.5	2100
2	16	1	6.7	4	1700
9	17	1	5.23	5.5	2100
16	18	1	6.15	5.5	2100
14	19	1	6.15	5.5	2772.72
8	20	1	6.7	7	2500

### 3.4.2. Analysis of results

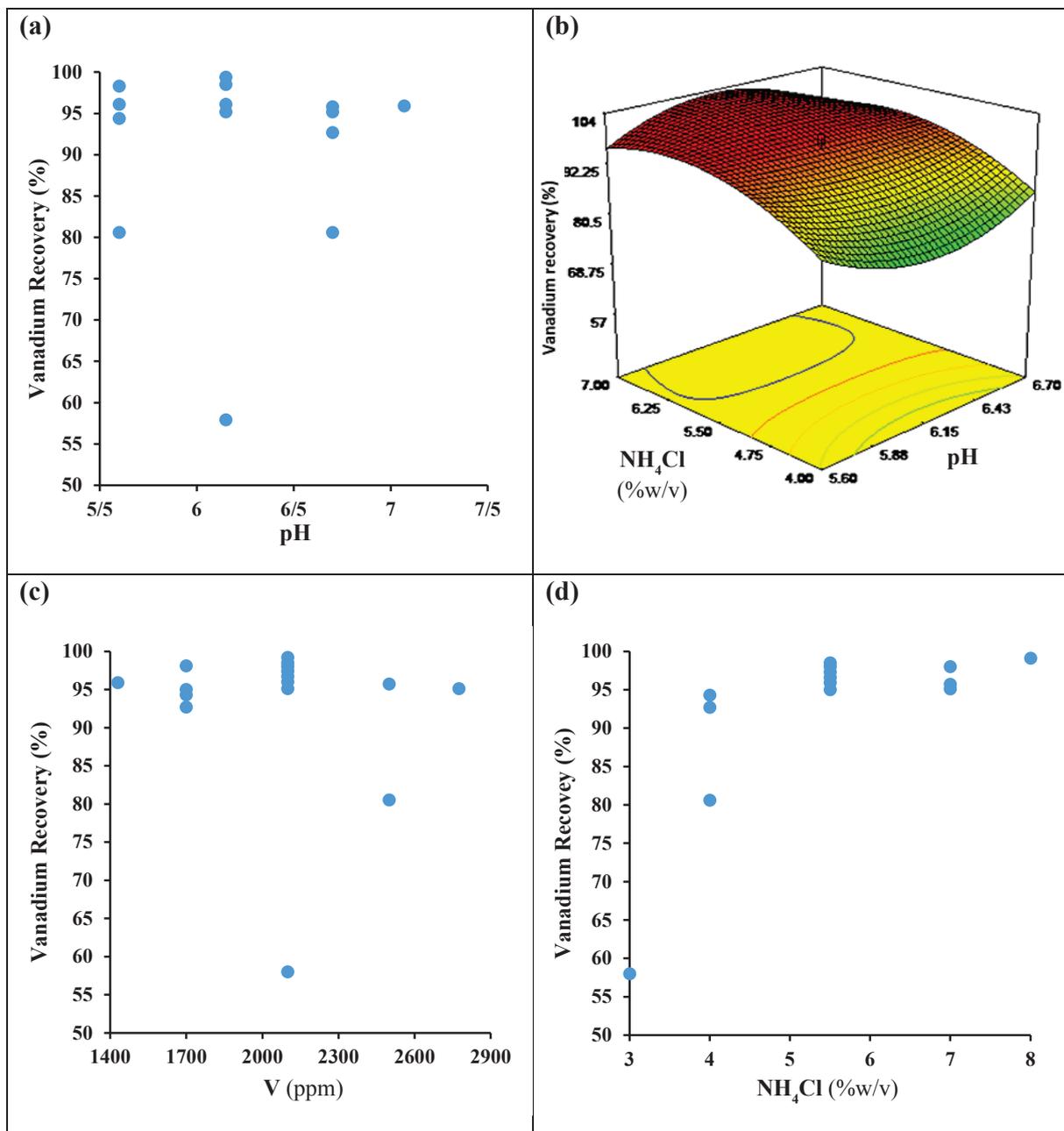
As shown in Figure 3a, pH changes have no significant effect on the increase or decrease in vanadium recovery. The recovery rate was almost high in the pH range under study. The low vanadium recovery was due to the low concentration of ammonium chloride. The pH values in the range of 5 to 7, with which the white precipitate of ammonium metavanadate is to be captured, can achieve high recovery of vanadium. So, the selection of all pH values in this range is acceptable. As shown in Figure 3b, the effect of pH on increasing vanadium recovery is not significant in this range. It has a maximum recovery for vanadium at pH=6.15 with an ammonium chloride ( $\text{NH}_4\text{Cl}$ ) concentration of 7% (w/v). The arc curvature in the diagram (2b) at  $\text{NH}_4\text{Cl}$  concentration of 4 to 7% (w/v) and pH of 5.6 is approximately similar to the curvature of the arc at  $\text{NH}_4\text{Cl}$  concentration of 4 to 7% (w/v) and pH value of 5.88. Based on Figure 3C, at some vanadium concentrations (2100 mg/L), the recovery is below 60% of vanadium. This significant difference is due to the insufficient concentration of the ammonium chloride used (the minimum concentration used was 2.98% (w/v)). It can be concluded that the vanadium precipitation depends on both the concentration of ammonium chloride and the concentration of vanadium in the leaching solution. It was also found that the minimum concentration of ammonium chloride used, i.e., 2.98% (w/v), is what was considered for the formation of ammonium metavanadate. According to Figure 3b, it is evident that the vanadium recovery continues to grow with increasing ammonium chloride concentration. In this connection, the concentrated leaching solution leads to the high recovery of up to 100% vanadium. Fig.c also shows that the recovery of over 80% of vanadium can be achieved with the ammonium chloride concentration in the range of 4 to 6% (w/v), which is economically and industrially justified. As shown in Figure 3d, the vanadium recovery increased from 57% to 99% with growing ammonium chloride concentration

from 2.98% to 8.02% (w/v). It is clear that to achieve vanadium recovery above 80%, ammonium chloride concentrations above 4% (w/v) must be used. From the results of the tests, it can be concluded that the vanadium and ammonium chloride concentrations have to be correlated with the inverse ratio in the leaching solution so that the vanadium concentration in the leaching solution is less than  $1000 \text{ mg L}^{-1}$ , which means that the ammonium chloride requires a concentration about 12% (w/v) to achieve vanadium recovery of over 90%.

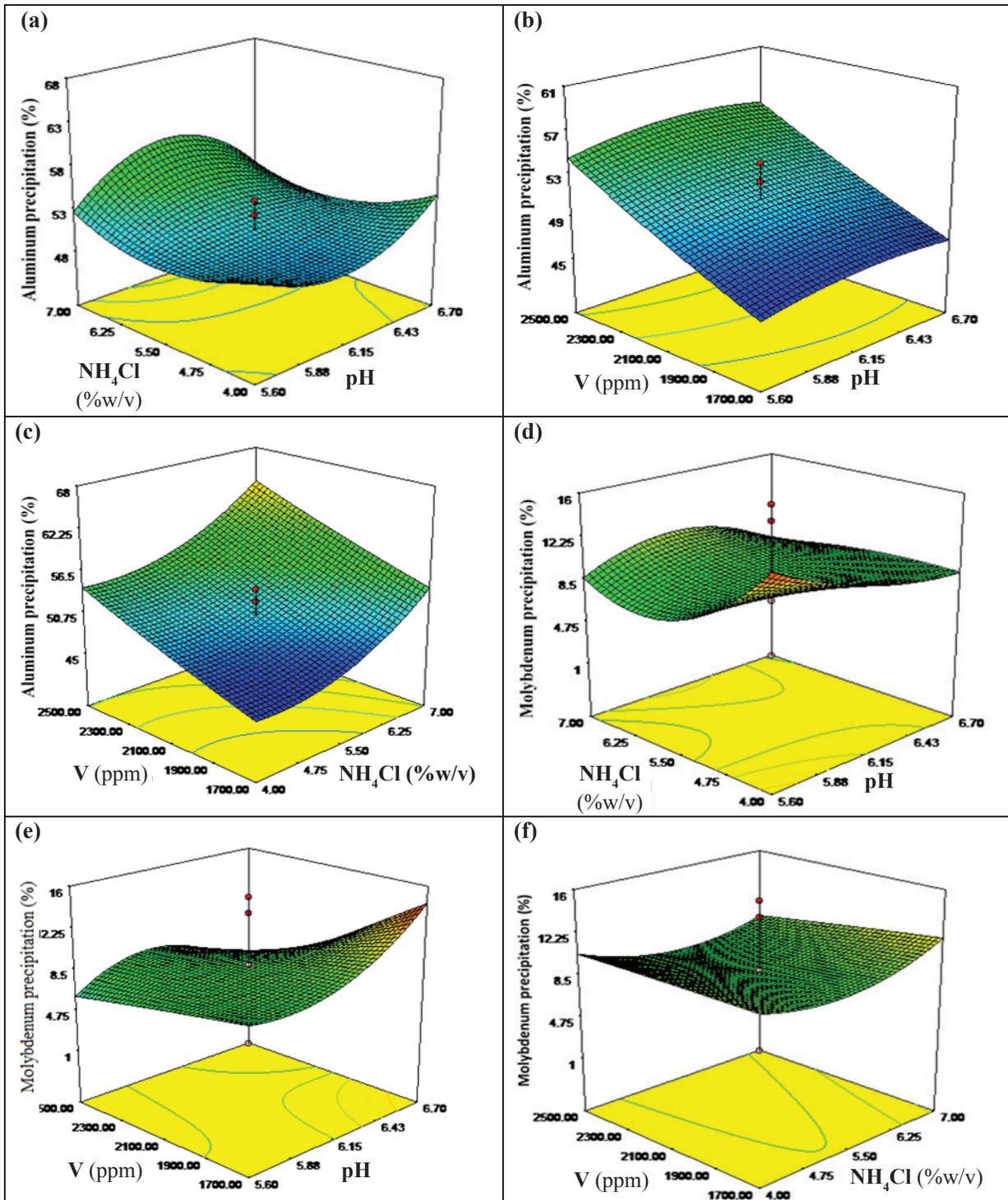
### 3.5. The effect of important parameters on recovery of impurities

#### 3.5.1. Aluminum recovery

Figure 4a shows the effect of pH and ammonium chloride concentration on aluminum precipitation. As can be seen, the amount of aluminum precipitation grew slightly with increasing pH and ammonium chloride concentration. In order to reduce impurities in vanadium to a minimum, the ammonium chloride concentration and pH value were chosen to be in the range of 4 - 6% (w/v) and 5.5-6.5, respectively. From Figure 4b, it is known that the higher the vanadium concentration in the leaching solution, the more aluminum is deposited, so that the effect of the pH value is negligible compared to the vanadium concentration in the leaching solution. Therefore, it is better to use leach solutions with a higher liquid-to-solid (L/S) ratio to minimize the amount of contamination in vanadium. According to Figure 4c, it is clear that the precipitation of aluminum rises with increasing concentrations of ammonium chloride and vanadium in the leaching solution. For example, in a leach solution with a vanadium concentration of  $1700 \text{ mg L}^{-1}$  and an ammonium chloride of 4% (w/v), the amount of aluminum precipitation reached about 40%, while in a leach solution with a vanadium concentration of  $2500 \text{ mg L}^{-1}$  and ammonium chloride with a concentration of 7% (w/v) is about 65%. Since our goal is to minimize the amount of impurities in vanadium, the first leaching solution is preferable.



**Fig. 3.** Influence of pH value (a), Effect of ammonium chloride concentration and pH value on vanadium recovery(b), vanadium concentration (c) and ammonium chloride concentration (d) on the recovery of vanadium



**Fig. 4.** Influence of pH value, vanadium concentration and ammonium chloride concentration on the recovery of Aluminium (**a – c**) Influence of pH value, vanadium concentration and ammonium chloride concentration on the recovery of Molybdenum (**d – f**)

### 3.5.2. Molybdenum recovery

It is clear from Figure 4d that the increase in pH, slightly reduces the amount of molybdenum precipitation. It is known that with increasing or decreasing the ammonium chloride concentration, the amount of molybdenum deposition varies between 8% and 10%. The minimal molybdenum precipitation is observed at an ammonium chloride concentration of 4.5 to 5.5% (w/v) and a pH of about 5.5 to 6.5. According to Figure 4e, it is observed that the rising in pH leads to an increase in the amount of molybdenum precipitation, but this increase is more pronounced for vanadium concentrations in leaching solution between 1700 to 2100 mg/L. Since our goal is to minimize the amount of molybdenum precipitation, a pH in the range of 5.5 to 6 was chosen. It is understandable from Fig. 3f that changes in the concentrations of ammonium chloride and vanadium in the leaching solution have little effect on molybdenum precipitation. According to the figure, the least amount of molybdenum precipitation is observed at concentrations of 5.5% (w/v) and 1200 mg L<sup>-1</sup> for ammonium chloride and vanadium, respectively. In

order to minimize the molybdenum precipitation, it is better to carry out experiments in this medium.

### 3.5.3. Sodium recovery

Based on Figure 5a, the sodium precipitation goes up with increasing vanadium concentration in the leaching solution. The highest amount of sodium precipitation was at a pH of 6.5 and a vanadium concentration of 2500 mg L<sup>-1</sup>, and the lowest amount was at a pH range between 5.5 to 6.5 and a vanadium concentration of about 1700 mg L<sup>-1</sup>. In this case, it is advisable to carry out the tests in the minimum point range. From Figure 5b, we can find that that increasing the vanadium concentration in the leaching solution leads to an expansion in the amount of sodium precipitate. In fact, the higher the concentration of the leach solution, the greater the deposition of other contaminants, including sodium along with ammonium metavanadate. Figure 5b also shows that increasing the ammonium chloride concentration at high vanadium concentrations reduces sodium precipitation. On the other hand, sodium formation is minimized at the minimum concentration of ammonium chloride and vanadium.

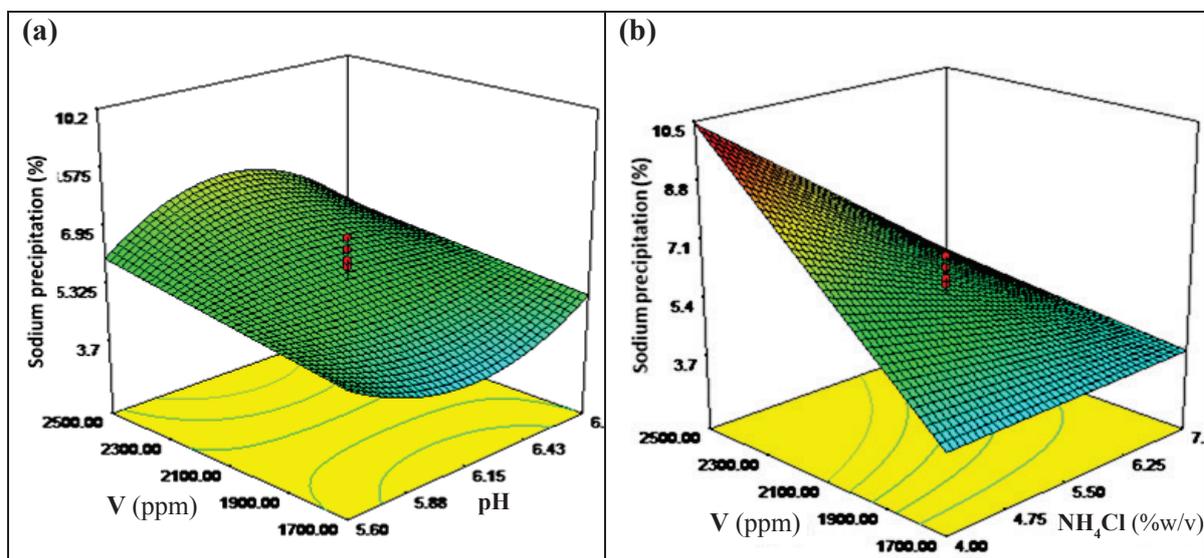
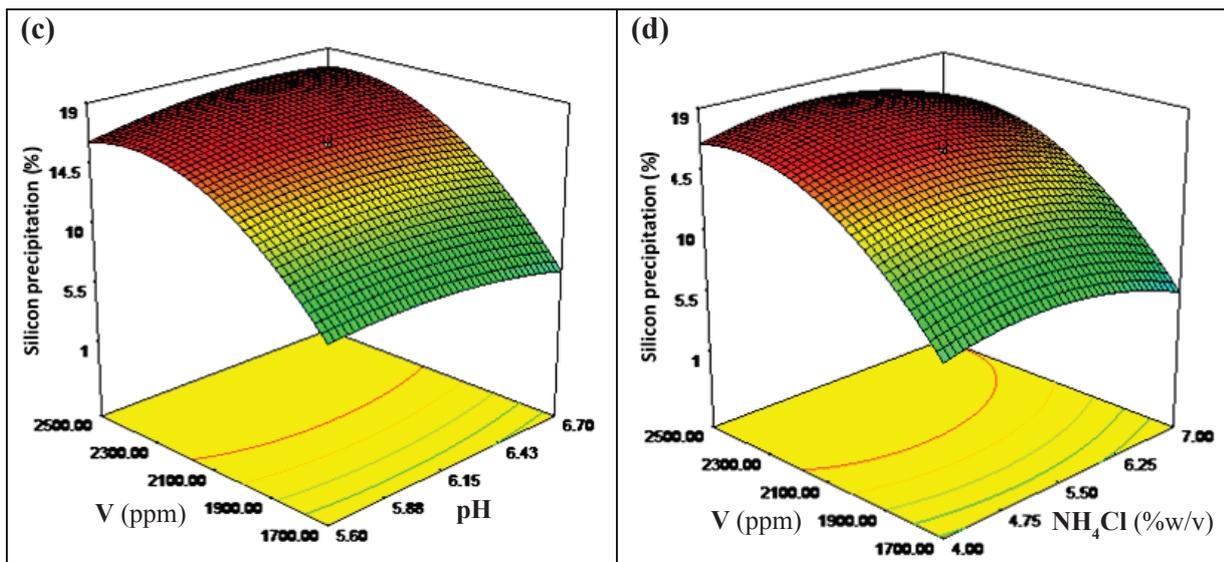


Fig. 5. Influence of pH value, vanadium concentration and ammonium chloride concentration on the recovery of Sodium (a, b)



**Fig. 5.** Influence of pH value, vanadium concentration and ammonium chloride concentration on the recovery of Silicon (c, d)

### 3.5.4. Silicon recovery

The effect of the vanadium concentration and pH on the silicon precipitation in the leaching solution is shown in Figure 5c. One can deduce that the higher the vanadium concentration in the leaching solution, the higher the amount of silicon precipitation. The pH parameter had no significant influence on the formation of the silicon deposit. The vanadium concentrations below 2000 mg L<sup>-1</sup> and a pH of around 5.5 to 6.15 should be selected to minimize silicon sedimentation. It can be seen in Figure 5d that increasing the vanadium concentration in the leach solution increases the amount of silicon precipitation. An increase in the ammonium chloride concentration also has a minor influence on the amount of silicon deposit. The minimum amount of impurities can be achieved at a concentration of 4 to 5% (w/v) ammonium chloride and a vanadium concentration below 1000 mg L<sup>-1</sup>.

### 3.6. The optimal point with maximum vanadium recovery

At the optimal point, we have the maximum recovery of vanadium and minimum precipitation of contaminants in the leach solution. The specified optimal point suggested by the software has the following conditions (Eq.1)

NH<sub>4</sub>Cl conc. = 5.48% (w/v), pH = 5.82, Vanadium concentration in the leach solution = 1700 mg L<sup>-1</sup> (Eq.1)

The important factors during designing the tests are shown in Table 5. The p-value for the parameters determines the significance and influence of the factor. The more the p-value is less than 0.05, the more effective. The parameter of Lack of fit specifies the fitting of the data with the model. The more the p-value for the Lack of fit exceeds 0.05, the better the fit. Also, the amount of (R-Sq = 98.83% or R-Sq (Adj) = 97.10%) should be taken into account, which is acceptable for the design of the test.

The equation 2 obtained by the software is as follows:  

$$R.V = (+5709.94005) - (1843.48600 * pH) - (612.88936 * NH_4Cl) - (1.05601 * V) + (208.76649 * pH * NH_4Cl) + (0.33175 * pH * V) + (5.05000E-003 * NH_4Cl * V) + (149.50072 * pH^2) - (2.79322 * NH_4Cl^2) - (16.99333 * pH^2 * NH_4Cl) - (0.026768 * pH^2 * V)$$

Where: NH<sub>4</sub>Cl is the concentration of ammonium chloride, and V is the vanadium concentration in the leach solution. According to Table 6, vanadium with a high recovery and high purity (low contamination) can be obtained at the point where the software determines to be the optimal point. Therefore, this point was considered as the optimal point for the set of these tests.

**Table 5.** Results obtained from Design-Expert ANOVA

Source	p-value
pH	0.3742
V <sub>2</sub> O <sub>5</sub>	0.8193
NH <sub>4</sub> Cl	0.0001 <
pH * V <sub>2</sub> O <sub>5</sub>	0.3713
pH * NH <sub>4</sub> Cl	0.7308
NH <sub>4</sub> Cl * V <sub>2</sub> O <sub>5</sub>	0.0006
Lack of fit	0.2031 not significant

**Table 6.** Results obtained from the experiment at the optimal point

Vanadium mg L <sup>-1</sup>	ammonium chloride % w/v	pH	Vanadium recovery %	Vanadium Purity %
1700	5.48	5.82	97.29	88.89

#### 4. Conclusions

The white ammonium metavanadate was formed with a pH value of 5 to 7. Vanadium had a high recovery at optimized pH. The effect of time on the vanadium recovery was examined, and it was found that the vanadium recovery rate does not change with increasing precipitation time. The time parameter had only a slight influence on the recovery rate of impurities in the leach solution. Since our goal is to maximize the vanadium recovery in the leach solution and minimize the recovery of impurities, we consider the shortest precipitation time of 2 hours. The vanadium concentration in the leach solution plays an effective role in the formation of precipitates. If the vanadium concentration in the leach solution is less than 1000 mg L<sup>-1</sup>, we have to use more concentrated ammonium chloride (12% (w/v)) to achieve a vanadium recovery of over 90%. The higher the vanadium concentration in the leach solution than 1000 mg L<sup>-1</sup>, the lower the concentration of ammonium chloride (4% (w/v)) must be used to achieve a vanadium recovery

above 90%. The ammonium chloride concentration plays the most important role in the vanadium precipitation. A high concentration of ammonium chloride leads to an increase in the recovery rate of vanadium. The optimal concentration of ammonium chloride for vanadium precipitation depends on the vanadium concentration in the leach solution. At high vanadium concentrations, a low concentration of ammonium chloride can lead to a high vanadium recovery. Concentrated ammonium chloride leads to a high recovery of vanadium at low vanadium concentrations.

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#### 6. Competing interests

The authors declare that they have no competing interests.

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