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## Study on extraction behavior of vanadium from acidic sulfate solutions

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### ABSTRACT

Extraction behavior of vanadium (V(V)) from the acidic sulfate solutions was investigated using trioctylamine (TOA). The extraction efficiency of V(V) from the acidic sulfate solutions increased with an increase in pH value, extractant concentration and organic to aqueous phase ratio. The optimum condition for V(V) extraction from the acidic sulfate solutions containing 100 mg/L V(V) was found to be at pH 2.5 using 0.005 M TOA. The V(V) from the loaded TOA was completely stripped by the use of 0.5 M NaOH solution. The regeneration of TOA after stripping process was obtained by washing with distilled water, and the recycling capacity of regenerated TOA had no appreciable change.

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## 1 INTRODUCTION

Vanadium was widely used in ferrous metallurgy, non-ferrous metallurgy, aerospace, nuclear and chemical industry due to its unique properties (Zhang *et al.*, 2016). Since the rapid increase of vanadium demand in industry leads to the depletion of vanadium primary sources, the recovery of vanadium from secondary sources such as spent hydrodesulphurization catalyst (Zeng and Cheng, 2009; Xue *et al.*, 2017), stone coal (Hu *et al.*, 2017), low-grade vanadium-bearing titanomagnetite (Zhao *et al.*, 2014) and petroleum fly ash (Navarro *et al.*, 2007) is paid more attention. In recovery of vanadium and other metals from the secondary sources, acid/alkaline leaching followed by solvent extraction (Zhang *et al.*, 1996; Zeng and Cheng, 2010) and ion exchange (Li *et al.*, 2009; Nguyen and Lee, 2014) is commonly used to separate and recover these metals. Among these methods, solvent extraction is chosen as a promising method for extraction and separation either vanadium or other metals from leach liquors of the secondary sources (Zeng and Cheng, 2009).

According to reported literatures, the formation vanadium species in solutions depends on pH value and metal ion concentration (Li *et al.*, 2009; Zeng and Cheng, 2009). Cationic species,  $\text{VO}_2^+$  are predominant at  $\text{pH} < 2$  while anionic vanadium complexes including polynuclear and mononuclear anionic species exist in the mildly acidic and alkaline solutions. Therefore, acidic extractants and amines were used to extract vanadium (Zeng and Cheng, 2009; Shi *et al.*, 2017). The main disadvantages encountered for acidic extractants such as di-(2-ethylhexyl)-phosphoric acid (D2EHPA), 2-ethylhexyl phosphonic acid mono 2-ethylhexylester (EHEPA) and bis(2,4,4-trimethylpentyl) phosphonic acid (Cyanex 272) are low extraction efficiency and the formation of third phase during stripping with ammonia solution (Zhang *et al.*, 1996). In a study by Nguyen and Lee (2015), 5,8-diethyl-7-hydroxydodecane-6-oxime (LIX 63) was used to extract V(V) from acidic solutions. Although solvent extraction with LIX 63 can prevent the formation of the third phase, but the extraction efficiency of V by LIX 63 was not high at  $\text{pH} > 2$ . Basic extractants such as tri-octyl/dodecyl amine (Alamine 336), tricaprylmethylammonium chloride

(Aliquat 336), 1-tridecanol, and tri-isooctyl amine (Alamine 308) offered high extraction efficiency of vanadium, but modifiers should be added to organic phases to avoid the third phase during solvent extraction process (Zeng and Cheng, 2009). Recently, the extraction behavior of vanadium from sulfuric acid solutions have been investigated by employing trioctylamine (TOA) in the presence of modifiers; however, little information on stripping of V(V) from loaded TOA was reported (Changes *et al.*, 2010; Kurbatova *et al.*, 2015). Therefore, in the present study, the extraction behavior of V(V) from acidic sulfate solutions by TOA was investigated as a function of pH value, extractant and metal concentration and types of stripping reagents. Moreover, the regeneration and recycling capacity of TOA after extraction and stripping process was studied in details.

## 2 MATERIALS AND METHODS

Commercial extractant, TOA (Sigma-Aldrich Co., Korea), is used without further purification, and

toluene (Merck Co., Korea) was used as a diluent. The synthetic solution of V(V) was prepared by dissolving  $\text{NH}_4\text{VO}_3$  (Samchun Pure Chem. Co., Korea) in distilled water. The acidity of the solution was adjusted by using NaOH (Junsei Chem. Co., Japan) and  $\text{H}_2\text{SO}_4$  solution (Duksan Co., Korea). The extraction experiments were carried out by mixing 10 mL of organic and aqueous phases in a 100 mL screwed cap bottle, and the mixtures were shaken for 30 minutes. After shaking, the organic and aqueous phases were separated using separating funnels. The pH of the aqueous phase was determined by a pH meter (Orion Star A211, USA). The vanadium concentration in the solutions before and after extraction was measured by ultraviolet spectrophotometer (UV730, Jasco, Japan) through formation of vanadium complexes,  $(\text{VO})_2(\text{SO}_4)_3$  in the mixture of  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{O}_2$  solution (Daejung Co., Korea). The concentration of metal ions in the loaded organic phases was calculated by mass balance.

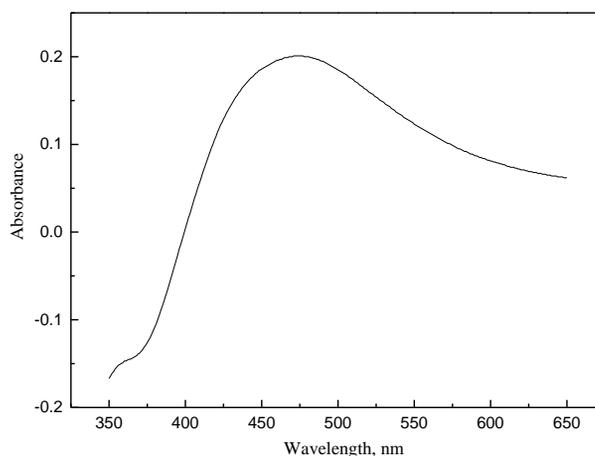


Fig. 1: UV-Vis spectrum of  $(\text{VO})_2(\text{SO}_4)_3$  complex in the mixture of  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{O}_2$  solution

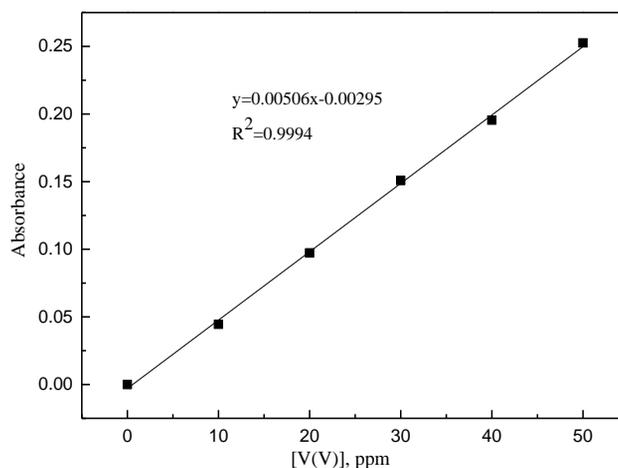


Fig. 2: Calibration curve for  $(\text{VO})_2(\text{SO}_4)_3$  complex ( $\lambda = 450 \text{ nm}$ )

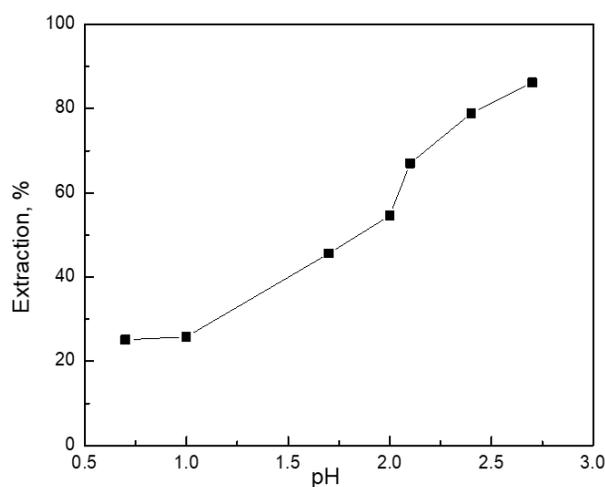
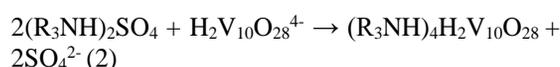
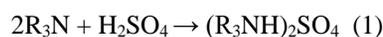
In order to prepare vanadium standard solutions and calibration curve, a series of 20 mL for vanadium standard solutions (0-50 mg/L V(V) in 0.8 M H<sub>2</sub>SO<sub>4</sub> and 0.08% v/v H<sub>2</sub>O<sub>2</sub>) were used for calibration curve. The UV-Vis spectrum of (VO)<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> complex, and its calibration curve was shown in Fig.1 and Fig. 2. The obtained linear regression equation of vanadium was  $A = 0.005 C - 0.003$  ( $R^2 = 0.9994$ ), where A and C were absorbance and metal concentration, respectively.

### 3 RESULTS AND DISCUSSION

#### 3.1 Effect of pH value

In these experiments, the solution pH was varied from 0.7 to 2.7, and the concentration of TOA was fixed at 0.01 M. The obtained results were shown in Fig. 3. The extraction percentage of V(V) steadily increased from 20 to 83% with increase of pH value from 0.7 to 2.7. As the pH value increased,

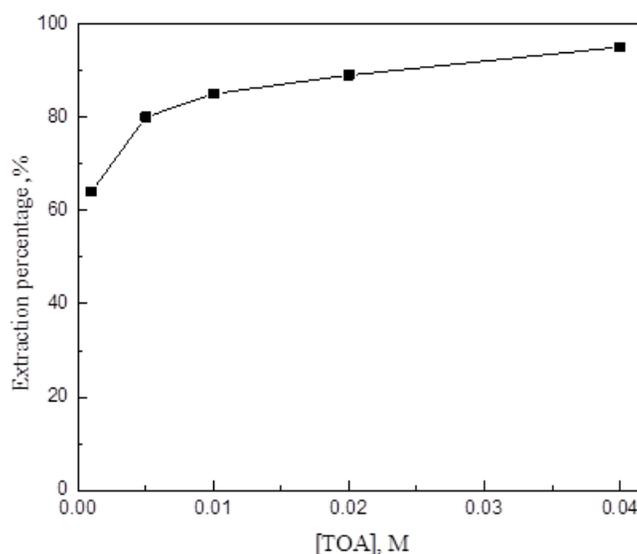
more fraction of vanadium anionic species formed (Li *et al.*, 2009), leading to increase in the extraction efficiency of V(V) by TOA. In order to extract V(V), TOA (R<sub>3</sub>N) was first reacted with sulfuric acid solution to form (R<sub>3</sub>NH)<sub>2</sub>SO<sub>4</sub>, and then the new form of extractant extracted vanadium anionic species (Chagnes *et al.*, 2010; Nguyen and Lee, 2016). At pH 2.5, H<sub>2</sub>V<sub>10</sub>O<sub>28</sub><sup>4-</sup> was predominant in the acidic sulfate solutions (Kurbatova *et al.*, 2015), so the extraction reaction between V(V) and TOA was represented in equations. (1) and (2). Since third phase was formed at pH 2.7, the optimum condition for extraction of V(V) by TOA was chosen at pH 2.5 in term of extraction efficiency and none of third phase.



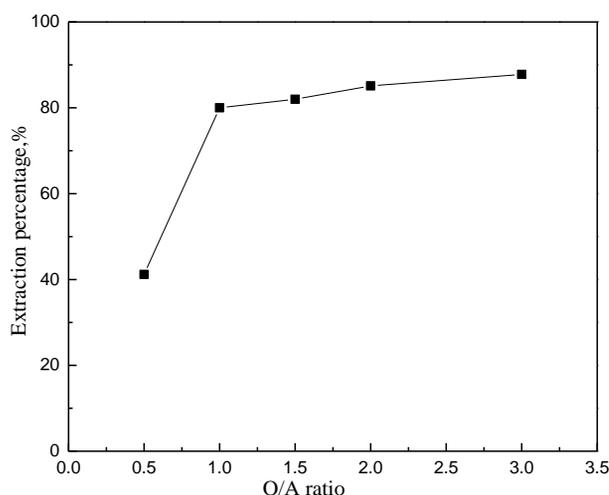
**Fig. 3: Effect of pH on extraction of V(V) from sulfuric acid solution by TOA. Aqueous: 100 mg/L V(V) pH = 0.7-2.7; Organic: 0.01 M TOA, O/A = 1/13.2 Effect of TOA concentration and O/A phase ratio**

The influence of TOA concentration on the extraction of V(V) was studied by varying TOA concentration from 0.001 to 0.04 M and keeping the pH of the solution at 2.5. The concentration of V(V) in the solution was fixed at 100 mg/L, and the organic to aqueous phase ratio was unity. Fig. 4 showed that extraction percentage of V(V) increased from 63 to 95% as TOA concentration increased from 0.001 to 0.04 M. Based on the obtained result in Fig. 4, 0.005 M TOA was suggested as the optimum condition in further experiments in term of extraction efficiency and low extractant consumption.

The relationship between O/A phase ratio and extraction percentage of V(V) is presented in Fig. 5. The extraction percentage of V(V) significantly increased from 40 to 81% with increase of O/A phase ratio from 0.5 to 1.5 using 0.005 M TOA, and then slightly rose in further increase of O/A phase ratio. The extraction behavior of V(V) by TOA at high O/A ratio might be related to the protonation reaction of TOA and H<sub>2</sub>SO<sub>4</sub>. Since the concentration of sulfuric acid was not enough for TOA to be protonated at high O/A ratio, the extraction behavior of V(V) was nearly unchanged with increase of O/A ratio from 1.5 to 3.



**Fig. 4:** Effect of TOA concentration on extraction of V(V) from sulfuric acid solution by TOA. Aqueous: 100 mg/L V, pH = 2.5; Organic: 0.001-0.04 M TOA, O/A = 1/1

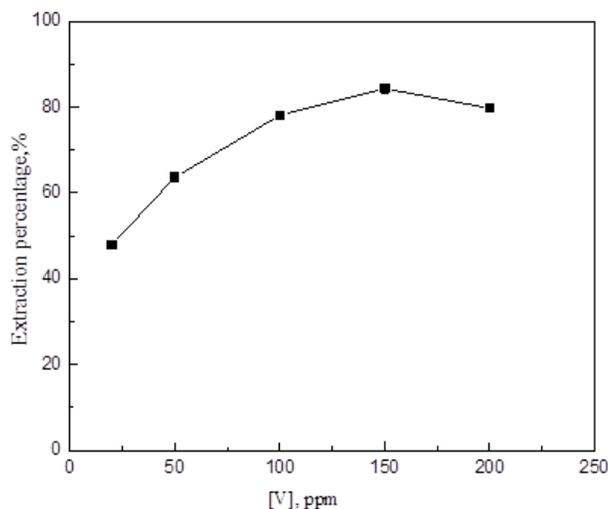


**Fig. 5:** Effect of O/A ratio on extraction of V(V) from sulfuric acid solution by TOA. Aqueous: 100 mg/L V(V), pH = 2.5; Organic: 0.005 M TOA, O/A = 1/2-3/1

### 3.2 Effect of vanadium concentration

In order to study on effect of V(V) concentration on the extraction behavior of V(V), the solutions at pH 2.5 were prepared by varying the V(V) concentrations between 20-200 mg/L. These solutions were employed to 0.005 M TOA at O/A phase ratio of unity. Fig. 6 shows variations in extraction percentage of V(V) with metal concentration. It was

observed that the extraction percentage of V(V) steadily rose from 48 to 85% with increase of vanadium concentration from 20 to 150 mg/L, and then slowly decreased in further vanadium concentration increase. The slow decrease in extraction behavior of V(V) at high vanadium concentration might relate to loading capacity of 0.005 M TOA with V(V).



**Fig. 6: Effect of vanadium concentration on extraction of V(V) by TOA. Aqueous: 20-200 mg/L V(V), pH = 2.5; Organic: 0.005 M TOA, O/A = 1/1**

### 3.3 Stripping

For the stripping purpose of V(V) from loaded TOA, H<sub>2</sub>SO<sub>4</sub> and NaOH (0.1-2 M) solutions were used in these experiments. The loaded TOA containing 83 mg/L V(V) was prepared by contacting 0.005 M TOA with the acidic sulfate solution containing 100 mg/L V(V) at pH 2.5. Table 1 shows variations in stripping percentage of V(V) with H<sub>2</sub>SO<sub>4</sub>/NaOH concentration. The stripping percentage of V(V) by H<sub>2</sub>SO<sub>4</sub> solution was much lower than that by NaOH solution. Low stripping percentage of V(V) using H<sub>2</sub>SO<sub>4</sub> solution was due to the formation of vanadium cationic species which were impossible to extract by basic extractants (Zeng and Cheng, 2009). According to equation (2), the reaction will be reversible as SO<sub>4</sub><sup>2-</sup> ion concentration increase. This was a reason why the stripping percentage of V(V) slowly increased with increase of H<sub>2</sub>SO<sub>4</sub> concentration. The obtained results indicated that NaOH solution was more effective to strip V(V) from the loaded TOA. The stripping percentage of V(V) from loaded TOA slowly rose from 90 to 99.8 % with increase for NaOH concentration from 0.1 to 0.5 M, and then was unchanged in further NaOH concentration increase. Therefore, 0.5 M NaOH was suggested as an optimum condition for complete stripping of V(V) from the loaded TOA.

**Table 1: Stripping of V(V) from loaded TOA. Loaded TOA: 83 mg/L V; Stripping reagents: H<sub>2</sub>SO<sub>4</sub>/NaOH (0.5-2 M)**

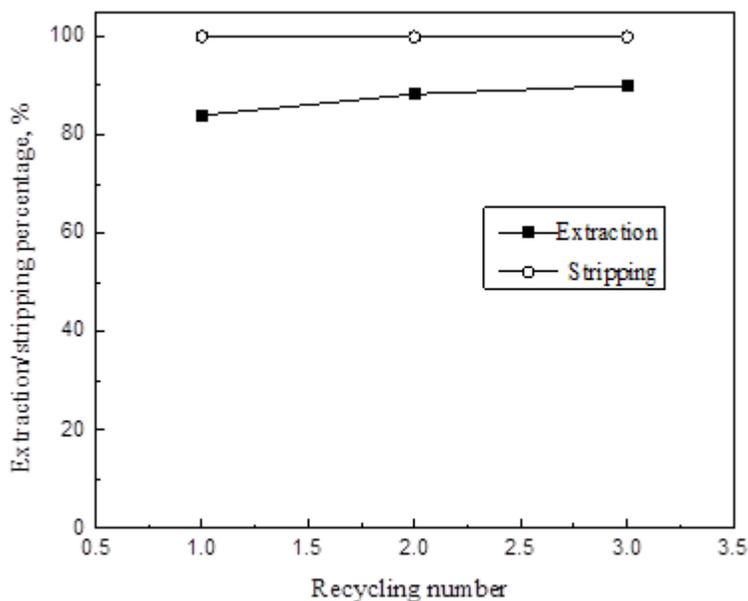
[H <sub>2</sub> SO <sub>4</sub> /NaOH] (M)	Stripping percentage (%)	
	H <sub>2</sub> SO <sub>4</sub>	NaOH
0.1	-	90.5
0.5	15.0	99.8
1	18.4	99.9
1.5	37.8	99.9
2	37.1	99.9

### 3.4 Regeneration and recycling capacity of TOA

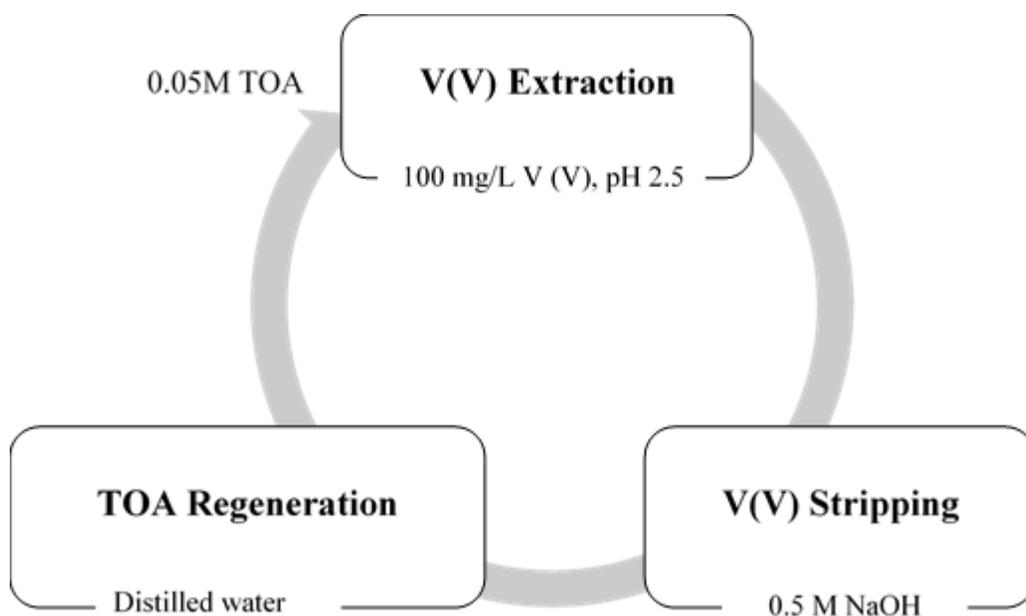
All experiments on the regeneration and recycling capacity of TOA were conducted under the optimum condition in extraction and stripping process. An acidic sulfate solution containing 100 mg/L V(V) at pH 2.5 was employed to 0.005 M TOA at O/A ratio of unity. Single stage extraction of V(V) gave loaded TOA containing 83 mg/L corresponding to 83% V extraction efficiency. The loaded TOA was further stripped with 0.5 M NaOH solution, resulting in 100% V(V) stripping efficiency. The stripped organic phase was washed by distilled water, and then used again for extraction and stripping. Two extraction and stripping cycles were carried out at the same experimental conditions, and the recovery of each stage was calculated from

the amount of V(V) extracted into the organic phase at each particular cycle. The obtained results are shown in Fig. 7. The extraction and stripping percentage of V(V) was unchanged up to three cycles, indicating that the regeneration and recycling capacity of TOA was obtained in the present study.

A process for extraction and stripping of V(V) from sulfate solutions by TOA was shown in Fig. 8.



**Fig. 7: Regeneration and recycling capacity of TOA. Aqueous: 100 mg/L V, pH =2.5; Organic: 0.005 M TOA; Stripping reagent: 0.5 M NaOH**



**Fig. 8: A schematic process of extraction and stripping of V(V) from sulfate solutions by TOA**

#### 4 CONCLUSIONS

Extraction behavior of V(V) from acidic sulfate solutions using TOA was investigated as a function of pH value, extractant and vanadium concentration, O/A phase ratio and stripping reagents. The extraction percentage of V(V) increased with the increase of pH value, extractant concentration and O/A phase ratio. The extraction behavior of vanadium steadily increased as vanadium concentration increased from 20 to 150 mg/L, and then slowly decreased in further vanadium concentration increase due to maximum loading capacity of TOA. The optimum condition for extraction of V(V) from the acidic sulfate solution containing 100 mg/L was found to be at pH 2.5 using 0.005 M TOA. The stripping percentage of V(V) from loaded TOA by NaOH solution was much higher than that by H<sub>2</sub>SO<sub>4</sub> solution. Complete stripping of V(V) from the loaded TOA was obtained using 0.5 M NaOH solution. After stripping process, stripped organic phase was regenerated by washing with distilled water, and the recycling capacity of regenerated TOA was unchanged. This technique can be applied for selective extraction of vanadium from leach liquors of secondary resources.

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