



## LIQUID – LIQUID EXTRACTION OF VANADIUM (V) FROM PERCHLORIC ACID SOLUTIONS BY TRIOCTYLPHOSPHINE OXIDE

J.O. Ojo

Department of Chemistry, Federal University of Technology, P.M.B. 704,  
Akure, Nigeria.

E-mail: oluwasanjo85@yahoo.com

### ABSTRACT

Many inorganic acids lack counter-ions required for the formation of extractable metal species thereby necessitating a continuous search, which has been extended to perchloric acid ( $\text{HClO}_4$ ) used in the current work with trioctylphosphine oxide (TOPO) extractant dissolved in purified kerosene to extract vanadium (V). Batch extractions were carried out in a separating funnel mechanically shaken at 120 rpm. The analysis of the V (V) content of the aqueous and organic phases were by UV – visible spectrophotometry based on hydrogen peroxide complex formation method. Various experimental conditions that could affect the percentage V(V) extraction (extraction efficiency, E%) were investigated. With increase in concentration of  $\text{HClO}_4$  at the studied range (1.0 – 6.0 mol  $\text{dm}^{-3}$ ), the extraction efficiency increased to an optimal value of 43.3 % at  $[\text{HClO}_4] = 6.0 \text{ mol dm}^{-3}$  at an ionic strength of  $[\text{NaClO}_4] = 0.1 \text{ mol dm}^{-3}$  and extractant concentration of  $\log [\text{TOPO}] = -1.19 \text{ mol dm}^{-3}$ , and least (E % = 10.0) at  $[\text{HClO}_4] = 5.0 \text{ mol dm}^{-3}$ , while an intermediate value of E% = 33.3 was observed at  $[\text{HClO}_4] = 3.0 \text{ mol dm}^{-3}$ , which was employed for a substantial part of the work to avoid TOPO degradation at higher concentrations.

The mixing of other extractants with TOPO was found non synergistic to V (V) extraction. Increased ionic strength was observed to have no appreciable effect on the extraction efficiency. All the added foreign ions increased the E% for V (V), highest with  $\text{V}^{4+}$  (E% = 50.0) and  $\text{Sr}^{2+}$  (E% = 46.7) compared with E% = 33.3 without added foreign ion.

Based on analytical and spectra data, the mechanism of extraction was deduced to be by the formation of two different extractable species  $\text{VO}_2\text{ClO}_4 \cdot \text{TOPO}$  and  $(\text{VO}_2\text{ClO}_4)_m \cdot n\text{TOPO}$  (where  $m \gg n$ ) at lower and higher concentrations, respectively. It could be inferred at the studied conditions that TOPO was slightly efficient for the removal of V (V) from  $\text{HClO}_4$  solutions.

**Keywords:** Extraction, Vanadium (V), Perchloric acid, Trioctylphosphine oxide.

### INTRODUCTION

The versatile applications of vanadium in various spheres of modern technology have been highlighted in previous reports by the author (Ojo *et al.*, 2009; Ojo and Adeeyinwo, 2011).

This has made the exploitation of the element from depleted primary sources by solvent extraction of utmost importance. The extractive recovery of the element as V (V) from HCl by organophosphorous extractants has been substantially reported (Ojo, 2010; Ojo *et al.*, 2012; Ojo, 2013).

In the later study vanadium (V) was appreciably extracted from concentrated HCl solutions using tri-n-butyl phosphate (TBP) with percentage extraction (E%) reaching a maximum of E% = 81.4. while di(2-ethylhexyl) phosphoric acid

(D2EHPA) efficiently removed V(V) up to E% = 80.0 at pH = 1.4 from  $\text{HNO}_3$  medium. Kurbatova *et al.* (2004) investigated the mechanism of extraction of V(V) from  $\text{H}_2\text{SO}_4$  solutions with di(2-ethylhexyl) phosphoric acid (D2EHPA), which was followed by another reported work where the parameters affecting the recovery of V (V) from sulphuric acid solutions were studied (Kurbatova and Kurbatov, 2006). Mixed trialkylphosphine oxide (TRPO or cyanex 923) similar to the extractant utilized in the current work has also been employed for V (V) extraction from hydrochloric acid solutions (Remya *et al.*, 2003). Perchloric acid behaves as an oxidizing medium (likewise  $\text{HNO}_3$ ) which can possibly enhance the stability of fully oxidized vanadium, and in addition provide the much needed counter-ion for

its extraction, hence, it is thought worthwhile to investigate V (V) extraction with trioctylphosphine oxide (TOPO) from it, in order to serve as an alternative to previously used oxidizing media (aqueous acids), and more so that hitherto reports on its use are rare.

## MATERIALS AND METHODS

### Materials used and their sources

The chemicals  $\text{NH}_4\text{VO}_3$ ,  $\text{HClO}_4$  and  $\text{HNO}_3$ , TBP, D2EHPA, TRIPO were purchased from the British Drug House (BDH),  $\text{NaClO}_4 \cdot \text{H}_2\text{O}$  from Sigma Limited and trioctylphosphoric oxide (TOPO) from Cytec, Canada. Kerosene was purified before use. All the chemicals were of analytical grade except TOPO and D2EHPA and were used without further purification.

Ammonium metavanadate (3.51 g, 0.03 mol) was dissolved in various concentrations of  $\text{HClO}_4$  (1.0 - 6.0 mol  $\text{dm}^{-3}$ ), 14.05 g (0.01 mol)  $\text{NaClO}_4 \cdot \text{H}_2\text{O}$  was added and made up to the 1 - litre mark to obtain solution counting  $\text{VO}_2^+$  ion (Greenwood and Earnshaw, 1997).

Different concentrations of TOPO in the range 0.5 - 2.5 % w/v were prepared by dissolving appropriate amounts of TOPO in purified kerosene (washed with  $\text{H}_2\text{SO}_4$  and NaOH). Mixtures of extractants with TOPO were prepared by mixing a fixed weight of TOPO with appropriate volumes of other extractants and diluted with kerosene to give the desired concentrations.

Solutions of different ionic strengths (0.01 - 1.0 mol  $\text{dm}^{-3}$ ) were also prepared by varying the amounts of added  $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ . Foreign ions were added to appropriate volumes of stock solutions to obtain desired concentration (0.003 mol  $\text{dm}^{-3}$ ) of the ions.

### Equilibrium studies and analytical procedure

Portions of 10  $\text{cm}^3$  V (V) solution were transferred with portions of 10  $\text{cm}^3$  TOPO solution into 100  $\text{cm}^3$  separating funnel, and shaken at 120 rpm for 5 mins (found optimum). The phases were allowed to settle, disengaged and separated. The vanadium extracted into the organic phase was stripped with 2.0 mol  $\text{dm}^{-3}$   $\text{HNO}_3$ . The effects of acidity of the aqueous medium, ionic strength, extractant concentration, mixing of extractants and foreign ions were studied by varying the one under investigation while keeping the others constant (temperature was however maintained at 28°C throughout) as follows: acidity of the  $\text{HClO}_4$  aqueous medium was varied (1.0 - 6.0 mol  $\text{dm}^{-3}$ ) by dissolving

$\text{NH}_4\text{VO}_3$  in the right concentration of  $\text{HClO}_4$  and made up to 1.0  $\text{dm}^3$ ; ionic strength varied (1.0 - 1.0 mol  $\text{dm}^{-3}$ ) by dissolving appropriate amounts of  $\text{NaClO}_4 \cdot \text{H}_2\text{O}$  in 1.0  $\text{dm}^3$  of the aqueous medium; extractant concentration (0.013 - 0.065 mol  $\text{dm}^{-3}$ ) by making a solution of TOPO in purified kerosene (Sato *et al.*, 2008); mixing of extractants, involving the dissolution of varied extractants (TBP, D2EHPA, TRPO) of the concentration 30% (v/v) with TOPO (0.065 mol  $\text{dm}^{-3}$ ); foreign ions,  $\text{V}^{4+}$ , citrate, oxalate,  $\text{Sr}^{2+}$ ,  $\text{K}^+$  and  $\text{Ce}^{4+}$  were added (using their compounds) to stock solutions to obtain an individual concentration of 0.003 mol  $\text{dm}^{-3}$ .

The amount of vanadium present in the aqueous and organic phases was determined by the V (V) -  $\text{H}_2\text{O}_2$  method (Vogel, 1978) which involves measuring the absorbance at 450 nm of the red complex formed. The electronic spectra (200 - 900 nm) was recorded on Alpha spectrophotometer and the infrared spectra on Buck Scientific Model 500 spectrophotometer (4400 - 350  $\text{cm}^{-1}$  range) at Obafemi Awolowo University, Ile - Ife and Ladoko Akintola University, Ogbomoso, respectively.

## RESULTS

### Effect of concentration of $\text{HClO}_4$

The effect of increased concentration of  $\text{HClO}_4$  medium on percentage V (V) extraction is presented in Figure 1.

With increase in  $[\text{HClO}_4]$  within the range 1.0 - 3.0 mol  $\text{dm}^{-3}$ , the percentage V (V) extraction increased gradually from  $E\% = 16.7$  to 33.3. Above  $[\text{HClO}_4] = 3.0$  mol  $\text{dm}^{-3}$ , the percentage V(V) extraction varied irregularly, however, it reached a highest value of  $E\% = 43.3$  at  $[\text{HClO}_4] = 6.0$  mol  $\text{dm}^{-3}$  (extraction at lower  $[\text{HClO}_4] = 3.0$  mol  $\text{dm}^{-3}$  was used for most of the work because of degradation of V(V) at the higher concentrations).

### The effect of ionic strength

The effect of ionic strength on percentage V (V) extraction is shown in Table 1.

Increasing the ionic strength of  $\text{NaClO}_4$  between 0.1 - 1.0 mol  $\text{dm}^{-3}$  produced no appreciable effect on percentage V(V) extraction,  $E\%$  merely varied between 23.3 and 16.7%.

### Effect of trioctylphosphine oxide concentration

The effect of increased TOPO concentration on percentage V (V) extraction is illustrated with Figure 2. At  $\log [\text{TOPO}] = -1.87$  i.e. 0.013 mol

$\text{dm}^{-3}$ ,  $\log D = -0.30$  ( $E\% = 33.3$ ) with the  $\log D$  increasing up to  $-0.06$  ( $E\% = 46.6$ ) at  $\log [\text{TOPO}] = -1.41$  and subsequently decreased.

**Effect of mixing of extractants with trioctylphosphine oxide**

Effect of mixing of extractants (30% v/v) with  $0.065 \text{ mol dm}^{-3}$  TOPO on percentage V(V) extraction is presented in Table 2. The mixing of TBP, D2EHPA and TRIPO at a concentration of 30% v/v with a fixed TOPO concentration of  $0.065 \text{ mol dm}^{-3}$ , changed the percentage V(V) extraction from  $E\% = 33.3$  (for TOPO only) to 10.0, 26.7 and 36.7% in the order listed.

**Effect of added foreign ion**

The effect of added foreign ion on percentage V(V) extraction is presented in Table 3. All the added foreign ion ( $0.003 \text{ mol dm}^{-3}$ ) increased percentage V(V) extraction. The highest increase ( $E\% = 50.0$ ) was observed with V(IV) and least ( $E\% = 42.5$ ) with citrate ion.

**Electronic and Infrared spectra for the extracted V(V) complex.**

The electronic absorption and infrared spectra bands are presented in Table 4.

The electronic absorption band of the aqueous V(V) feed (i.e. V(V) dissolved in  $3.0 \text{ mol dm}^{-3}$   $\text{HClO}_4$ ) was observed at  $27778 \text{ cm}^{-1}$  ( $\epsilon = 67.0 \text{ M}^{-1} \text{cm}^{-1}$ ) which shifted to  $25773 \text{ cm}^{-1}$  in the V(V) – TOPO extracted complex. The infrared absorption band observed at  $1227 \text{ cm}^{-1}$  assigned to  $\nu(\text{P} = \text{O})$  vibration in the TOPO ligand shifted negatively to  $1210 \text{ cm}^{-1}$  in the extracted V(V) – TOPO complex, and also a new but weak band was observed at  $870 \text{ cm}^{-1}$  assigned to  $\nu(\text{V} = \text{O})$  in the extracted complex.

**Table 1: Effect of ionic strength on percentage V(V) extraction from  $\text{HClO}_4$  solution by TOPO dissolved in kerosene.**

Concentration of $\text{NaClO}_4 / \text{mol dm}^{-3}$	Percentage V(V) extraction /%
0.1	23.3
0.2	23.3
0.5	20.0
1.0	16.7

$[\text{V(V)}] = 0.03 \text{ mol dm}^{-3}$ ;  $[\text{TOPO}] = 0.065 \text{ mol dm}^{-3}$ ;  $[\text{HClO}_4] = 3.0 \text{ mol dm}^{-3}$

TOPO = trioctylphosphine oxide;  $\text{HClO}_4$  = perchloric acid

**Table 2: Effect of mixing of extractants with TOPO (0.065 mol dm<sup>-3</sup>) on percentage V(V) extraction from HClO<sub>4</sub> solution.**

Extractant	Concentration of extraction / v/v/ %	Percentage V(V) extraction / %
TBP	30.0	10.0
D2EHPA	30.0	26.7
TRIPO	30.0	36.7
TOPO (only)	–	33.3

$$[\text{HClO}_4] = 3.0 \text{ mol dm}^{-3}$$

TOPO = trioctylphosphine oxide; HClO<sub>4</sub> = perchloric acid

**Table 3: Effect of added foreign ions on percentage V(V) extraction from HClO<sub>4</sub> solution.**

Foreign ions	Added as	Percentage V(V) extraction / %
Citrate	Sodium citrate	42.5
C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	Na <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	43.3
Sr <sup>2+</sup>	Sr(NO <sub>3</sub> ) <sub>2</sub>	46.7
K <sup>+</sup>	KCl	43.9
Ce <sup>4+</sup>	(NH <sub>4</sub> ) <sub>2</sub> Ce(SO <sub>4</sub> ) <sub>2</sub>	43.3
V <sup>4+</sup>	VOSO <sub>4</sub>	50.0
–	–	33.3 <sup>a</sup>

<sup>a</sup> = Percentage V(V) extraction without foreign ion ; HClO<sub>4</sub> = perchloric acid

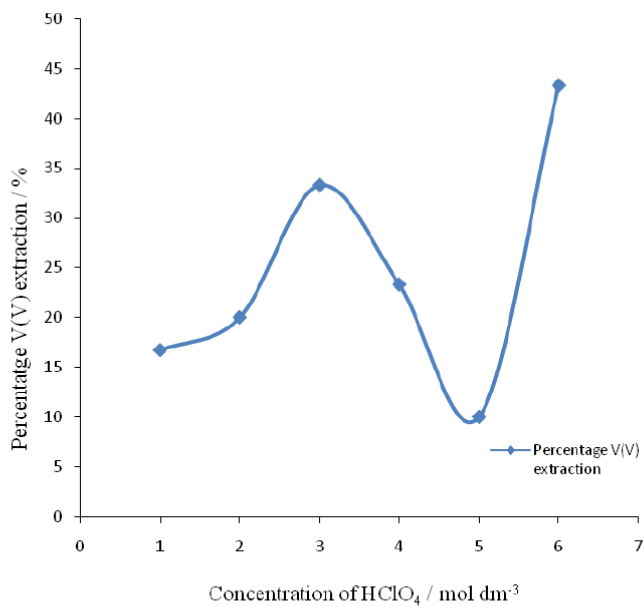
$$[\text{HClO}_4] = 3.0 \text{ mol dm}^{-3}; [\text{NaClO}_4] = 0.1 \text{ mol dm}^{-3};$$

$$[\text{TOPO}] = 0.065 \text{ mol dm}^{-3}; [\text{foreign ion}] = 0.003 \text{ mol dm}^{-3}$$

**Table 4: Electronic and Infrared Spectra data for the Extracted Vanadium (V) complexes.**

Compound	Wave number (cm <sup>-1</sup> )	Assignment
<b>Electronic</b>		
V(V) / HClO <sub>4(aq)</sub>	27,778 (67 M <sup>-1</sup> cm <sup>-1</sup> )	Charge transfer
V(V) – TOPO	25,778 (50 M <sup>-1</sup> cm <sup>-1</sup> )	Charge transfer
<b>Infrared</b>		
TOPO	1227	υ (P = 0)
V(V) - TOPO	1210	υ (P = 0)
	870	υ (V = 0)

TOPO = trioctylphosphorine oxide; HClO<sub>4</sub> = perchloric acid



**Figure 1: Effect of concentration of HClO<sub>4</sub> on Percentage V(V) extraction from HClO<sub>4</sub> solution with TOPO**

[V(V)] = 0.03 mol dm<sup>-3</sup>; [TOPO] = 0.065 mol dm<sup>-3</sup>

HClO<sub>4</sub> = perchloric acid

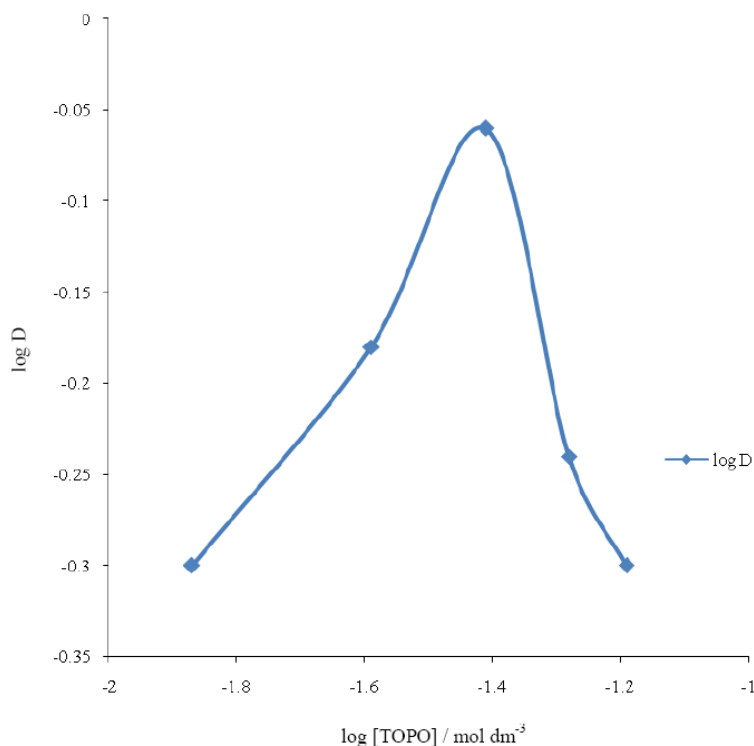


Figure 2: A plot of log D against log [TOPO] for the extraction of V(V) from HClO<sub>4</sub> solution.

[V(V)] = 0.03 mol dm<sup>-3</sup>; [HClO<sub>4</sub>] = 0.065 mol dm<sup>-3</sup>

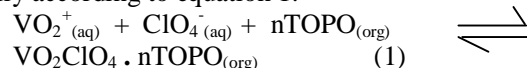
TOPO = trioctylphosphorine oxide

## DISCUSSION

The observed irregular trend in percentage V(V) extraction at studied range of [HClO<sub>4</sub>] = 1.0 - 6.0 mol dm<sup>-3</sup> might be due to the presence of different extracted V(V) species, which is similar to the trend reported by the author in V(V) extraction from HCl solutions with D2EHPA (Ojo, 2012). The observed low percentage V(V) extraction in this work, despite the well-known efficiency of TOPO for V(V) extraction with other media, attracts attention. It could be due to the poor binding characteristics of ClO<sub>4</sub><sup>-</sup> ion to V(V) consequently hindering the formation of an extractable complex, a feature earlier remarked in the author's reported investigative study involving V(IV) extraction from HClO<sub>4</sub> solution using TBP, a solvating extractant similar to TOPO employed for current work (Ojo, 2009). This further buttressed the fact that the perchlorate ion is a weak counter – ion, unable to

properly desolvate the aquated VO<sub>2</sub><sup>+</sup>, a condition required for high extractability.

The observation of two trends as the extractant concentration increased suggests the extraction of two different species at lower and higher concentrations which can be deduced as follows: If the extraction of VO<sub>2</sub><sup>+</sup> can be represented generally according to equation 1.



Then, the extraction equilibrium constant, K<sub>ex</sub>, can be expressed according to equation 2.

$$K_{\text{ex}} = \frac{[\text{VO}_2\text{ClO}_4 \cdot n\text{TOPO}]_{\text{org}}}{[\text{VO}_2^+]_{\text{aq}} \cdot [\text{ClO}_4^-]_{\text{aq}} \cdot [\text{TOPO}]_{\text{org}}^n} \quad (2)$$

$$D = \frac{[\text{VO}_2\text{ClO}_4 \cdot n\text{TOPO}]_{\text{org}}}{[\text{VO}_2^+]_{\text{aq}}} \quad (3)$$

where K<sub>ex</sub>, D, 'aq' and 'org' represent extraction equilibrium constant, distribution co-efficient, aqueous and organic phases, respectively.

Combining equations 2 and 3 and keeping  $[\text{ClO}_4^-]$  constant, we have

$$K_{\text{ex}} = D / [\text{TOPO}]_{\text{org}}^n \quad (4)$$

Taking logarithm, equation (4) reduces to

$$\log D = n \log [\text{TOPO}]_{\text{org}} + \log K_{\text{ex}} \quad (5)$$

It is expected that a plot of  $\log D$  against  $\log [\text{TOPO}]$  (Figure 2) should yield a straight line of slope equal to 'n', the number of TOPO molecules solvated to extracted  $\text{VO}_2^+$ . Two different portions were observed in the plot; a region of positive slope equal to 0.6 ( $\approx 1$ ) and that of negative slope equal to  $-1.0$  which suggest the extraction of two different species.

The former implies that one molecules of TOPO was solvated to the extracted complex, while the later shows that polymeric  $\text{VO}_2^+$  were associated with a TOPO molecule, with the deduced stoichiometries being  $\text{VO}_2\text{ClO}_4 \cdot \text{TOPO}$  and  $(\text{VO}_2\text{ClO}_4)_m \cdot n\text{TOPO}$  (where  $m \gg n$ ) respectively. From the intersection of the two linear portions,  $\log K_{\text{ex}}$  was determined to be equal to  $-1.4$  (i.e.  $K_{\text{ex}} = 0.04$ ), which is quite low, and justifies the low percentage V(V) extraction observed throughout the study.

This indicated that TBP and D2EHPA were antagonistic while TRIPO, structurally similar to TOPO enhanced the extraction.

On the effect of added foreign ion on V(V) extraction, the observed increase in the extraction efficiency might indicate that the ions formed more extractable species with V(V).

With regard to the electronic spectra bands, they have been assigned to ligand-metal charge transfer (LMCT).

The negative shift (bathochromic shift) in the bands of the V(V) – TOPO extracted complex indicated the binding of  $\text{VO}_2^+$  to TOPO which is similar to what we reported recently on V(V) extraction from HCl solutions (Ojo and Adeeyinwo, 2011).

With respect to the infrared spectra bands, the shift in the  $\nu(\text{P} = \text{O})$  band by  $17 \text{ cm}^{-1}$  and the presence of the  $\nu(\text{V} = \text{O})$  band in the extracted complex, which is absent in the TOPO ligand serve as evidences of coordination of the  $\text{VO}_2^+$  to the TOPO ligand. This is in agreement with the spectral observations on V(V) extraction from

$\text{HNO}_3$  solution with D2EHPA reported by the author (Ojo, 2010).

#### CONCLUSION

Vanadium (V) extraction from  $\text{HClO}_4$  solutions with TOPO is not quantitative and may not be feasible for commercial exploitation except if a counter – current extraction is employed.

#### ACKNOWLEDGEMENTS

The effort of Mr. Oladipo and the technical assistance of Mr. Akinola of Obafemi Awolowo University are well appreciated.

#### REFERENCES

- Greenwood, N.N. and Earnshaw, N.** (1997). Chemistry of the Elements. 2<sup>nd</sup> edition, Pergamon Press Plc., England, pp. 983-985.
- Kurbatova, L.D., Kurbatov, D.I. and Medvedeva, N.I.** (2004). Mechanism of extraction of vanadium (V) from sulphuric acid solutions with di(2-ethylhexyl) phosphoric acid. Russian Journal of Applied Chemistry 77 (4): 676 -679.
- Ojo, J.O.** (2009). Extractive recovery of vanadium (IV) from HCl,  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$  and  $\text{H}_3\text{PO}_4$  solutions with tri-n-butyl phosphate. International Journal of Chemical Sciences 2(1): 41 - 47.
- Ojo, J.O., Ojo, O.I. and Olugbayin, O.P.** (2009). Recovery and mechanism of vanadium (V) extraction from phosphoric acid solutions with tri-n-butyl phosphate and di(2-ethylhexyl) phosphoric acid. Journal of Chemical Society of Nigeria 34 (1): 75-84.
- Ojo, J.O.** (2010). Solvent extraction of vanadium (V) from nitric acid solutions with di(2-ethylhexyl) phosphoric acid. Malaysian Journal of Chemistry 12 (1): 40 – 48.
- Ojo, J.O. and Adeeyinwo, C.E.** (2011). Dependence of vanadium recovery on oxidation state in its solvent extraction from hydrochloric acid solutions with tri-n-butyl phosphate. Ife Journal of Science 13 (1): 175 – 183.
- Ojo, J.O., Adebayo, A.O. and Ojo, O.I.** (2012). Comparative study of the extraction of V(V) and V(IV) from hydrochloric acid solutions with di(2-ethylhexyl) phosphoric acid. Ife Journal of Science 14 (1): 15- 22.
- Ojo, J.O.** (2013). Separation of simulated mixed Mo(VI) and V(V) from  $\text{HNO}_3$  and HCl solutions by selective extraction and stripping with tri-n-butyl phosphate as extractant.

Separation Science and Technology 48 (10):  
1577 – 1584.

**Remya, P.N., Saji, J. and Reddy, M.L.P.**  
(2003). Solvent extraction and separation of  
V(V) from multivalent metal chloride solutions  
by Cyanex 923. Solvent Extraction and Ion  
Exchange 24 (6): 877- 892.

**Sato, T., Suzuki, H. and Sato, K.** (2008).  
Liquid – liquid extraction of molybdenum (VI)  
from nitric and sulphuric acids solutions by  
di(2-ethylhexyl) phosphoric acid. Journal of  
Mining and Materials Processing Institute of  
Japan, 124, 467 – 472.