Separation and Purification Technology 122 (2014) 270–277

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur

Separation of vanadium using both hollow fiber membrane and solvent extraction technique – A comparative study

P.C. Rout [a,b,*], K. Sarangi [a,b]

[a] Academy of Scientific and Innovative Research, India
[b] CSIR – Institute of Minerals and Materials Technology, Bhubaneswar, Odisha 751013, India

ARTICLE INFO

Article history:
Received 9 July 2013
Received in revised form 4 November 2013
Accepted 6 November 2013
Available online 14 November 2013

Keywords:
Vanadium
Hollow fiber
Solvent extraction
LIX 84I
Vanadium pentoxide

ABSTRACT

A comparative study between solvent extraction and hollow fiber membrane technique has been carried out for the extraction of V (V) from an aqueous chloride solution. LIX 84I has been used as carrier/extractant. Also the extraction of vanadium in presence of various other metals, such as iron, copper, zinc, cobalt, nickel and manganese using hollow fiber supported liquid membrane (HFSLM) has been studied. Effect of different parameters such as pH of feed solution, flow rate, extractant concentration, metal ion concentration and strip solution concentration on vanadium extraction has been investigated. With increase of pH, extractant concentration and flow rate, the flux value increased up to certain level and then decreases. The flux increased from 1.0 to 1.82×10^{-5}, 0.97 to 1.82×10^{-5} and from 0.6 to 1.82×10^{-5} -mol/m^2.s with increase of pH, [extractant] and flow rate from 1.0 to 1.75, 0.08 to 0.32 M and from 105 to 290 mL/min, respectively. The extracted species was determined to be $VO_2R{\cdot}RH$. Vanadium was extracted selectively and separated completely from a multi metal bearing solution by using hollow fiber membrane module and the separation factor values were found to be in the order of $\alpha_{V/Cu} < \alpha_{V/Fe} < \alpha_{V/Zn} < \alpha_{V/Co} < \alpha_{V/Mn} < \alpha_{V/Ni}$. The data generated from the hollow fiber study were compared with that of conventional mixer-settler study. High purity (99%) V_2O_5 was produced from the strip solution by precipitation with H_2SO_4 at pH around 2.0.

1. Introduction

Vanadium is commercially important as a constituent of several alloys and catalysts. Oxides of vanadium are used in the manufacture of sulfuric acid which is an important industrial chemical. Due to high coefficient of thermal resistance, vanadium (V) oxide finds application as a detector material for thermal imaging and an ethanol sensor in ppm levels (up to 0.1 ppm). Now a days vanadium is mostly recovered as a co-product from secondary resources or from industrial waste streams such as titaniferrous magnetite, vanadium bearing ferrophosphorus slag, fly ash, spent catalysts and Bayer's sludge. The waste chloride liquors from the titanium minerals processing industry represent another potential source for vanadium. Different processes such as ion exchange [1], leaching and precipitation [2,3] and solvent extraction [3] are being used for recovery of vanadium from above resources. To obtain pure vanadium from leach solution, solvent extraction technique is the most suitable process for industries and many authors have studied its extraction using different extractants [4–10].

Organophosphorus acid derivative such as di-(2-ethylhexyl)phosphoric acid (D2EHPA) has been widely used for the extraction of vanadium (V) from both acidic chloride and nitrate solutions [4–7]. Vanadium was recovered from heavy oil desulphurization waste catalyst by liquid–liquid extraction using D2EHPA and tri-n-octylamine (TOA) followed by stripping and precipitation as NH_4VO_3 [4]. From diluted and concentrated nitric acid solutions vanadium (V) was extracted using D2EHPA in various diluents and the nature of extracted species with the corresponding diluents were studied [5]. Tributylphosphate (TBP) has been used for the extraction of vanadium (V) from hydrochloric acid solutions [8–10]. The extraction behavior of vanadium (V) from a multi metal solution containing vanadium, magnesium, aluminum, titanium, chromium, manganese and iron from acidic chloride medium was investigated using TBP [8]. The effect of HCl concentration, extractant concentration and metal ion concentration on extraction of vanadium was studied. The extraction and stripping isotherms were constructed for recovery of vanadium. The extracted vanadium (V) complex was determined to be $VO_2Cl{\cdot}2HCl{\cdot}2TBP$. The extraction of vanadium (V) from bitumen in Nigeria was carried out with TBP in nitric acid medium [9]. The extraction of vanadium was maximum at pH 2.8, 41.5 °C, and 7.8×10^{-4} M concentration of aqueous vanadium. The ammine extractant Aliquat 336 has also been extensively used by different authors for

* Corresponding author at: CSIR – Institute of Minerals and Materials Technology, Bhubaneswar, Odisha 751013, India. Tel.: +91 9861204567; fax: +91 6742581637.
E-mail address: pradeep2005_chem@yahoo.co.in (P.C. Rout).

1383-5866/$ - see front matter © 2013 Published by Elsevier B.V.
http://dx.doi.org/10.1016/j.seppur.2013.11.010

Nomenclature

A	effective membrane area, m^2
$VO_2R{\cdot}RH$	V – complex
D	distribution coefficient
J	flux, $mol/m^2.s$
K_{ext}	extraction equilibrium constant
M	concentration of metal ion, mol/m^3
P	permeability coefficient, m/s
RH	concentration of LIX 84I
t	time, s
V	volume of the feed and strip solutions, m^3

Greek letters

α	separation factor

Subscript and superscript

f	feed
1	major extracted metal ion
2	minor extracted metal ion
Org	organic

extraction of vanadium. The extraction of vanadium from both acidic and alkaline media was studied with Aliquat 336 [11]. The effect of different parameters such as acid, alkali, extractant, metal concentration, phase ratio and loading capacity were separately studied for both the medium. The vanadium species for acid and alkaline solution were determined to be $(H_2V_{10}O_{28})^{4-}$ and $(VO_3{\cdot}OH)^{2-}$, respectively. The extraction of vanadium was better from sodium hydroxide solution than from hydrochloric acid solution. A survey of published researches showed that some authors have also worked for the extraction of vanadium using Cyanex 923 [12,13], Alamine 336 [14,15], TOA [16], LIX 860 [17].

LIX 84I is a commercially used extractant for copper and nickel by solvent extraction [18] and supported liquid membrane technique [19,20]. Also it has been used for the extraction of refractory metal like molybdenum [21,22]. Although there are some literatures available on extraction of vanadium by supported liquid membranes using various extractants [15,16,23], the studies with hollow fiber membrane using LIX 84I has not been reported yet.

Hence in the present study, LIX 84I has been explored for the extraction of vanadium (V) from acidic chloride solutions with hollow fiber membrane. The effects of different parameters such as pH, flow rate, LIX 84I concentration, metal ion concentration, NaOH concentration in the strip solution have been studied in detail to investigate vanadium (V) mass transfer through HFSLM for practical applications. Also a comparison has been made between the hollow fiber and the solvent extraction data which is very useful for industries.

2. Theory

Vanadium is known to form several chemical species (usually oxoanions/oxocations) in aqueous solution as a function of pH with different oxidation states [24]. At pH > 2 vanadium forms anionic species [25] and in more acidic solution (pH < 2) it generally remains in cationic form [5,17,25]. From some preliminary experiments it was observed that maximum extraction of V (V) with LIX 84I occurred at equilibrium pH 1.53. At this pH the predominant species of vanadium is VO_2^+ [5]. So the reaction mechanism of V with LIX 84I can be written by Eq. (1).

$$VO_2^+ + 2RH_{Org.} \Longleftrightarrow VO_2R \cdot RH_{Org} + H^+ \quad (1)$$

The extraction equilibrium constant (K_{ext}) can be written as:

$$K_{ext} = \frac{[VO_2R \cdot RH]_{Org}[H^+]}{[VO_2^+][RH]^2_{Org}} \quad (2)$$

The distribution coefficient, D of the system is defined as:

$$D = \frac{[VO_2R \cdot RH]_{Org}}{[VO_2^+]} \quad (3)$$

By substituting Eq. (3) in Eq. (2), Eq. (4) was obtained as follows

$$K_{ext.} = D\frac{[H^+]}{[RH]^2_{Org}} \quad (4)$$

Taking logarithm of Eq. (4) and rearranging,

$$\log D = \log K_{ext.} + pH + 2\log[RH]_{Org} \quad (5)$$

For hollow fiber membrane experiments, the flux of vanadium was calculated from the initial slope of $(V/A)d[M]$ vs. 'dt' plot [20].

The permeability coefficient P is defined as

$$P = \frac{J_M}{[M]} \quad (6)$$

When two or more metal ions are present in the feed solution, the metal ions can be separated depending on their permeability coefficient values and the separation factor (α) is defined as:

$$\alpha = \frac{P_1}{P_2} = \frac{(J_{M_1}/[M_1]_f)}{(J_{M_2}/[M_2]_f)} \quad (7)$$

where M_1 and M_2 are the major and minor extracted components [20].

3. Experimental

3.1. Membranes and reagents

The hollow fiber membrane Liqui-Cel 2.5 × 8 Extra-Flow was used as the solid support for the liquid membrane and was supplied by Membrana-Charlotte, NC, USA. The effective length of the hollow fiber module was 0.15 m and within the module 10,200 numbers of fibers were arranged in a compact modular form having effective surface area of 1.4 m^2. The porosity of the hollow fiber membrane was 25%. The membranes were made up of polypropylene which was not affected by regular contact with acid/alkali. The inner and outer diameters of a single fiber were 200 and 300 μm, respectively and the thickness of the fiber was 50 μm.

The extractant LIX 84I (2-hydroxy-5-nonylacetophenoneoxime) used as the mobile carrier for the hollow fiber membrane and was supplied by Cognis Corporation, USA. The extractant was used without any purification. Distilled kerosene (b.p. 180–240 °C) was used as the diluent. The feed solution was prepared by dissolving ammonium vanadate (NH_4VO_3) in hot distilled water. Few drops of sulfuric acid were added for complete dissolution of the salt. All chemicals used were of analytical reagent grade and obtained from BDH, Merck, India. The experiments were carried out from a synthetic solution bearing 20 mol/m^3 vanadium.