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# Solvent Extraction of Niobium from Oxalic Acid-Sulphuric Acid Medium Using Furfuryl Thioalcohol: Thermodynamic and Mechanistic Investigations

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Solvent extraction equilibria of niobium(V) from aqueous acetic-sulphuric acid solutions with furfuryl thioalcohol (FTA) dissolved in kerosene and the stripping were investigated. Results showed that proposed media can significantly improve the extraction efficiency of niobium. The distribution coefficients were significantly depends upon the media concentrations of oxalic-sulphuric acid and FTA in organic phase. Extraction efficiency (95.80%) was found from aqueous phase of 1.6 mol $L^{-1}$ $C_2H_2O_4$-0.6 mol $L^{-1}$ $H_2SO_4$ media with 10% (v/v) FTA dissolved in kerosene. In addition to this, extraction mechanism of niobium was proposed. On the basis of thermodynamics analysis and values of ΔH and ΔS, extraction reaction of niobium was exothermic. Dielectric constants of different diluents used for the preparation of organic phase and its significant role on extraction efficiency of niobium have been studied. In the stripping process, the ability to strip the niobium from organic phase is $H_2SO_4$ > $HNO_3$ > HCl solutions.

**Keywords: Solvent extraction, Niobium, Furfuryl thioalcohol, Stripping, Exothermic.**

## INTRODUCTION

Niobium and tantalum are strategically important metals owing to their extensive industrial applications. Niobium compounds and niobium-based alloys are widely employed in the fabrication of superconducting equipment owing to their excellent electrical and mechanical properties [1]. High-purity niobium is extensively used in the aerospace sector, where niobium alloys serve as heat-resistant materials for rocket components, spacecraft and jet engine parts operating under extreme conditions [2]. Its excellent corrosion resistance, high thermal conductivity and low neutron absorption cross-section make niobium well suited for applications in the nuclear energy industry [3,4]. The expanding use of niobium across these advanced technological sectors has led to a steady increase in its global demand. This growing requirement has intensified research efforts aimed at developing efficient and selective methods for the extraction and separation of niobium from complex mineral resources.

Solvent extraction is one of the most effective techniques for the selective recovery of niobium from aqueous solutions due to its high separation efficiency and operational flexibility [5-9]. A wide range of extractants containing nitrogen-, phosphorus- and oxygen-donor atoms has been investigated for niobium extraction [10-14]. Rodriguez *et al.* [15] employed Cyanex 923, a mixture of trialkylphosphine oxides, for the extraction of niobium and tantalum from HF/$H_2SO_4$ media. The process achieved 97.70% extraction of niobium, while selective stripping was accomplished using a solution containing 0.3 mol $L^{-1}$ $NH_4F$ and 0.1 mol $L^{-1}$ $NH_3$. Deblonde *et al.* [16] investigated the extraction of niobium and tantalum from alkaline solutions (pH 12) using Aliquat 336 and isotridecanol diluted in Elixore 205. The extraction efficiency for niobium reached 96.10% in the presence of tantalum and 96.60% of the loaded niobium was selectively stripped with a mixture of 0.5 mol $L^{-1}$ oxalic acid, 0.3 mol $L^{-1}$ $HNO_3$ and 0.15 mol $L^{-1}$ $NH_4NO_3$.

El-Hazek *et al.* [17] examined octan-2-ol diluted in kerosene for the extraction of niobium and tantalum from sulphate liquor at pH 0.7. Pure octan-2-ol provided 99.50% niobium extraction, while a mixture of 6 mol $L^{-1}$ $H_2SO_4$ and 7 mol $L^{-1}$ HF achieved 99.20% stripping efficiency. Sun *et al.* [18] introduced a mixed extractant system comprising 50% trioctyl tertiary amine (N235) and 4-methyl-2-pentanone

(MIBK), which extracted 94.60% of niobium from sulphuric acid solutions containing oxalate ions. Equilibrium was established within 15 min and saturated $NH_4F$ solution stripped 89.10% of the loaded niobium. Thermodynamic evaluation yielded an enthalpy change (ΔH) of -11.0 kJ $mol^{-1}$ for an exothermic extraction process.

Tanvar *et al*. [19] reported the extraction of niobium and tantalum using methyltrioctylammonium chloride, obtaining 96.20% niobium extraction from aqueous solutions. Quantitative stripping was achieved with a mixture of 0.5 mol $L^{-1}$ $HNO_3$ and oxalic acid. In another investigation, the 50% N235-MIBK system extracted 99.10% of niobium from solutions containing 8.17 mol $L^{-1}$ hydrogen ions after four extraction stages, while 99.70% stripping was obtained with 2 mol $L^{-1}$ $HNO_3$ after three stripping stages. The corresponding thermodynamic parameters (ΔH = -14.4 kJ $mol^{-1}$ and ΔS = -38.7 J $K^{-1}$ $mol^{-1}$) confirmed the exothermic nature of the extraction reaction [20]. More recently, 1,2-propylene glycol has been explored as an extractant for niobium recovery from concentrated sulphate solutions and the loaded metal was stripped using 1 mol $L^{-1}$ HF [21].

Sulphur-containing extractants have attracted considerable interest for the selective separation of metal ions as their strong affinity toward metal species [22-25]. Their extraction performance is commonly attributed to the presence of high-energy non-bonding electron pairs on sulphur and the availability of vacant orbitals that facilitate stable extractant-metal complex formation [26,27]. Furfuryl thioalcohol represents one such sulphur-containing reagent and has been successfully applied for the selective extraction of copper in the presence of nickel [24]. An additional advantage of furfuryl thioalcohol is its sustainable origin, as it can be prepared from agricultural byproducts such as sugarcane bagasse and corn cobs without requiring complex synthetic procedures or catalysts.

Efficient separation of niobium from its associated elements remains a major challenge in solvent extraction. Most reported extraction systems employ hydrofluoric acid (HF) or highly concentrated acidic media because stable fluoride complexes of niobium facilitate efficient extraction [28]. Industrial solvent extraction processes are therefore largely dependent on fluoride-containing systems. Fluorine-free extraction has received limited attention and the extraction behaviour of niobium under such conditions remains poorly understood. Developing an efficient fluorine-free extraction process is still an important research objective. This study evaluates furfuryl thioalcohol (FTA) as an alternative extractant for the fluorine-free extraction of niobium. The effects of aqueous phase composition, FTA concentration, diluent, extraction equilibrium time and stripping conditions were investigated. The extraction mechanism and thermodynamic behaviour of the niobium-FTA system were also examined.

## EXPERIMENTAL

All chemicals used in this study were of analytical reagent grade and obtained from Alfa Aesar (Thermo-Fisher Scientific, India) and Spectrochem Pvt. Ltd. (India). The reagents were used without further purification. Stock solutions were prepared by dissolving appropriate quantities of the respective salts in doubly distilled water and the required working solutions were obtained by dilution. Doubly distilled water was used throughout the study. Niobium concentrations were determined using a Shimadzu UV-Visible spectrophotometer (UV-1800) equipped with a 1 cm quartz cuvette.

**Solvent extraction of niobium:** Solvent extraction experiments were carried out at room temperature. Equal volumes of the aqueous niobium solution and the organic phase containing furfuryl thioalcohol (FTA) were transferred to a glass tube and equilibrated in an orbital shaker for 20 min. After equilibration, the phases were separated using a glass separating funnel. The niobium concentration in the aqueous phase before and after extraction was determined spectrophotometrically [29]. The extraction efficiency (%EE) and distribution coefficient (DC) were calculated using the following equations:

$$\%EE = \frac{[M]_{org}}{[M]_{aq}} \times 100 \quad (1)$$

$$DC = \frac{[M]_{org}}{[M]_{aq}} \quad (2)$$

where $[M]_{org} = [M]_{aq.in} - [M]_{aq}$, $[M]_{org}$ is the concentration of niobium in organic phase, $[M]_{aq.in}$ and $[M]_{aq}$ is the concentration of niobium in aqueous phase before and after the extraction, respectively in the test solutions.

## RESULTS AND DISCUSSION

**Effect of media concentration:** The extraction behaviour of niobium by FTA with various binary acid systems was investigated. Series different concentrations of HCl, $HNO_3$, $H_2SO_4$ and $C_2H_2O_4$ mixed with or without HF in the aqueous phase were employed to develop fluorine free media for selective and efficient extraction of niobium. Extraction experiments of 100 mg $L^{-1}$ niobium were carried out with 10% (v/v) FTA dissolved in xylene, A/O phase ratio=1 and extraction equilibrium time was 10 min. The concentration range of these aqueous phase media were varied over the range 0.2 mol $L^{-1}$ to 4.0 mol $L^{-1}$. As shown in Fig. 1, the increasing concentration of HCl, $HNO_3$, $H_2SO_4$ and $C_2H_2O_4$ showed positive effect on the niobium extraction performance upto certain limit. At 0.2 mol $L^{-1}$ HCl-0.8 mol $L^{-1}$ HF, the extraction efficiency of niobium was 4.10%, the extraction efficiency increased to 72.48% at 3.6 mol $L^{-1}$ HCl-0.8 mol $L^{-1}$ HF. Similarly, the maximum extraction efficiency of niobium was 54.82%, 92.44% and 38.80% showed by 3.4 mol $L^{-1}$ $HNO_3$-0.8 mol $L^{-1}$ HF, 2.6 mol $L^{-1}$ $H_2SO_4$-0.8 HF and 1.8 mol $L^{-1}$ $C_2H_2O_4$-0.6 mol $L^{-1}$ HF, respectively. HF concentration exerted a pronounced influence on niobium extraction. In oxalate media, an HF concentration of 0.8 mol $L^{-1}$ suppressed the formation of the extractable FTA–niobium–oxalate complex, possibly due to the oxalate protonation under highly acidic conditions [18].

Niobium extraction with FTA from the binary acid system of $C_2H_2O_4$-$H_2SO_4$ was investigated in the concentration range of 0.2 mol $L^{-1}$ to 4.0 mol $L^{-1}$. As shown in Fig. 2, with increase in concentration of $C_2H_2O_4$ from 0.2 mol $L^{-1}$ to 4.0 mol $L^{-1}$, the extraction efficiency of niobium increased upto

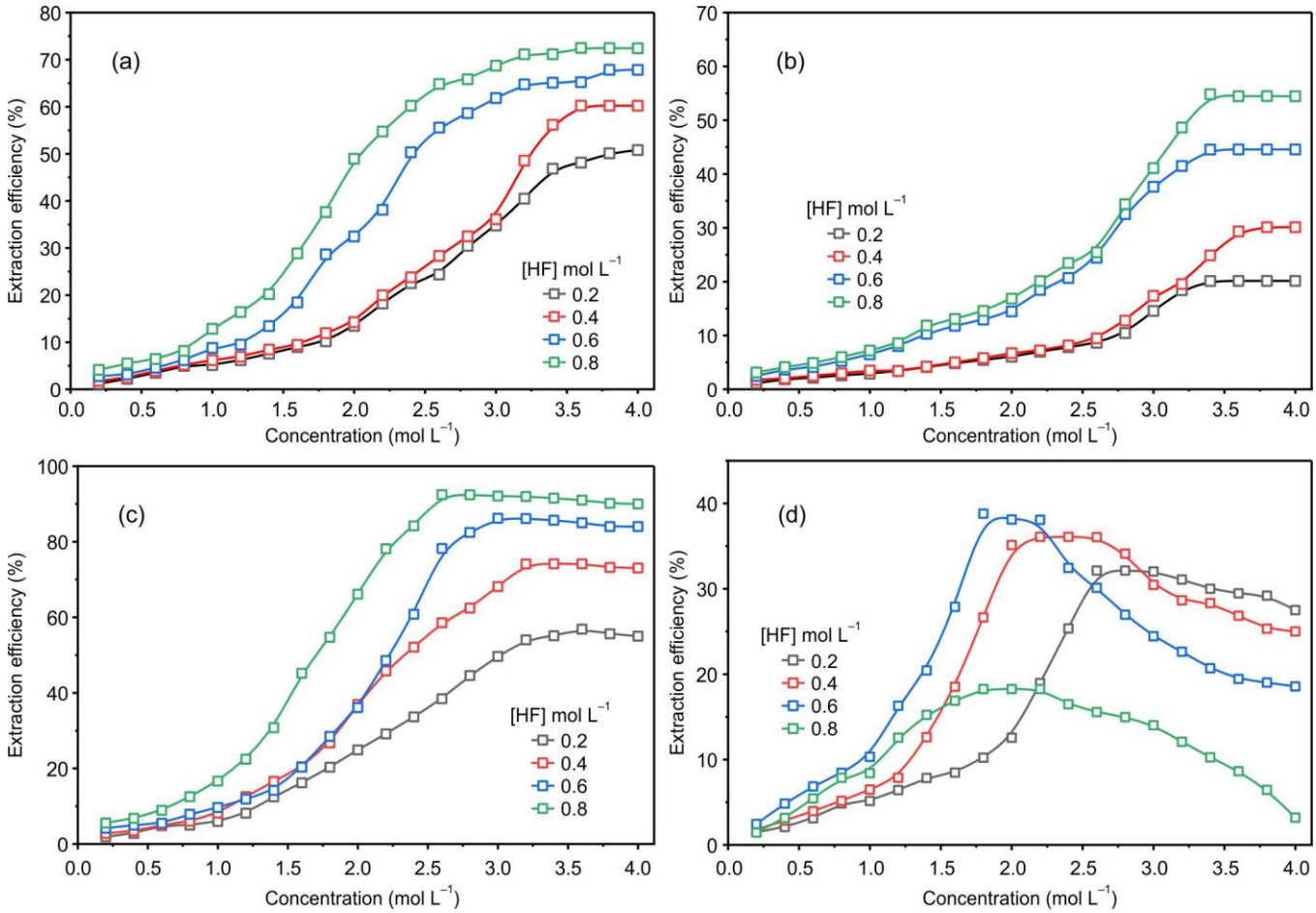


Fig. 1. Effect of media concentration on extraction of niobium. Conditions: [FTA] = 10%(v/v) in kerosene, O/A= 1, Equilibrium time 10 min, (a) HCl-HF, (b) $HNO_3$-HF, (c) $H_2SO_4$-HF and (d) $C_2H_2O_4$-HF

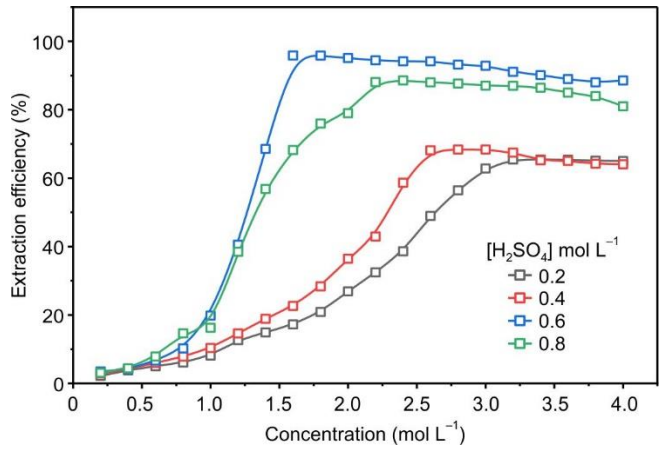


Fig. 2. Effect of $C_2H_2O_4$-$H_2SO_4$ concentration on extraction of niobium. Conditions: [FTA] = 10%(v/v) in kerosene, O/A = 1, Equilibrium time 10 min

65.44% by 3.2 mol $L^{-1}$ $C_2H_2O_4$-0.2 mol $L^{-1}$ $H_2SO_4$, 68.36% by 2.8 mol $L^{-1}$ $C_2H_2O_4$-0.4 mol $L^{-1}$ $H_2SO_4$, 95.84% by 1.6 mol $L^{-1}$ $C_2H_2O_4$-0.6 mol $L^{-1}$ $H_2SO_4$ and 88.56% by 2.4 mol $L^{-1}$ $C_2H_2O_4$-0.8 mol $L^{-1}$ $H_2SO_4$. The extraction results identified the binary acid system comprising 1.6 mol $L^{-1}$ $C_2H_2O_4$ and 0.6 mol $L^{-1}$ $H_2SO_4$ as more effective than the reported fluoride-based single or binary acid systems. The enhanced extraction efficiency can be attributed to the ability of oxalic acid to coordinate with niobium and form extractable complexes. The high charge density and small ionic radius of Nb(V) promote strong interactions with hard oxygen-donor ligands such as oxalate [30,31]. The formation of niobium-oxalate species in the presence of $H_2SO_4$ facilitates their association with FTA at the liquid-liquid interface, leading to improved extraction efficiency [20]. These findings establish FTA as a promising extractant for the efficient recovery of niobium from fluorine-free media.

**Effect of FTA concentration:** The effect of FTA concentrations on extraction of niobium(V) was investigated in the range of 2.0% to 20.0% (v/v). Extraction experiments were performed by 20 mL organic phase of FTA dissolved in toluene, 100 mg $L^{-1}$ niobium, 1.6 mol $L^{-1}$ $C_2H_2O_4$-0.6 mol $L^{-1}$ $H_2SO_4$ in aqueous phase, O/A phase ratio = 1 and extraction equilibrium time 10 min. The extraction results (Fig. 3) show that the extraction efficiency of niobium increased from 42.24% to 95.80% as the FTA concentration increased from 2.0% (v/v) to 10% (v/v) and remained unchanged up to 20% (v/v) confirmed that 10% (v/v) FTA was sufficient for efficient extraction of niobium. The extraction results (Fig. 3) show that the extraction efficiency of niobium increased from 42.24% to 95.80% as the FTA concentration increased from 2.0% (v/v) to 10% (v/v) and remained unchanged up to 20% (v/v) with

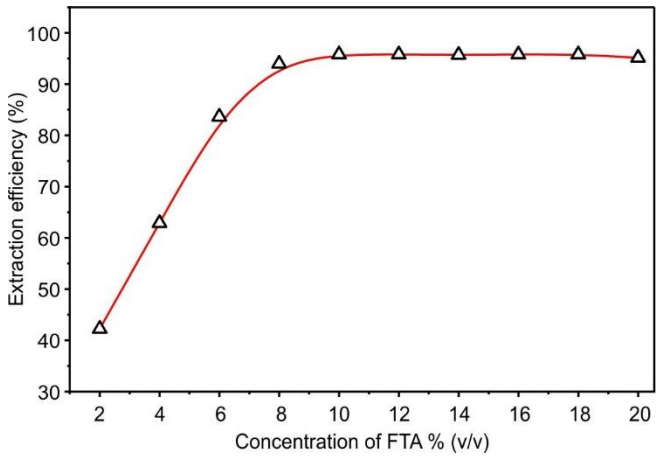


Fig. 3. Effect of FTA concentration on extraction of niobium. Conditions: Aqueous phase media = 1.6 mol $L^{-1}$ $C_2H_2O_4$-0.6 mol $L^{-1}$ $H_2SO_4$, O/A = 1, equilibrium time 10 min

10% (v/v) FTA being sufficient for the efficient niobium extraction.

**Extraction thermodynamics:** The final extraction stage is strongly influenced by temperature since alloying elements exhibit similar thermodynamic behaviour that complicates their separation [32]. To study the effect of temperature on the extraction of niobium from two different aqueous phases containing 100 mg $L^{-1}$ niobium, 1.6 mol $L^{-1}$ $C_2H_2O_4$-0.6 mol $L^{-1}$ $H_2SO_4$ and 100 mg $L^{-1}$ niobium, 2.6 mol $L^{-1}$ $H_2SO_4$-0.8 mol $L^{-1}$ HF by organic phase of 10% (v/v) FTA in kerosene, experiments were carried out in thermostatic water bath oscillators and the temperature range varied from 298 K to 328 K. Fig. 4 showed that an increase in the temperature from 298 K to 328 K leads to decrease in extraction efficiency of niobium from 95.80% to 87.10% and 92.40% to 84.43% through the medium of 1.6 mol $L^{-1}$ $C_2H_2O_4$-0.6 mol $L^{-1}$ $H_2SO_4$ and 2.6 mol $L^{-1}$ $H_2SO_4$-0.8 mol $L^{-1}$ HF, respectively.

The thermodynamic parameters such are Gibbs free energy (ΔG), enthalpy change (ΔH) and entropy change (ΔS) of extr-action system was calculated by following equations:

$$\Delta G = -2.303RT \log D \quad (3)$$

where R is the universal gas constant (8.314 J $K^{-1}$ $mol^{-1}$), T is the absolute temperature. From the plot (Fig. 5), enthalpy change (ΔH) and entropy change (ΔS) were calculated from slope and intercept of log D *vs.* 1/T $K^{-1}$ and yielded a slope of 1752.3 with an intercept of 4.5717 and a correlation coefficient of $R^2$ =0.9456, ΔH and ΔS were found to be -33.55 kJ

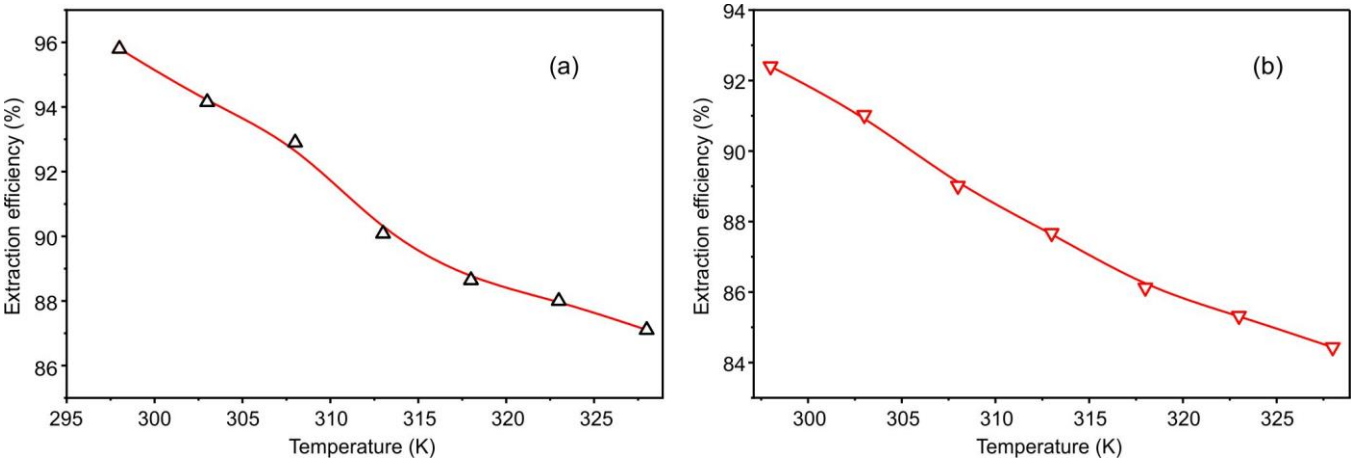


Fig. 4. Effect of temperature on extraction of niobium. Conditions: [FTA] = 10% (v/v) in kerosene, O/A = 1, equilibrium time 10 min, (a) aqueous phase media: 1.6 mol $L^{-1}$ $C_2H_2O_4$-0.6 mol $L^{-1}$ $H_2SO_4$, (b) aqueous phase media: 2.6 mol $L^{-1}$ $H_2SO_4$-0.8 mol $L^{-1}$ HF

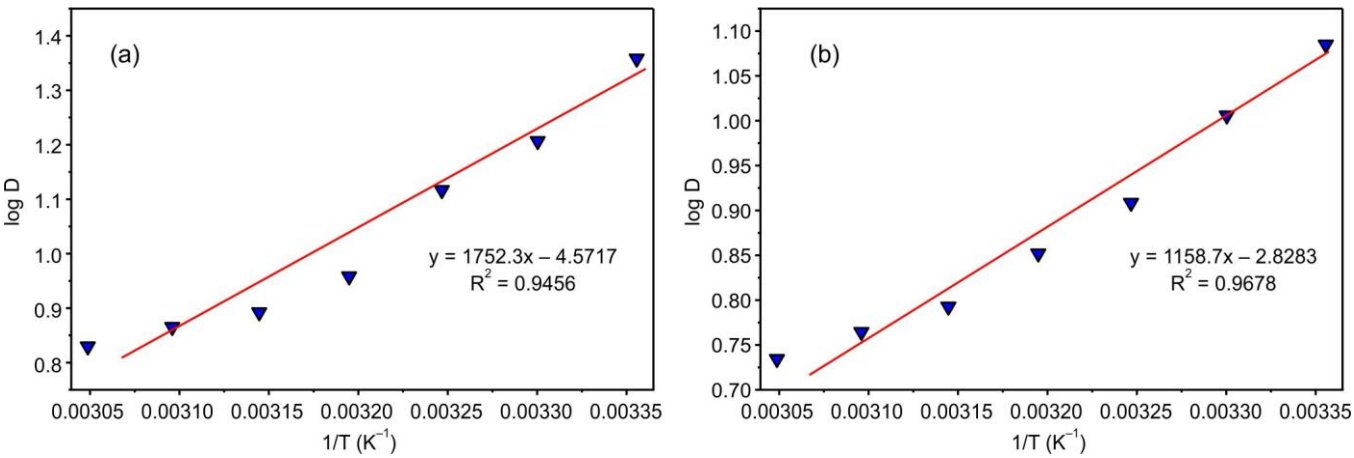


Fig. 5. Plot of Log D *vs.* 1/T for extraction of niobium. Conditions: [FTA] = 10% (v/v) in kerosene, O/A = 1, equilibrium time 10 min, (a) aqueous phase media: 1.6 mol $L^{-1}$ $C_2H_2O_4$-0.6 mol $L^{-1}$ $H_2SO_4$, (b) aqueous phase media: 2.6 mol $L^{-1}$ $H_2SO_4$-0.8 mol $L^{-1}$ HF

mol$^{-1}$ and -87.53 J K$^{-1}$ mol$^{-1}$, respectively for 1.6 mol L$^{-1}$ $C_2H_2O_4$-0.6 mol L$^{-1}$ $H_2SO_4$ system. And, from Fig. 5b, $\Delta H$ = -22.18 kJ mol$^{-1}$ and $\Delta S$ = -54.15 J K$^{-1}$ mol$^{-1}$ were obtained by the extraction experiments of niobium from 2.6 mol L$^{-1}$ $H_2SO_4$-0.8 mol L$^{-1}$ HF aqueous system. The negative values of $\Delta H$ signified the exothermic nature of the extraction experiments by FTA extractant. The values of $\Delta S$ suggested that the degree of order had increased during the extraction of niobium.

Fig. 6 shows that the distribution coefficient decreased from 22.809 to 6.751 for the 1.6 mol L$^{-1}$ $C_2H_2O_4$-0.6 mol L$^{-1}$ $H_2SO_4$ system and from 12.157 to 5.422 for the 2.6 mol L$^{-1}$ $H_2SO_4$-0.8 mol L$^{-1}$ HF system. Negative Gibbs free energy ($\Delta G$) values at all investigated temperatures established the spontaneous and feasible nature of niobium extraction with FTA. The oxalic acid-sulphuric acid medium yielded more negative $\Delta G$ values than the $H_2SO_4$-HF system shows better thermodynamic favourability for niobium extraction.

**Effect of diluents:** The choice of extractant and diluent plays a critical role in solvent extraction as the physico-chemical interactions between them influence metal distribution in the organic phase. This effect was examined by extracting 100 mg L$^{-1}$ niobium from a 1.6 mol L$^{-1}$ $C_2H_2O_4$-0.6 mol L$^{-1}$ $H_2SO_4$ system using 10% (v/v) FTA dissolved in toluene, chloroform, benzene, kerosene, carbon tetrachloride and xylene. As listed in Table-1, the dielectric constant of the diluent markedly influenced niobium extraction. Kerosene and carbon tetrachloride achieved the highest extraction efficiencies of 95.80% and 88.25%, whereas chloroform gave the lowest extraction efficiency of 66.22%. No third-phase formation or emulsion was observed during phase separation. The extraction efficiency decreased with increasing dielectric constant of the diluent owing to the stronger FTA-diluent interactions that limit the association of FTA with niobium at the aqueous-organic interface. These results establish that the extraction performance of FTA is strongly governed by the physico-chemical properties of the diluent.

**Effect of extraction equilibrium time:** The effect of extraction equilibrium time on the extraction of niobium was also studied. The extraction equilibrium time was investigated over the range of 2-20 min using an aqueous phase containing 100 mg L$^{-1}$ niobium in 1.6 mol L$^{-1}$ $C_2H_2O_4$-0.6 mol L$^{-1}$ $H_2SO_4$ and an organic phase comprising 10% (v/v) FTA in kerosene. Fig. 7 shows that equilibrium was reached within 10 min with quantitative extraction of niobium. No measurable improvement in extraction efficiency was observed between 10 and 20 min and an equilibration time of 10 min was adopted for all subsequent experiments.

**Effect of stripping reagents:** Stripping efficiency is a key criterion for evaluating the performance of a solvent extraction system. The decrease in niobium extraction at higher acid concentrations suggested that strong mineral acids could effectively recover the loaded metal from the organic phase. Following a single extraction stage, 95.80% of niobium was transferred to the FTA-kerosene phase. Stripping experiments were carried out using $H_2SO_4$, $HNO_3$ and HCl at concentrations ranging from 0.5 to 4.0 mol L$^{-1}$. Fig. 8 shows that 3.5 mol L$^{-1}$ HCl and $HNO_3$ stripped 68.84% and 76.34% of

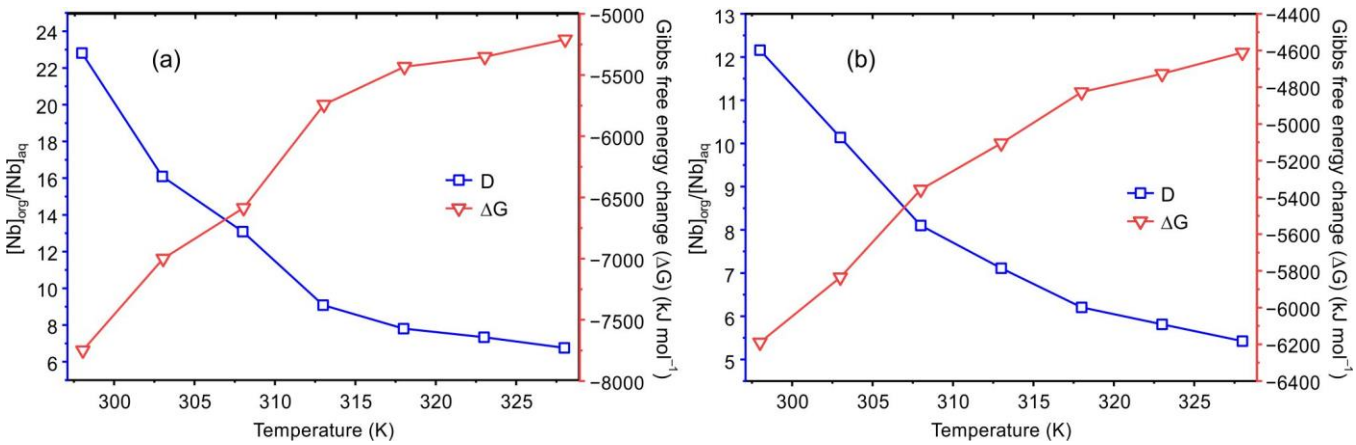


Fig. 6. Effect of temperature on Gibbs free energy change ($\Delta G$) and distribution coefficient (D). Conditions: [FTA] = 10% (v/v) in kerosene, O/A = 1, equilibrium time 10 min, (a) aqueous phase media: 1.6 mol L$^{-1}$ $C_2H_2O_4$-0.6 mol L$^{-1}$ $H_2SO_4$, (b) aqueous phase media: 2.6 mol L$^{-1}$ $H_2SO_4$-0.8 mol L$^{-1}$ HF

TABLE-1
EFFECT OF DILUENTS ON THE EXTRACTION OF NIOBIUM

| Diluents | Dielectric constant | Density (g cm$^{-3}$) | Extraction efficiency (%) | Distribution coefficient (D) |
|---|---|---|---|---|
| Kerosene | 1.80 | 0.800 | 95.80 | 22.809 |
| Carbon tetrachloride | 2.24 | 1.590 | 88.67 | 7.826 |
| Benzene | 2.27 | 0.876 | 82.54 | 4.727 |
| Toluene | 2.38 | 0.867 | 76.12 | 3.187 |
| Xylene | 2.57 | 0.879 | 70.94 | 2.441 |
| Chloroform | 4.81 | 1.489 | 65.63 | 1.909 |

Conditions: [FTA] = 10% (v/v), O/A =1, aqueous phase media: 1.6 mol L$^{-1}$ $C_2H_2O_4$-0.6 mol L$^{-1}$ $H_2SO_4$, equilibrium time 10 min.

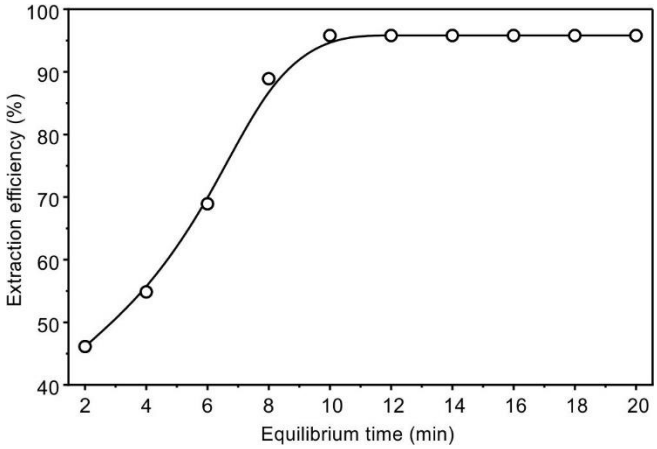


Fig. 7. Effect of equilibrium time on extraction of niobium. Condition: [FTA] = 10% (v/v) in kerosene, aqueous phase media = 1.6 mol $L^{-1}$ $C_2H_2O_4$-0.6 mol $L^{-1}$ $H_2SO_4$, O/A = 1

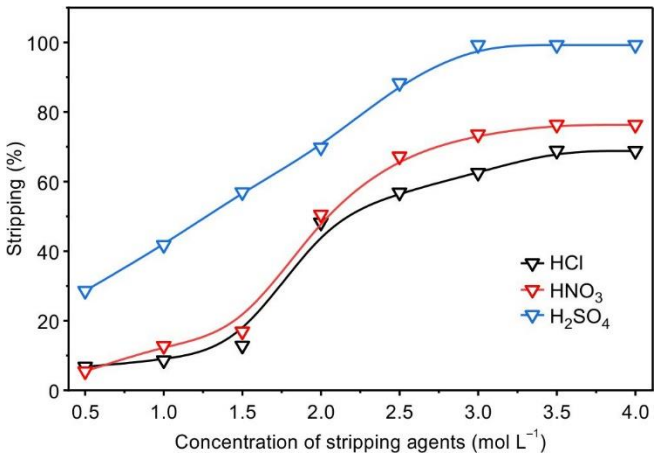


Fig. 8. Effect of concentration of stripping reagents on niobium loaded in organic phase

niobium, respectively, whereas 3.0 mol $L^{-1}$ $H_2SO_4$ achieved 99.26% stripping from the FTA-kerosene organic phase.

**Extraction mechanism analysis:** FTA exhibited high extraction efficiency for niobium under the proposed conditions. The extraction process is initiated by the interaction of niobium with the $C_2H_2O_4$-$H_2SO_4$ medium, which lowers the effective charge density of Nb(V) through oxalate complexation and facilitates its interaction with FTA [33]. The extraction mechanism was investigated using UV-visible spectrophotometry and slope analysis, which have been widely applied for determining the composition of niobium extractable species [10,17,29,34].

The stoichiometry of the extracted complex was established from the relationship between log D and log [FTA]. At a fixed aqueous phase composition of 1.6 mol $L^{-1}$ $C_2H_2O_4$-0.6 mol $L^{-1}$ $H_2SO_4$, the slope of 1.0117 obtained from Fig. 9a corresponds to the participation of one FTA molecule in the extracted complex. The contribution of oxalic acid was evaluated by varying its concentration while maintaining constant FTA and $H_2SO_4$ concentrations. The slope of 1.9336 obtained from the log D *versus* log [$C_2H_2O_4$] plot (Fig. 9b) corresponds to the participation of two oxalate molecules. The role of $H_2SO_4$ was examined under constant oxalic acid concentration and the slope of 1.0482 from the log D *versus* log [$H_2SO_4$] plot (Fig. 9c) corresponds to the participation of one sulphuric acid molecule in the extracted species. The extraction reactions proposed for the FTA–niobium system are based on these stoichiometric relationships and are represented by the following equations:

$$Nb(V)_{aq} + 2(C_2O_4^{-2})_{aq} + (HSO_4^{-1})_{aq} + RH_{org} \longrightarrow [Nb(C_2O_4)_2(HSO_4)R]_{org} + H^+_{aq} \quad (4)$$

$$K_{ex} = \frac{[Nb(C_2O_4)_2(HSO_4)R]_{org}[H^+]_{aq}}{[RH]_{org}[Nb(V)]_{aq}[C_2O_4^{-2}]^2_{aq}[HSO_4^-]_{aq}} \quad (5)$$

$$K_{ex} = \frac{D[H^+]_{aq}}{[C_2O_4^{-2}]^2[HSO_4^-][RH]_{org}} \quad (6)$$

$$LogD = LogK_{ex} + 2Log[C_2O_4^{-2}]_{aq} + Log[HSO_4^-]_{aq} + Log[RH]_{org} + pH \quad (7)$$

where subscript aq and org denote the aqueous phase and organic phase, respectively. The extraction equilibrium constant $K_{ex}$ is only related to the temperature of extraction reaction and D is the distribution coefficient of niobium.

**Selective extraction of niobium:** The extraction behaviour of niobium and tantalum was initially evaluated using synthetic solutions containing 100 mg $L^{-1}$ niobium and 50 mg $L^{-1}$ tantalum with FTA dissolved in kerosene. Media optimisation was carried out by extracting niobium and tantalum individually from 0.6 mol $L^{-1}$ $H_2SO_4$ solutions containing different concentrations of oxalic acid while maintaining all

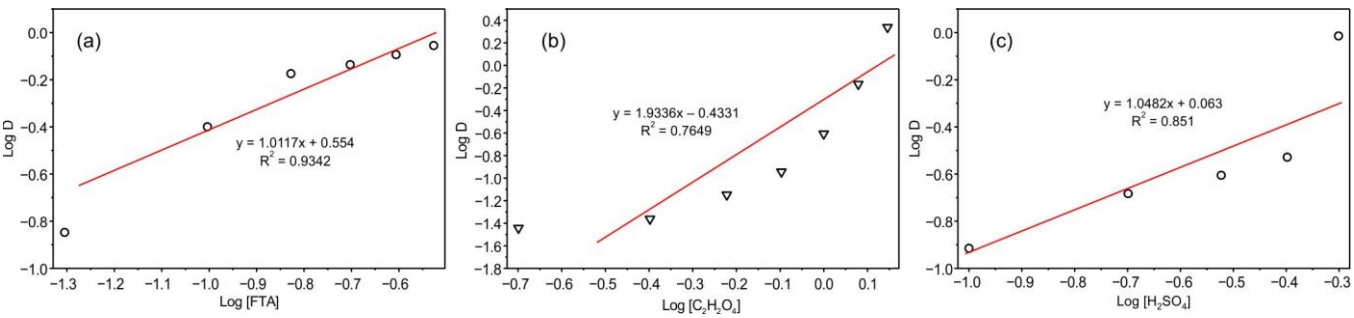


Fig. 9. Plots of Log D *versus* (a) log [FTA], (b) log [$C_2H_2O_4$] and (c) log [$H_2SO_4$]. Experimental conditions: aqueous phase medium = 1.6 mol $L^{-1}$ $C_2H_2O_4$-0.6 mol $L^{-1}$ $H_2SO_4$ for (a); 10% (v/v) FTA in kerosene for (b) and (c); O/A = 1 and equilibrium time = 10 min for all experiments

TABLE-2
SEPARATION OF NIOBIUM FROM BINARY MIXTURE

| Compositions (mg $L^{-1}$) | Recovery of niobium (%) | R.S.D.* | Recovery of added metals (%) | R.S.D* |
|---|---|---|---|---|
| Nb 100, Ta 50 | 95.75 | 0.092 | 98.84 | 0.094 |
| Nb 100, Ti 100 | 95.80 | 0.003 | 99.23 | 0.041 |
| Nb 100, Fe 100 | 95.78 | 0.064 | 99.12 | 0.680 |
| Nb 100, Mn 100 | 95.79 | 0.038 | 99.63 | 0.024 |

R.S.D. = Relative standard deviation, *Average six determinations

other extraction parameters constant. Fig. 10 shows that niobium extraction increased with increasing oxalic acid concentration and reached 95.84% at 1.6 mol $L^{-1}$ $C_2H_2O_4$, whereas tantalum extraction decreased from 54.46% to 2.31% over the concentration range of 0.2-1.6 mol $L^{-1}$ $C_2H_2O_4$.

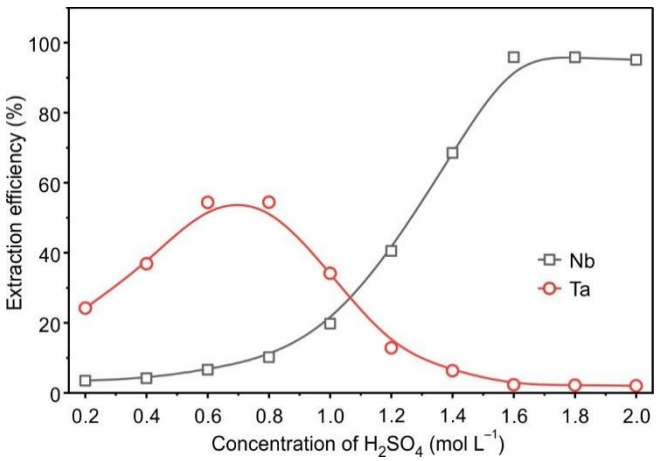


Fig. 10. Effect of $C_2H_2O_4$ concentration on niobium and tantalum extraction. Conditions: [FTA] = 10% (v/v) in kerosene, O/A = 1, equilibrium time 10 min, aqueous phase media: 0.6 mol $L^{-1}$ $H_2SO_4$

The extraction performance of FTA was subsequently evaluated for the selective separation of niobium from binary mixtures containing tantalum, titanium, iron and manganese. The extraction was carried out using an aqueous phase containing 100 mg $L^{-1}$ niobium in 1.6 mol $L^{-1}$ $C_2H_2O_4$-0.6 mol $L^{-1}$ $H_2SO_4$, an organic phase of 10% (v/v) FTA in kerosene, an O/A phase ratio of 1, an equilibration time of 10 min and 3.0 mol $L^{-1}$ $H_2SO_4$ as the stripping agent. Under these conditions, tantalum, titanium, iron and manganese remained quantitatively in the aqueous phase and were determined spectrophotometrically [35]. The proposed method achieved selective and efficient recovery of niobium from the investigated metal ions and the results are shown in Table-2.

## Conclusion

Systematic investigation established that 10% (v/v) furfuryl thioalcohol (FTA) in 1.6 mol $L^{-1}$ $C_2H_2O_4$-0.6 mol $L^{-1}$ $H_2SO_4$ provides an efficient fluorine-free extraction system for the selective recovery of niobium from commonly associated metals. Kerosene was the most suitable diluent and the extraction efficiency decreased with increasing dielectric constant of the diluent. The extraction process was exothermic with ΔH and ΔS values of −33.55 kJ $mol^{-1}$ and -87.53 J $K^{-1}$ $mol^{-1}$, respectively, for the $C_2H_2O_4$- $H_2SO_4$ system, compared with –22.18 kJ $mol^{-1}$ and –54.15 J $K^{-1}$ $mol^{-1}$, respectively, for the $H_2SO_4$-HF system. Quantitative stripping of niobium was achieved using 3.0 mol $L^{-1}$ $H_2SO_4$. The proposed method offers high selectivity for niobium and provides a practical fluorine-free alternative for its separation from associated metal ions.

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## CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

## DECLARATION OF AI-ASSISTED TECHNOLOGIES

During the preparation of this manuscript, the authors used an AI-assisted tool(s) to improve the language and no data, results or scientific conclusions were generated by AI. All analyses, interpretations and conclusions are the authors' own. The authors reviewed and edited the content and take full responsibility for the published work.

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