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Separation of uranium (VI) using dispersive liquid-liquid extraction from leach liquor

Meysam Hadadian [a], Mohammad H. Mallah [b], *, Mohammad A. Moosavian [a], Jaber Safdari [b], Mehrdad Davoudi [b]

[a] School of Chemical Engineering, University of Tehran, Enqelab Square, Tehran, Iran
[b] Nuclear Fuel Cycle Research School, Nuclear Science &Technology Research Institute, End of North Karegar Ave, Tehran, Iran

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ABSTRACT

A dispersive liquid–liquid extraction technique was applied for evaluation of optimal conditions of uranium (VI) separation from aqueous solution (It is actual leach liquor, containing uranium (VI), thorium (IV), iron (III), Cl^-, SO_4^{2-}, etc). In this procedure, an appropriate mixture of the disperser and extraction solvents was added rapidly to the aqueous sample containing uranium ion; as a result, a cloudy solution was formed which consisted of fine droplets of extraction solvent dispersed entirely throughout the aqueous phase. The cloudy solution was centrifuged and the fine droplets of the extraction solvent were settled at the bottom of the conical test tube. The analytes were extracted from the source solution into the receiving phase and were concentrated to a small volume of the settled phase and finally, the inductively coupled plasma optical emission spectrometry was used to determine the analyte concentration in the settled phase. The conditions for the batch extraction performance were optimized; Furthermore, the continuous packed tower with 5 cm of diameter and 30 cm of height was applied to examine the batch results of continuous condition on an industrial-scale. The results showed that for 41.2% and 90% recovery factors of uranium (VI) from the leach liquor solution, one equilibrium stage and five equilibrium stages are needed, respectively.

1. Introduction

Uranium is a relatively rare metal element often found in association with other elements in the earth's crust. It plays an important role in daily life because of its use in nuclear power plants. Different processes are available for uranium extraction and separation from the associated elements in natural resources as well as from nuclear wastes. Conventional methods such as liquid-liquid extraction (LLE) (Kumar et al., 2010a; Sahoo et al., 2002; Takahashi et al., 2009; Mohanty et al., 1991; Lin and Freiser, 1983) and solid-phase extraction (SPE) (Shamsipur et al., 1999; Sadeghi and Sheikhzadeh, 2009; Funda and Soylak, 2007) have been used for extraction of uranium. However, these techniques are tedious and time also solvent consuming. Recent research activities are oriented towards the development of efficient, economical, and miniaturized sample preparation methods. Therefore, extraction methods such as supercritical fluid extraction (SFE) (Yuehe. et al., 1995; Yuehe et al., 2003), supported liquid membrane (SLM) (Kenichi and Takuji, 2006; Surajit et al., 2009), cloud point extraction (CPE) (Hadla et al., 2006; Alain et al., 2006; Ghasemi et al., 2012), solvent microextraction (SME) (John, 2012, 2013), and single drop microextraction (SDME) (Michael et al., 2010) were used. For the fist time, a novel, simple and efficient solvent extraction technique, termed dispersive liquid-liquid extraction (DLLE), has been developed by the authors.

This technique, in principle, is similar to the dispersive liquid-liquid microextraction (DLLME) introduced by Assadi et al., in 2006 (Rezaee et al., 2006a). In this method, the appropriate mixture of extraction solvent and disperser solvent is injected into the aqueous sample by a syringe rapidly. Thereby, a cloudy solution is formed. The dispersing solvent, in DLLME, is applied to create fine droplets of the extracting solvent in the extraction media. In such a process, as the mass transfer area between the extracting solvent and analytes increases, the yield of extraction would be much higher than that of the conventional extraction methods (Rezaee et al., 2006b; Mallah et al., 2009; Mallah and Davoudi, 2012;

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* Corresponding author.
E-mail address: mmallah@aeoi.org.ir (M.H. Mallah).

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Maya et al., 2014). The volume of aqueous solution in DLLE is much larger than the required volume in DLLME; consequently, the volumes of the extracting and disperser solvents are also more than their volumes in DLLME. In other words, the DLLE technique can be regarded as a method between LLE and DLLME which simultaneously provides the advantages of both techniques. The use of a centrifuge for separation of organic phase in DLLE could be avoided due to the increase in volumes.

The recovery of the small amount of the extractant solvent after the phase separation is troublesome, particularly when the solvents with lighter molecular weights than water are used. Moreover, the handling of the minute amounts of an extractant solvent influences the reproducibility of the technique, albeit unsuitable for the routine analysis due to the low analysis throughputs, a laborious and time-consuming procedure. In addition, it requires manual glassware cleaning or disposal, implying an increase in costs and waste generation. In order to overcome these limitations, different approaches have been developed for the automation of the DLLME technique using flow-analysis techniques (Ruzicka and Hansen, 1975; Ruzicka and Marshall, 1990; Silvestre et al., 2009) such as flow-injection analysis (FIA) (Ruzicka and Hansen, 1975) and sequential-injection analysis (SIA) (Ruzicka and Marshall, 1990).

In this research, DLLE technique was investigated for the first time to remove uranium from the leach liquor. Therefore, this work has been done in two stages: The first section deals with the batch processing through which the optimum parameters can be specified by DLLE technique for uranium separation. The second section is the industrial scale and continuous status of the first section in a packed tower which has a porosity of 60%. The number of equilibrium stages and packed tower height for uranium separation can be determined at this step by McCabe-Thiele technique. Several extractants have been used for uranium extraction using DLLE technique. These extractants are categorized into four types:

1. Nitrogen-based extractants (Gupta et al., 2000; Zhu et al., 2004; Kumar et al., 2010b),
2. Phosphorous-based extractants (Stas et al., 2005; Singh et al., 2009; Sahu et al., 2000),
3. Sulfur-based extractants (Gamare et al., 2009; Sato et al., 2006; Khan et al., 2008),
4. Other extractants (Reddy et al., 2000; Banerjee et al., 2003; Guo et al., 2006; Agrawal et al., 2006).

2. Experimental

2.1. Reagents and chemicals

All chemicals used in the present experiment such as trioctylamine (TOA), di-(2-ethylhexyl) phosphoric acid (DEHPA), amines, methanol, ethanol, acetone, and so on, were of analytical grade reagents produced by Merck Co. (Darmstadt, Germany). Vessels used for the trace analysis were kept in a 1.0 mol L^{-1} HNO_3 solution at least 24 h, and subsequently washed twice with distilled water before use. Sample holders were polyethylene bottles which were rinsed with concentrated nitric acid, then washed with distilled water.

2.2. Apparatus

An inductively coupled plasma-optical emission spectroscopy (ICP-OES) was used for the uranium (VI) ion determination. The stock solution of uranium (VI) was prepared from the standard solutions of 1000 ppm. The phase separation was assisted by a centrifuge (Mistral 1000, MSB 100/CE 1.4). The pH values were measured with a Schot pH-meter (CG 841) equipped with a glass-combined electrode. The pH measurements were done in the wake of the compensation of deviations caused by the ionic strength by following these steps:

1. Prepare 100 mL each of 2.0, 1.5, 1.0, 0.5, 0.1 and 0.001 M of aqueous NaCl solutions. Start with the 1 L of the 2.0 M solutions and make more dilute samples by dilution.
2. Provide a buffer solution from Sigma 79 tris (hydroxymethyl) aminomethane (TRIS') by adding 0.124 g to 100 mL of distilled water.
3. Adjust the pH meter using appropriate calibration buffer solutions. If the value shown is different from that of the standard solution, continue this adjustment procedure until the indicated value is within ±0.02 of the pH of the standard solution.
4. Measure the pH of each of the NaCl solutions. Plot the measured pH versus the ionic strength of the solution.

2.3. Procedure

Under the optimal conditions, 10 mL of a solution containing uranium (VI) at a concentration of 45.71 mg L^{-1} as the source phase (s.p.: aqueous sample) was placed into a 15 mL sample holder with a conic bottom. Then 1.2 mL of methanol as a disperser solvent which contained 0.4 mL of DEHPA as extraction solvent, whose pH was fixed by the aqueous hydrochloric (11.8 mol L^{-1}) solution within the range of 1–1.5, was added rapidly to the aqueous sample solution. A cloudy solution was formed in the sample holder. At this step, uranium ion reacted with the extraction solvent and was transferred into the fine droplets of DEHPA. The mixture was whirled for 3 min and then centrifuged for 10 min at 4000 rpm.

Accordingly, the dispersed fine droplets of uranium oxide (VI) were precipitated at the bottom of the conical sample holder. After separating the upper phase including aqueous phase, the receiving phase (r.p.: the sum of dispersive solvent and organic extractant solvents), was dried in a furnace at 160 (±5 °C), near the boiling point of the extraction solvent (DEHPA), then were diluted to 5 mL by adding distillated water (Davoudi and Mallah, 2013) and finally, were analyzed under the ICP-OES operating conditions for determination of Uranium (VI), (Table 1) and the wavelength of 409.014 nm in curve uranium (VI).

The measurements of precision and accuracy management of the matrix effects are very important. Although, among all commonly used analytical atomic spectrometry techniques, ICP-OES is probably the one with the fewest interferences, the most common interference problem in ICP-OES is the spectral interference. These interferences can be listed into four categories:

1 Simple background shift,
2 Sloping background shift,

Table 1
Operating conditions of ICP-OES in measurement of uranium (VI).

Power of plasma	1300 W
RF generator	40 MHz
Vista axial-position	Horizontal: 0 mm Vertical: 15 mm
Nebulizer	Glass, Meinhard
Gas flow of plasma	15 L/min
Gas flow of auxiliar	0.2 L/min
Gas flow of nebulizer	0.8 L/min
Aspiration	1.5 mL/min
Integration time	10 s
Number of replicates	3