



# Supercritical fluid extraction and purification of uranium from crude sodium diuranate



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## ABSTRACT

Supercritical Fluid Extraction (SFE) and purification of uranium, from crude sodium diuranate (SDU) containing uranium (53%), iron (22.2% of U) and rare earth impurities (4% of U), has been studied. Adduct of tri-butyl phosphate (TBP) and nitric acid (HNO<sub>3</sub>) has been used for uranium dissolution and extraction. Carbon dioxide has been used as supercritical fluid. For 200 mg of crude SDU, operating parameters such as temperature, pressure, quantity of TBP·HNO<sub>3</sub> adduct, static and collection time have been optimized at 323 K temperature, 15.20 MPa pressure, 1 mL of TBP·HNO<sub>3</sub> adduct, 20 min. static time and 20 min. collection time. Under these conditions, uranium extraction efficiency was 95 ± 5%. Addition of free nitric acid leads to improvement in purity of uranium. Uranium was stripped from SFE extract and precipitated as ammonium diuranate (ADU), which was then subjected to second cycle of SFE. After two cycles of SFE, purification factor of uranium was found to be 4970, 90, 110 and 60 with respect to iron, yttrium, ytterbium and erbium respectively.

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## 1. Introduction

Uranium is used worldwide as fuel for nuclear power reactors to produce electricity. The conventional resources of uranium are limited and available in few countries. Uranium recovery from unconventional sources is being explored worldwide for sustainable nuclear power generation. Rock phosphate ore is a valuable unconventional source of uranium which, depending upon its source, contains uranium in the range of 50 to 200 ppm. Total uranium content present in rock phosphate ore is estimated to be around 9 million ton which is higher than that in conventional resources (*Resources, Production and Demand, 2014*). Rock phosphates are employed for production of phosphatic fertilizer. During fertilizer production, phosphoric acid is produced as an intermediate product which contains ppm level of uranium. Several solvent extraction processes have been developed to recover this uranium (*Hurst et al., 1972; Bunus, 2000; IAEA Techdoc, 1989; Rawajfeh and Al-Matar, 2000; Singh et al., 2009; Nazari et al., 2004; Singh et al., 2004; Krea and Khalaf, 2000; Abdel-Khalik et al., 2011*). Among these processes, solvent extraction using D2EHPA/TBP or D2EHPA/TOPO as extractant is most successful for sustained industrial scale operation (*Singh et al., 2007; Singh et al., 2003*). Uranium has been successfully recovered as by-product during fertilizer production in several countries. However,

crude yellow cake (sodium diuranate or ammonium diuranate) produced from this source contains several impurities viz. transition and rare earth elements. These elements possess high neutron absorption cross section and unfavorable metallurgical properties (*Wilson, 1996*). Conventional purification methodologies to purify these crude yellow cakes to nuclear grade involve several process steps such as dissolution, pretreatment and filtration followed by solvent extraction as the key step which leads to the generation of significant quantity of liquid waste.

Supercritical Fluid Extraction (SFE) is a method of separation that employs Supercritical Fluid (SCF) as extraction media. Solubility of a substance, and hence extraction behavior in SCF is dependent on density of SCF which can be tuned by changing pressure and temperature conditions. Also, SCF possesses diffusivity, viscosity and surface tension intermediate to that of liquid and gas. Due to high diffusivity, it can extract materials of interest directly from solid phase. Low viscosity and surface tension leads to faster mass transfer and kinetics (*Mchugh and Krukoni, 1994*). Carbon dioxide is a preferred choice for supercritical fluid (SCF) owing to its moderate critical constants ( $P_c = 7.38$  MPa and  $T_c = 304.1$  K) coupled with radiation and chemical stability, non-toxic nature and commercial availability at reasonable rate. CO<sub>2</sub> used for this purpose is mostly produced as by-product from chemical industries making it an environmental friendly process. Also, after extraction CO<sub>2</sub> escapes as gas leading to a compact extract (*Mchugh and Krukoni, 1994; Mukhopadhyay, 2000*). SFE has been successfully developed and being used for several industries such as separation of natural extracts,

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organic compounds, medicines, food products and cosmetics (Mukhopadhyay, 2000). SC CO<sub>2</sub> and Supercritical H<sub>2</sub>O have also been used for extraction of heavy metal ions from sand and sewage sludge (Yabalak and Gizir, 2013). But Supercritical CO<sub>2</sub> (SC CO<sub>2</sub>), being non polar in nature, is very inefficient in dissolution of metals due to charge neutralization requirement and weak solute-solvent interactions. Hence, SFE with SC CO<sub>2</sub> modified with suitable complexing agents has been employed to extract various metals from liquid and solid matrices (Wai, 1997; Hanny and Hogarth, 1879). In the context of nuclear industry, SFE is very attractive, as it leads to minimization of liquid waste generation, reduction of process steps, increase in the process efficiency and minimization of use of corrosive chemicals (Rao et al., 2010; Kumar et al., 2008).

Uranium oxide has been successfully dissolved with TBP·HNO<sub>3</sub> adduct in SC CO<sub>2</sub> medium and extracted quantitatively. Several studies have been reported on SFE of actinides and lanthanides with TBP·HNO<sub>3</sub> adduct from various matrices viz. assorted radioactive waste matrices and spent nuclear fuels from different nuclear reactors (Shadrin et al., 2008; Zhu et al., 2012; Shamsipur et al., 2001; Shimada et al., 2006). Uranium present in spent nuclear fuel has been selectively recovered with good separation factors from fission products by SFE followed by counter current chromatographic separation (Myasoedov et al., 2009).

In present study, feasibility of direct dissolution and SFE of uranium from crude sodium diuranate (SDU) matrix, containing impurities such as iron, transition and rare earth elements, has been explored. TBP·HNO<sub>3</sub> adduct has been employed in the in-situ mode of complexation for the same. Effect of operating parameters such as temperature, pressure, TBP·HNO<sub>3</sub> adduct amount, static time and collection time on extraction efficiency of uranium has been studied. Possibility of purification of uranium from impurities has been investigated. Effect of SDU quantity and addition of free acid on uranium extraction efficiency and its purification from impurities has been studied. ADU prepared from stripped SFE extract has been subjected to second cycle of SFE to improve purity of recovered uranium.

## 2. Experimental

### 2.1. Materials

Analytical Reagent (AR) grade TBP and nitric acid have been used in the study. Ultrapure water obtained from Millipore ultrapure water system was used for preparing reagents. Chloroform used for collecting SFE extracts and ammonium hydroxide used for uranium precipitation were of AR grade (Merck make). Calibration standards used during analysis by Inductively Coupled Plasma-Optical Emission

Spectrophotometer (ICP-OES) were prepared from single elemental standard solution (Inorganic Ventures, Virginia, USA).

### 2.2. Instruments

Schematic diagram of the SFE set up is shown in Fig. 1. The SFE system consists of CO<sub>2</sub> pump, co-solvent pump, thermostat, extraction vessel, back pressure regulator and a collection vessel. The detailed working of instrument is described elsewhere (Rao et al., 2010).

Inductively Coupled Plasma-Optical Emission Spectrophotometer (ICP-OES) of Horiba Jobin make (Ultima 2) has been used for analysis of uranium and other impurities. The instrument consists of RF Generator (40.68 MHz), monochromator (Czerny Turner mounting) with Dual holographic gratings (4320 and 2400 line/mm) and Photomultiplier Tube (PMT) as detector. It has wavelength resolution of 5 nm (between 170 to 320 nm) and 10 nm (between 320 to 800 nm). Argon was used as plasma gas. Spectral lines used for elemental analysis are 409.014, 259.940, 371.300, 369.420 and 369.265 nm for uranium, iron, yttrium, ytterbium and erbium respectively.

### 2.3. Method

#### 2.3.1. Preparation of TBP·HNO<sub>3</sub> adduct

TBP·HNO<sub>3</sub> adduct was prepared by mixing pure TBP with HNO<sub>3</sub> of desired molarity in a beaker under stirring for 45 min. TBP·HNO<sub>3</sub> adduct phase was separated from aqueous phase with the help of separating funnel and used for SFE studies.

#### 2.3.2. SFE studies

Dried SDU (200 mg) and TBP·HNO<sub>3</sub> adduct was taken in the extraction vessel. On obtaining the desired temperature in thermostat, CO<sub>2</sub> was pumped to achieve desired pressure. This is known as the in-situ mode of complexation. The system was kept at desired pressure and temperature for desired time period for dissolution of SDU and complexation of uranium (static time). Subsequently, extraction was achieved by flowing CO<sub>2</sub> at 2 mL min<sup>-1</sup> and collecting the extract in collection vessel (collection time) at atmospheric pressure where CO<sub>2</sub> escapes as gas. The unextracted uranium left in extraction vessel was analyzed for uranium content and extraction efficiency was calculated [Eq. (1)].

$$\text{Extraction Efficiency (\%)} = \frac{[U_i - U_r]}{U_i} \times 100\% \quad (1)$$

where U<sub>i</sub> = Amount of initial uranium loaded in extraction vessel. U<sub>r</sub> = Amount of residual uranium left over in extraction vessel after SFE.

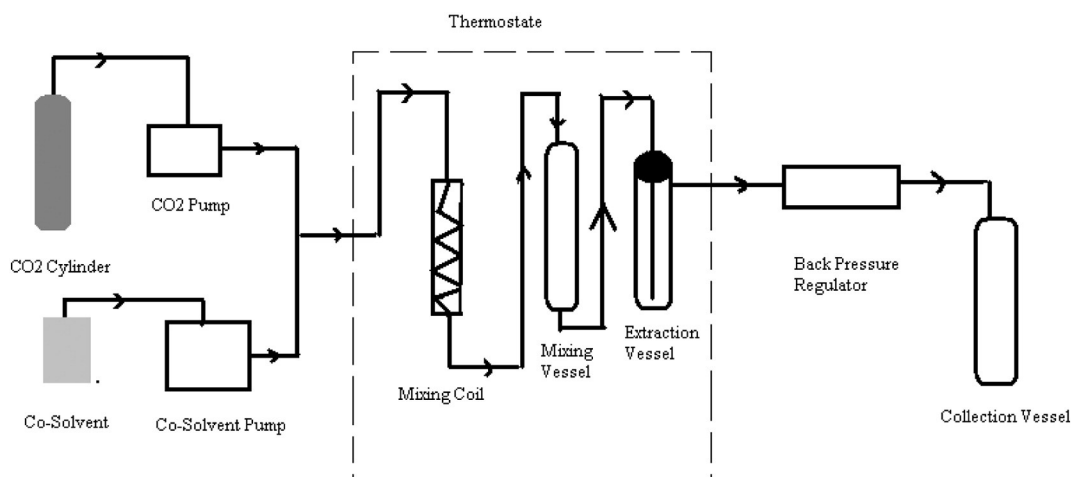


Fig. 1. Schematic of Supercritical Fluid Extraction Set up.

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