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Supercritical fluid extraction of uranium from sintered oxides (UO_2, $(U,Th)O_2$), soil and ore samples using tri-*n*-butylphosphate and *N*,*N*-di-(2-ethylhexyl) isobutyramide as extractants

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ABSTRACT

Direct extraction of uranium from different samples viz. sintered UO_2, $(U,Th)O_2$, soil, and ores was carried out by modifier free supercritical fluid containing tri-*n*-butylphosphate (TBP) and/or *N*,*N*-di-(2-ethylhexyl)isobutyramide (D2EHIBA) as extractants. These extractants were pre-equilibrated with nitric acid prior to their use in supercritical fluid extraction experiments. Uranium extraction studies from sintered UO_2 showed that pre-equilibration with more concentrated nitric acid helped in its better dissolution and extraction. The extraction of uranium from $(U,Th)O_2$ samples was significantly lower for both TBP–HNO_3 (~17%) and D2EHIBA–HNO_3 (~12%) adducts in 2 h, under the conditions of present study. Modifier free supercritical fluid extraction appears attractive with respect to minimization of secondary wastes. This method resulted 80–100% extraction of uranium from different soil/ore samples. The results were confirmed by performing neutron activation analysis of original (before extraction) and residue (after extraction) samples.

Keywords: Supercritical fluid extraction; Uranium; Thorium; Soil; Ore; Neutron Activation Analysis

1. Introduction

Recovery and purification of uranium from ores and from the spent fuel are key steps in the nuclear fuel cycle. Though the conventional processes have been successfully utilized for this purpose, generation of large volumes of liquid wastes is a cause of concern. In this context, supercritical fluid carbon dioxide (SF-CO_2) is being accepted as a potential *green solvent* for chemical separations and reactions. It has the potential of minimizing liquid waste generation, easy separation of solutes, and the ability to penetrate into small pores of solid matrices. As CO_2 is not regarded as a volatile organic compound, CO_2-based extraction processes are generally environmentally acceptable and its release during different CO_2 based industrial processes does not contribute to the *green house* effect. The processes, however, can be modified to recycle CO_2 with no release in the environment. SF-CO_2 extraction has been successfully demonstrated for removal of organic pollutants from solid materials and is a known technique for environmental analysis [1–3]. Attempts have also been made on the optimization of experimental conditions for the extraction of toxic/radioactive metal ions from diverse solid samples including environmental samples [4–6]. Conventionally, the metal ions are

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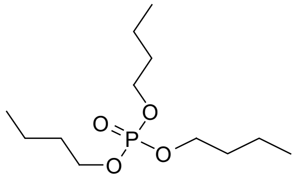
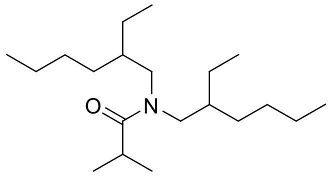
extracted using SF-CO_2 modified with ligand molecules dissolved in some solvents like alcohol etc. [7–9]. It was of interest to evaluate the metal extraction efficiency without pumping modifier solution in the extraction vessel, which appears promising for the reduction of secondary waste volume. In addition, the absence of a modifier is expected to help in stabilizing the supercritical phase of carbon dioxide [10]. The extraction behavior of uranium from uranyl nitrate crystals/the tissue paper matrix and the preferential extraction of uranyl nitrate over thorium nitrate employing modifier free delivery mode of different ligands was evaluated. Reagents such as hydrogen peroxide (H_2O_2) and/or alkali metal/ammonium carbonates have been reported to facilitate dissolution of UO_2 [11–13]. Hubert et al. investigated the dissolution of ThO_2 powdered samples under various conditions of pH (in both nitric and hydrochloric media) and concentration of anions in the leachate [14]. Whereas the presence of nitrate, chloride and perchlorate anions did not show significant influence on the dissolution of ThO_2; the presence of other ligands such as sulfate, and hydrogen peroxide enhanced the dissolution kinetics which was attributed to the complexing affinity of these ligands. The dissolution mechanism was explained in terms of the weakening of Th-O bonds through the formation of surface complexes at the solid/liquid interface, which enhanced the rate of detachment of the solid and thus accelerated the overall dissolution. Similar dissolution studies on $Th_{0.87}Pu_{0.13}O_2$ solid solution, showed an increase in the dissolution rate as compared to that of ThO_2, which was attributed to the presence of H_2O_2 formed by radiolysis. In addition, the redox properties of plutonium in acidic media may also influence the dissolution of plutonium.

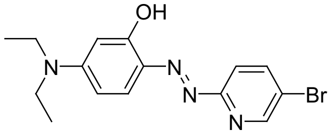
Myasoedov et al. reported direct extraction of actinides from their solid dioxides of U, Np and Pu employing the adducts of HNO_3 with tri-*n*-butylphosphate (TBP; Fig. 1a), methylisobutylketone (MIBK), *N*,*N*′-dimethyl-*N*,*N*′-dioctylhexylethoxymalonamide (DMDOHEMA) [15]. Samsonov et al. demonstrated that UO_2 can be dissolved in supercritical CO_2 carrying TBP–HNO_3 adduct to form a highly soluble $UO_2(NO_3)_2$ 2TBP complex. The diffusion of the oxidized products in the liquid phase was the limiting factor for dissolution rate [16]. Recently, dissolution/extraction of uranium and plutonium using TBP–HNO_3 adduct in supercritical and liquid carbon dioxide was examined on real spent fuel samples [17]. However, the use of organophosphorous extractants such as TBP is not considered environmentally benign due to the generation of large volume of solid waste (after incineration).



(a) Tributyl phosphate



(b) N,N-di-(2-ethylhexyl)isobutyramide



(c) 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (Br-PADAP)

Fig. 1. Structural formulae of different reagents used in this work.

In this context, completely incinerable *N*,*N*-dialkyl amides are being evaluated as alternative green extractants to TBP for spent fuel reprocessing in accord with the CHON principle. Studies carried out at BARC, India on the development of new extractants for reprocessing of spent fuel suggested that whereas straight chain *N*,*N*-di-*n*-hexyloctanamide (DHOA) is a promising extractant for reprocessing of uranium based spent fuels, branched chain *N*,*N*-di(2-ethylhexyl)-isobutyramide (D2EHIBA; Fig. 1b) was found suitable for selective extraction of uranium from thorium [18]. We investigated the extraction of uranium from tissue paper, synthetic soil, and from its oxides (UO_2, UO_3 and U_3O_8) using supercritical CO_2 modified with methanol solutions of extractants such as TBP or DHOA. The effects of temperature, pressure, extractant/nitric acid (nitrate) concentration, and of hydrogen peroxide on uranium extraction were investigated [9]. The dissolution and extraction of uranium in supercritical CO_2 modified with TBP or DHOA, from the oxide samples followed the order: $UO_3 \gg UO_2 > U_3O_8$. Addition of hydrogen peroxide in the modifier solution enhanced the dissolution/extraction of uranium in dynamic mode.

This paper presents the studies on the modifier free supercritical fluid extraction of uranium from sintered UO_2, $(U,Th)O_2$, soil, and ore samples, carried out employing TBP and D2EHIBA as the extractants. The latter was evaluated for selective extraction of uranium from $(U,Th)O_2$ matrix vis-à-vis TBP.

2. Experimental

2.1. Materials

The sintered UO_2 samples (95% theoretical density; sintered at 1,550°C/4 h in Argon +8% Hydrogen atmosphere) and $(U,Th)O_2$ samples (~4% U, 92–93% theoretical density; sintered at 1450°C/4 h in air) were procured from Radiometallurgy Division, BARC. Sintered samples were used to simulate with real spent nuclear fuels. These pellets were powdered and sieved to get uniform particle size of ~100 µm. These sintered and sieved powders were used for uranium extraction experiments. D2EHIBA was synthesized at Radiochemistry Division as per the reported method [18]. AR grade TBP was purified prior to its use in the present work. Both TBP and D2EHIBA were pre-equilibrated 1:1 (v/v) with nitric acid solutions of desired concentration (6, 8 M or concentrated HNO_3) for half an hour. Food grade CO_2 (99.99%) was used at 250 kg/cm^2 pressure and 40°C temperature to be in the supercritical phase.

2.2. Extraction experiments

JASCO-SFE set-up with a solvent delivery pump, modifier pump, constant temperature oven, back pressure regulator was used in the present study (Fig. 2). The sample is taken in the extraction vessel of 10 ml capacity (made of steel) which is then loaded inside the thermostat. CO_2 is delivered to the extraction vessel at a desired flow rate using delivery pump. Simultaneously, the modifier pump is used to mix a desired percentage of the modifier (containing extractant/complexant) to the CO_2 stream. It is important to mention that modifier concentration in CO_2 stream can not be increased beyond a certain level to ensure single-phase supercritical fluid for extraction.

Experiments were carried out by directly placing the samples (~20 mg for UO_2; ~50–100 mg for $(U,Th)O_2$; ~0.5–1 g for ore/zircon) in extraction vessel of 10 ml capacity under the desired experimental conditions. The extracted fractions were collected in glass collection tubes of 15 ml capacity containing 1–2 ml of methanol.

2.3. Analytical techniques

Generally, the collected fractions were diluted to 10 ml in ethanol and the resulting solutions were used for spectrophotometric estimation of uranium employing 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (Br-PADAP; Fig. 1c) as the chromophore. Br-PADAP forms red-violet colored 1:1 stable U(VI)-Br-PADAP complex at pH 7–8 (Triethanolamine (TEA) buffer) with λ_{max} = 578 nm, and ε = 48,000 M^{-1}cm^{-1} (organic phase). Each experiment was repeated for three to five times and the reproducibility of the results was within ±10%. In the data graph, if the symbol is without an uncertainty range, the uncertainty is less than the size of the symbol.

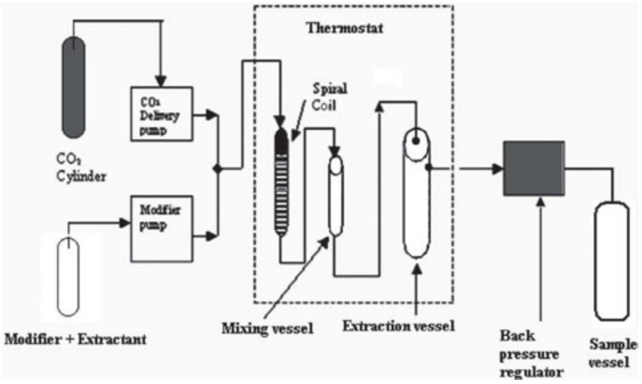


Fig. 2. SFE extraction set-up used in the present study.

Uranium concentrations in soil and ore samples were further authenticated by performing passive gamma and neutron activation analysis (NAA) before and after SFE experiment. A known weight (~10–20 mg) of these samples was sealed in polythene and irradiated in DHRUVA reactor Pneumatic Carrier Facility (PCF). The samples were analyzed by gamma-ray spectrometry.

3. Results and discussion

3.1. Uranium extraction from sintered UO_2 samples

Extraction experiments were carried out in static mode using ~20 mg sintered UO_2 sample and 3.0 ml of TBP–HNO_3 adducts (prepared using 6 and 8 M HNO_3 solutions) at P = 250 kg/cm^2, T = 40°C, and CO_2 flow rate = 2.5 ml/min (during equilibration and flushing of the extracted fraction). Whereas for TBP–HNO_3 adduct at 6 M HNO_3, uranium extraction (%) increased with equilibration time from 20% ± 2% (30 min) to 85% ± 3% (240 min), ~90% ± 5% uranium extraction was observed for TBP–HNO_3 adduct at 8 M HNO_3. It should be noted that TBP gets saturated with respect to HNO_3 after equilibration with ≥8 M HNO_3 solutions. A saturation behavior in uranium extraction was observed thereafter (Fig. 3). This experiment suggested that pre-equilibration of TBP with concentrated nitric acid facilitates faster dissolution and extraction of uranium from sintered oxide samples. It was worth noting that similar study on sintered UO_2 samples (20 mg) using ~3 ml of TBP–HNO_3 adduct (prepared with concentrated HNO_3) with 30 min equilibration time (static mode, P = 250 kg/cm^2, T = 40°C) followed by dynamic mode extraction using 30% TBP solution (equilibrated with concentrated HNO_3) in methanol at identical pressure and temperature and maintaining flow rates

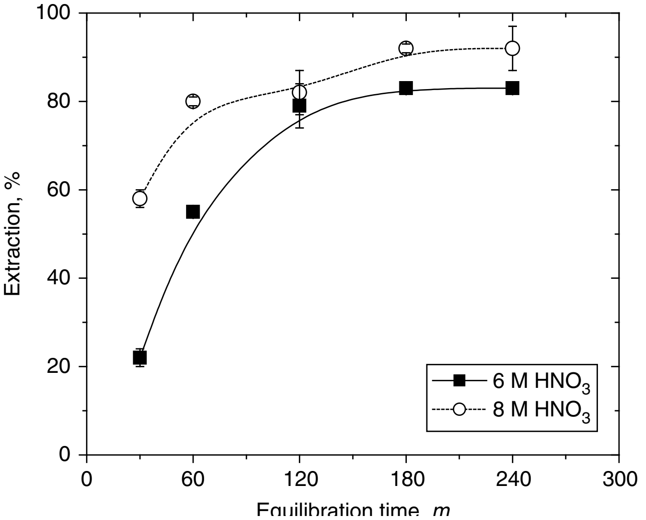


Fig. 3. Modifier free uranium extraction from sintered UO_2 sample using TBP as extractant; Sample size: 20 mg; Conditions: P = 250 kg/cm^2; T = 40°C and CO_2 flow rate = 2.5 ml/min.

(2.5 ml/min (CO_2) and 0.25 ml/min (modifier)) yielded ≥90% extraction in 60 min. Even though the later appears attractive option with respect to time required for 90% extraction of uranium, the former would be preferred in view of: (i) modifier free extraction, and (ii) the use of 8 M HNO_3 for pre-equilibration of TBP. This option will help in minimizing the generation of secondary waste volume and also the corrosion of different parts of the extraction unit. These dissolution studies were also carried out using D2EHIBA as extractant in the presence of H_2O_2 [9]. Whereas no significant improvement in uranium dissolution was observed even after 120 m (≥90%) using TBP as the extractant; D2EHIBA (pre-equilibrated with 8 M HNO_3) yielded only ~45% dissolution from the sintered UO_2 matrix.

3.2. Selective uranium extraction from sintered (U,Th)O_2 samples

Extraction experiments were carried out in static mode using ~20 mg sintered (U,Th)O_2 sample and 3.0 ml of TBP–HNO_3 and D2EHIBA–HNO_3 adducts (prepared using 8 M HNO_3 solutions) at P = 250 atm, T = 40°C, and CO_2 flow rate = 2.5 ml/min (during equilibration and flushing of the extracted fraction). 1 ml methanol was used as the collecting medium and the collection time was maintained as 120 min. In sharp contrast to sintered UO_2 samples, the extraction of uranium from (U,Th)O_2 samples was significantly lower for both TBP–HNO_3 (~17%) and D2EHIBA–HNO_3 (~12%) adducts. This observation can be attributed to two factors: (a) inertness of the major matrix ThO_2 towards dissolution, and (b) the acid concentration in TBP/D2EHIBA adducts. As discussed earlier, the presence of nitrate anions does not have significant influence on the dissolution of ThO_2 due to their relatively poor complexing affinity for Th^{4+} ions so as to weaken the Th–O bonds through the formation of surface complexes at the solid/liquid interface. The basicity of D2EHIBA (defined in terms of acid uptake constant, K_H) is lower than that of TBP, which is responsible for enhanced rate of detachment of uranium from the solid [19]. On the other hand, Kumar et al. demonstrated quantitative and selective extraction of uranium from a mixture of uranium and thorium nitrates (equal weights) using D2EHIBA as the extractant in modifier free mode [10]. This study clearly indicates that selective dissolution of uranium from sintered/ceramic ThO_2 (melting point: 3300°C) is very difficult. Conventionally, the dissolution of thorium oxide requires fluoride ion as catalyst in nitric acid medium. The highly electronegative fluoride ion attacks the Th–O bonds to facilitate the dissolution in nitric acid medium. However, the use of fluoride ion can cause corrosion problem in stainless steel equipment and therefore was not used in the present study.

3.3. Uranium extraction from soil and ore samples

These studies were carried out for the recovery of uranium from different soil and ore samples collected from different origins (Table 1). The extraction conditions used were: 3.0 ml of TBP–HNO_3 adduct (prepared using 8 M HNO_3) directly added to in the extraction vessel; 0.5–1.0 g of soil/ore sample; 250 atm pressure; 40°C temperature; 120 min equilibration time followed by collection for 30 min (no modifier). Uranium recovery was found to be between 80% and 100%. Variations

Table 1
Uranium recovery from different soil and ore samples using modifier free TBP–HNO_3 adduct in static mode; sample size: 0.5–1 g; pressure: 250 kg/cm^2; temperature: 40°C; equilibration time: 120 min; collection time: 30 min(no modifier)

Sample Id	U_{exp}^{a} (μg/g)	U_{meas} (μg/g)	% Recovery
IAEA-std-soil	400	415 ± 15	~100^b
Ore-1	350	380 ± 10	~100^b
Ore-2	350	273 ± 15	78 ± 5
Ore-3	200 (av)	232 ± 10	~100^b
Zircon-1	300 (av)	278 ± 20	93 ± 10
Zircon-2	300 (av)	260 ± 20	87 ± 10

[a] Determined by neutron activation analysis.
[b] These values refer to near quantitative recovery of uranium.

in uranium recovery from the ore and zircon samples reflected the variations in their origins. Uranium recovery was also cross checked by neutron activation analysis of the solid samples before and after supercritical fluid extraction experiments. These experiments also suggested that uranium recovery from soil and ore samples were between 80% and 100%.

4. Conclusions

Direct extraction of uranium from sintered UO_2 showed that pre-equilibration of TBP with more concentrated nitric acid helped in its better dissolution and extraction. By contrast, uranium extraction from $(U,Th)O_2$ samples was significantly lower for both TBP-HNO_3 (~17%) and D2EHIBA–HNO_3 (~12%) adducts in 2 h. This behavior was attributed to the inertness of the major matrix ThO_2 towards dissolution and the acid concentration in the extractant adduct. This method resulted 80–100% extraction of uranium from different soil/ore samples. Neutron activation analysis of the original (before extraction) and residue (after extraction) samples further confirmed these observations. These studies, however, suggest that modifier free supercritical fluid extraction appears attractive with respect to minimization of secondary wastes.

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