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Study of effects of different parameters on supercritical fluid extraction of uranium from acidic solutions employing TBP as co-solvent

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Summary. In the supercritical fluid extraction of uranium from acidic medium employing TBP as co-solvent, effects of various parameters on extraction efficiency were studied. Variation in pressure (80–300 atm), temperature (308–353 K), CO_2 flow rate (0.5–3 mL/min), co-solvent percentage (1–10%), molarity of nitric acid (0.5–10 M) were found to influence uranium extraction efficiency. The uranium extraction efficiency depends on distribution ratio and kinetics of transport of U-TBP complex into supercritical CO_2. In the 150–300 atm pressure range, variation in extraction efficiency was similar to that of uranium distribution ratio under equilibrium conditions. Whereas below 150 atm, it closely followed supercritical CO_2 density variation which could be attributed to non-equilibrium behavior that eventually attained equilibrium. In the non-equilibrium region, increased supercritical CO_2 density with pressure favored enhancement in solubility as well as extraction kinetics of the U-TBP complex. Increase in temperature generally resulted in enhanced volatility of U-TBP complex and a decrease in supercritical CO_2 density which in turn affected the extraction efficiency. Up to 333 K temperature, extraction efficiency gradually increased due to enhancement in volatility of U-TBP complex which more than compensates for decrease in the supercritical CO_2 density. Beyond this temperature, the steep fall in the extraction efficiency is attributed to combined effect of saturation in volatility of the U-TBP complex and significant decrease in the density of supercritical CO_2 approaching the critical value at which supercritical CO_2 tends to form large clusters thereby resulting in steep decrease in its solvating power. Extraction efficiency was found to increase with nitric acid molarity up to 7 M and afterwards showed small decrease possibly due to competitive co-extraction of HNO_3. Up to CO_2 flow rate of 1 mL/min increase in extraction efficiency was observed which attained saturation afterwards. Linear increase in extraction efficiency was observed with the amount of TBP. Extraction efficiency was found to increase linearly with logarithm of extraction time. Under optimised conditions (150 atm, 333 K, 1 mL/min CO_2 flowrate, 10% co-solvent, 7 M nitric acid and 30 min dynamic extraction time) extraction efficiency was found to be (98 ± 2) %. Also, (100 ± 1) % mass balance was observed. 30 min dynamic extraction mode was found equivalent to 40 min static mode. Online complexation mode was more efficient than *in situ* mode.

1. Introduction

Extraction and purification of actinides from various matrices is a key chemical process in the nuclear industry. The conventional process is acid dissolution followed by solvent extraction with suitable organic reagent. Large amount of radioactive liquid waste, comprising of used acid and organic solvents, is generated from conventional process. Recently, increasing attention has been directed towards supercritical fluid extraction (SFE) as a promising alternative to the conventional process, because of its inherent potential to minimize the amount of liquid waste generation and simplification of the extraction process. In comparison to conventional solvent extraction process SFE exhibits distinct advantages, such as enhanced extraction rate, rapid mass transfer and favorable modification of solvent properties like density by tuning pressure/temperature. Supercritical fluids (SCF) offer attractive extraction characteristics, such as favorable diffusivity, viscosity and surface tension. Higher diffusivity than liquids facilitates rapid mass transfer and faster completion of reaction. Due to low viscosity and surface tension, SCFs can penetrate deep inside the material, extracting the components. Liquid like characteristics enable dissolution of compounds whereas gas like characteristics provide conditions for high degree of extraction in shorter time duration.

Hanny and Hogarth [1] in 1879, first observed the unique solvent properties of supercritical fluids. In 1958, Lovelock [2] suggested its use in chromatography. Afterwards SCFs have been widely employed in extraction and separation of natural products [3]. For quite a long period supercritical CO_2 could not be employed for metal ion extraction as direct extraction of metal ions by supercritical CO_2 is highly inefficient owing to charge neutralization requirement and the weak solute–solvent interactions. However, Laintz *et al.* [4] reported the SFE of metal ion, Cu^{2+}, in 1992 by complexing with suitable complexing agents which opened a new realm in the field of SFE of metal ions. Since supercritical CO_2 behaves like solvent, in the present study

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complexing agents have been referred to as co-solvent. In 1993, Lin *et al.* [5] was successful in performing SFE of lanthanides and uranyl ion from solid materials by supercritical CO_2 containing a fluorinated β-diketone. The very next year they reported the SFE of thorium and uranium from solid and liquid materials with fluorinated β-diketones and tributyl phosphate [6]. In 1995, Lin *et al.* [7] carried out SFE of uranium and thorium from nitric acid solution with organophosphorus reagents. These studies opened a gateway for application of SFE in nuclear industry. Kumar *et al.* [8, 9] have carried out SFE of uranium from tissue paper matrix.

Extraction efficiency is significantly affected by pressure, temperature conditions. In order to achieve high extraction efficiency by means of tuning parameters, in depth understanding of effect of various parameters on extraction efficiency is of utmost importance and becomes useful in developing models for extraction processes. Few studies on effect of parameters have been reported in literature by Meguro *et al.* [10–12]. Meguro *et al.* have made attempts to decipher the extraction process by studying the effects of pressure and temperature on distribution ratio of uranium under equilibrium condition. Under equilibrium condition, a substance gets distributed between aqueous phase and supercritical fluid phase. Supercritical fluid phase is not renewed under equilibrium condition. Hence, equilibrium study provides only partial insight about the SFE process. Under extraction conditions, the supercritical phase is continuously renewed by flowing SCF. The SFE process is combined effect of equilibrium processes and extraction kinetics. The present study was taken up in view of examination of the effects of various parameters on extraction efficiency and optimization of the parameters. Extraction efficiency is a complicated function of various parameters *viz.* extraction pressure, extraction temperature, CO_2 flow rate, percentage of co-solvent, molarity of acid medium, extraction time, mode of chelation (online/*in situ*), mode of extraction (static/dynamic). TBP was chosen as co-solvent in the present study in view of its wide application in the conventional solvent extraction process *viz.* PUREX. In PUREX process nitric acid is employed for dissolution of fuel, hence chosen for the present study. CO_2 was selected as supercritical fluid owing to its moderate critical constants [13] (critical pressure = 72.9 atm, critical temperature = 304.3 K, critical density = 0.47 g/mL) and other attractive properties such as being easily recyclable, non-toxic, chemically and radio-chemically stable and less expensive.

2. Experimental

2.1 Chemicals

CO_2 gas employed for preparing supercritical fluid was of 99.9% purity. Uranium standard solution was prepared by dissolving high purity U_3O_8 powder in 4 M nitric acid. TBP used as co-solvent was of Merck grade (for extraction analysis). Aldrich grade arsenazo III was used for color development in the spectrophotometric uranium determination. Sulphamic acid was of Merck grade (99%), AR grade nitric acid and ammonium sulphate were employed.

2.2 Apparatus

The supercritical fluid extraction set-up mainly consists of CO_2 delivery pump, modifier pump, thermostat, back-pressure regulator and collection vessel [14]. CO_2 gas from cylinder was fed into the CO_2 delivery pump where it was liquefied to 263 K. The pump supplied liquid CO_2 at desired flow rates. The modifier pump provided the desired co-solvent flow rate. The CO_2 and co-solvent flow rates could be varied from 0.001 to 10 mL/min with a precision of 0.001 mL/min. The CO_2 and co-solvent streams were merged into a single stream by a T-joint to produce mixture of CO_2 containing the desired percentage of co-solvent. The stream was then allowed to pass through a 5-m long spiral coil for thorough mixing of CO_2 and co-solvent. High level of homogeneity was achieved by passing the stream through a 10 mL capacity cylindrical vessel containing spherical teflon pebbles. The stream then entered a six-port valve, which had provision for selecting/bypassing the extraction vessel. Spiral coil and mixing vessel are contained in the thermostat. The stainless steel extraction vessel (10 mL) were cylindrical in shape. Extraction vessel consists of inlet and outlet at the top. The inlet stainless steel tube (0.5 mm inner diameter), passing through center of extraction vessel from top, extended up to bottom for purging supercritical CO_2 through the sample solution. Back-pressure regulator controlled the pressure of the extraction vessel by means of opening/closing of variable stroke needle valve. Pressure could be varied from atmospheric pressure up to 500 atm with a precision of ± 1 atm. The temperature of thermostat could be varied from room temperature up to 353 K with a precision of ± 0.1 K. The extract coming out from the outlet of extraction vessel was collected in a collection tube at atmospheric pressure where CO_2 escaped as gas. Each unit of the set-up can be independently controlled by its inbuilt microprocessor. Additionally, provision exists for controlling all units collectively (except back-pressure regulator) through computer. All the parameters could be set, controlled and monitored by a software programme which can also control CO_2 delivery pump rate, modifier pump rate and temperature of the thermostat.

2.3 Supercritical fluid extraction procedure

Uranium solution in acidic medium, of known concentration was taken in the extraction vessel and loaded in the thermostat by fitting the inlet and outlet tubes. The desired temperature was allowed to be reached in the thermostat. Liquid CO_2 and co-solvent were pumped at desired flow rates which, after getting thoroughly mixed in the spiral coil and mixing vessel, entered the extraction vessel as supercritical fluid. The flow was continued until desired pressure in the extraction vessel achieved. The extraction vessel pressure was maintained by back-pressure regulator. SFE was performed by continuously flowing supercritical fluid and collecting the extract in collection tube kept at atmospheric pressure where CO_2 escaped as gas. CO_2 flow rates and modifier flow rates were increased, in steps of less than 0.5 mL/min as sudden pressurization/depressurization might damage the system. After extraction, system was depressurized gradually to atmospheric pressure and extraction vessel was unloaded. While loading/unloading, the extraction vessel was bypassed by means of the six-port valve.

2.4 Determination of uranium

Uranium amount in a sample was determined spectrophotometrically employing arsenazo III metal indicator [15]. Required volumes of uranium solution were aliquotted in a flask followed by the addition of 1 mL of 1 M sulphamic acid and 1 mL of arsenazo III (1 mg/mL). The volume was then made up to 10 mL using 4 M HNO_3. Uranium concentration was calculated from calibration graph between uranium amount (in μg/mL) *versus* absorbance at 655 nm. Uranium concentration was varied from 1–10 μg/mL. The uranium extraction efficiency was defined as the percentage ratio of the uranium amount collected to initial uranium amount taken the extraction vessel.

2.5 Back-extraction of uranium into aqueous phase

Uranium-TBP complex emerging from extraction vessel was collected in collection tube containing chloroform. For carrying out spectrophotometric determination, uranium was back-extracted into aqueous phase by employing 10% ammonium sulphate solution. Back-extraction efficiency was obtained by determining the uranium amount left unextracted in extraction vessel and uranium amount present in aqueous phase. Back-extraction efficiency was defined by Eq. (1).

$$\text{Back-extraction efficiency} = \frac{U_{\text{aq}}}{(U_{\text{init}} - U_{\text{unext}})} \times 100\,, \qquad (1)$$

where U_{init} and U_{unext} are the uranium amounts taken for extraction and left unextracted in the extraction vessel respectively. Whereas U_{aq} is the uranium amount back-extracted into the aqueous phase. Back-extraction was performed with $\sim 1:1$ volume ratio of organic and aqueous phase. In Table 1, back-extraction efficiency for three extractions is shown. While calculating uranium extraction efficiency, the back-extraction efficiency was taken into consideration.

3. Results and discussion

Supercritical fluid extraction can be compared to solvent extraction process. In solvent extraction metal-complex gets distributed between organic and aqueous phases. Extraction of solute is achieved by equilibrating the two immiscible phases, (organic and aqueous) and separating the organic phase. In SFE also metal-complex gets distributed between two phases *viz.* aqueous and supercritical CO_2 phase. However, extraction process in SFE is quite different to solvent extraction as extraction is achieved by flowing supercritical CO_2 through the extraction vessel for certain time period and collecting the extract in a collection vessel at atmospheric pressure allowing the CO_2 to escape as gas. Since extraction efficiency is governed by distribution ratio, factors enhancing distribution ratio would lead to higher extraction efficiency. However, one major difference between solvent extraction and supercritical fluid extraction is the density of supercritical fluid. In solvent extraction, fluid density does not vary much within operational temperature and pressure range, and apparently has insignificant effect on extraction efficiency. Whereas in SFE, SCF density plays a vital role as solvent strength is directly related to density. Moreover, SCF density is markedly affected by pressure and temperature conditions.

Table 1. Uranium back-extraction efficiency *versus* no. of extractions.

Total no. of extractions	Uranium back-extraction efficiency
1	$(62 \pm 3)\,\%$
2	$(72 \pm 3)\,\%$
3	$(85 \pm 3)\,\%$

Overtly in SFE, extraction efficiency depends on two basic factors: (i) distribution ratio of metal-complex and (ii) kinetics of transport of metal-complex into supercritical CO_2. The distribution ratio of meta-complex is determined under equilibrium conditions. Here at a certain pressure and temperature liquid phase and supercritical phase are thoroughly mixed by stirring (for ∼ 60 min) and aqueous phase is sampled at operational pressure and temperature so that equilibrium condition is not disturbed. In equilibrium study neither extract collection is performed nor SCF is purged through the solution. Whereas in SFE, SCF is continuously flown (purged) through solution and hence extraction efficiency is influenced by the kinetics of transport of metal-complex into supercritical CO_2.

3.1 Theoretical aspects of uranium SFE

A probable extraction scheme for uranium extraction from nitric acid medium into supercritical CO_2 is depicted in Fig. 1. Uranium extraction process into supercritical CO_2 involves many equilibria processes.

$$H^+ + NO_3^- + TBP \leftrightharpoons H(NO_3)\cdot TBP \qquad (2a)$$

$$UO_2^{2+} + 2NO_3^- + 2TBP \leftrightharpoons UO_2(NO_3)_2\cdot 2TBP \qquad (2b)$$

Meguro *et al.* [10] from equilibrium study found that the uranium is extracted as $UO_2(NO_3)_2\cdot 2(TBP)$ into supercritical CO_2 phase. They proposed uranium extraction mechanism for overall extraction reaction which is very similar

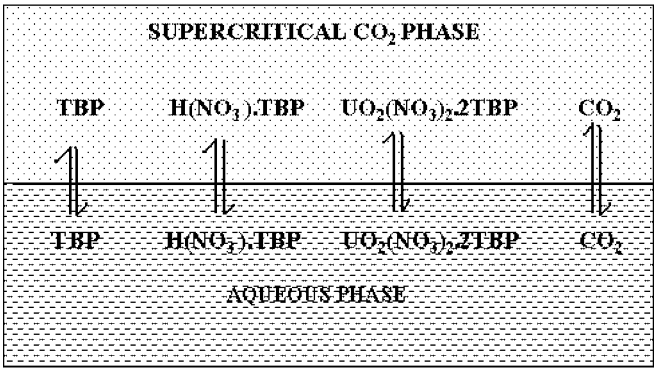

Fig. 1. Extraction scheme of UO_2^{2+} from nitric acid into supercritical CO_2 employing TBP as co-solvent.

to the conventional mechanism for uranium extraction from acidic medium by solvent extraction employing TBP asextractant. According to the proposed mechanism the extraction reaction involves at least three elemental processes: (i) distribution of TBP between aqueous and supercritical CO_2 phases (ii) formation of complex $UO_2(NO_3)_2 \cdot 2(TBP)$ in the aqueous phase and (iii) distribution of the complex between aqueous and supercritical CO_2 phases. The overall extraction reaction could be expressed by the following formula

$$\begin{aligned}&{UO_2}^{2+}{}_{aq} + 2TBP_{SF} + 2{NO_3}^{-}{}_{aq} \overset{K_{ex}}{\leftrightarrows} \\ &\quad \{UO_2(NO_3)_2 \cdot 2(TBP)\}_{SF}\,, \end{aligned} \tag{3}$$

where, K_{ex} is extraction constant defined by following equation

$$K_{ex} = \frac{[UO_2(NO_3)_2 \cdot 2(TBP)]_{SF}}{[{UO_2}^{2+}]_{aq}\,[TBP]^2_{SF}\,[{NO_3}^{-}]^2_{aq}}\,. \tag{4}$$

The phase distribution constants of TBP, $K_{D,TBP}$ and U-TBP complex, $K_{D,U\text{-}TBP}$ are defined as

$$K_{D,TBP} = \frac{[TBP]_{SF}}{[TBP]_{aq}}\,, \tag{5}$$

$$K_{D,U\text{-}TBP} = \frac{[UO_2(NO_3) \cdot 2TBP]_{SF}}{[UO_2(NO_3) \cdot 2TBP]_{aq}} \tag{6}$$

and formation constant of U-TBP complex in the acid solution, $K_{f,U\text{-}TBP}$ is defined as

$$K_{f,U\text{-}TBP} = \frac{[UO_2(NO_3) \cdot 2TBP]_{aq}}{[{UO_2}^{2+}]_{aq}\,[NO_3]^2_{aq}[TBP]^2_{aq}}\,. \tag{7}$$

Eq. (4) could also be written as

$$\begin{aligned}&K_{ex} = \\ &\frac{[UO_2(NO_3) \cdot 2TBP]_{SF}[UO_2(NO_3) \cdot 2TBP]_{aq}[TBP]^2_{aq}}{[UO_2(NO_3) \cdot 2TBP]_{aq}[TBP]^2_{SF}[TBP]^2_{aq}\,[{UO_2}^{2+}]_{aq}\,[{NO_3}^{-}]^2_{aq}}\,. \end{aligned} \tag{8}$$

From (5)–(8), K_{ex} can be expressed as

$$K_{ex} = \frac{K_{D,U\text{-}TBP}K_{f,U\text{-}TBP}}{K_{D,TBP}}\,. \tag{9}$$

By taking log on both sides, K_{ex} could be expressed by following equation

$$\log K_{ex} = \log K_{D,U\text{-}TBP} - 2 \log K_{D,TBP} + \log K_{f,U\text{-}TBP}\,. \tag{10}$$

The distribution ratio D_U of uranium between aqueous and supercritical CO_2 phase is given by

$$D_U = \frac{[UO_2(NO_3)_2 \cdot 2(TBP)]_{SF}}{[{UO_2}^{2+}]_{aq}}\,. \tag{11}$$

Eqs. (8) and (11) could be combined so that D_U can be related to K_{ex}

$$D_U = K_{ex}[NO_3]^2_{aq}[TBP]^2_{aq}\,. \tag{12}$$

By taking log on both sides and substituting the values of K_{ex} from Eq. (10), we get

$$\begin{aligned}\log D_U &= \log K_{D,U\text{-}TBP} + \log K_{f,U\text{-}TBP} - 2 \log K_{D,TBP} \\ &\quad + 2 \log[NO_3]_{aq} + 2 \log[TBP]_{SF}\,. \end{aligned} \tag{13}$$

Extraction efficiency depends upon solvating power of supercritical CO_2. Several models have been proposed to predict and quantitatively explain solubility behavior of solutes in supercritical fluids. These models are based on Hildebrand solubility parameter or Peng–Robinson equation of state [16, 17]. These models require a prior knowledge of thermodynamic properties of the solute. Peng–Robinson equation of state could successfully predict the solubility of many solid samples. But this equation is a complicated one and difficult to apply.

However, Chrastil [18] has arrived at a simple empirical correlation which relates the solubility of a solute to the density of supercritical fluid

$$\ln S = k \ln \rho + C\,, \tag{14}$$

where S and ρ are the solubility of the solute and density of the supercritical fluid respectively. Here k corresponds to the number of CO_2 molecules solvating around the solute molecule and the constant C is a temperature-dependent term consisting of thermal properties such as the solvation heat, vaporization heat and/or the volatility of the solute. C is independent of fluid density. Hence, the knowledge of values of k and C enables one to predict the solubility of a solute. Eq. (14) predicts a linear relationship between $\ln S$ and $\ln \rho$ with slope k and intercept C.

This simple empirical correlation proposed by Chrastil was meant for organic compounds such as carboxylic acid, carboxylic esters *etc.* However, in a review Smart *et al.* [19] mentioned the validity of the above correlation for metal-complexes also.

The phase distribution constant, K_D of a substance (extractant, extracted complex) can be correlated to solvent property of supercritical CO_2. K_D of a substance can be expressed in terms of its solubilities by Eq. (15)

$$K_D = \frac{S_I}{S_{II}}\,, \tag{15}$$

where S_I and S_{II} are the solublities of a substance in solvent I and solvent II.

Eqs. (5) and (6) can be generalized on the basis of Eqs. (15) in (16).

$$\log K_{Dj} = \log(S_{j,SF}/S_{j,aq})\,, \tag{16}$$

which on expansion gives

$$\log K_{Dj} = \log S_{j,SF} - \log S_{j,aq}\,, \tag{17}$$

where j denote a particular substance.

On substituting the value of $\log S$ from Eq. (14) into Eq. (17), we get

$$\log K_{Dj} = k_j \log \rho + C_j - \log S_{j,aq}\,. \tag{18}$$

3.2 Effect of operating parameters

In order to investigate the effect of an operating parameter on extraction efficiency, particular parameter was varied while keeping all other parameters fixed. During the study, online complexation mode and dynamic extraction mode were adopted. The experimental conditions under which the effect of various parameters was investigated are shown in Table 2.

3.2.1 Effect of pressure

Effect of pressure on extraction efficiency was studied at 333 K by varying the pressure of the extraction vessel from 80–300 atm. The variation in uranium extraction efficiency with pressure is depicted graphically in Fig. 2. In the figure, the variation in SC CO_2 density with pressure at 333 K, as obtained from Peng–Robinson equation of state [10], is also shown. As is evident from the graph, the variation in uranium extraction efficiency with pressure is not a straightforward affair, pressure affects extraction efficiency in a very complicated manner. The graph displays initial steep rise in extraction efficiency with increasing pressure followed by a gradual decline. Density *versus* pressure graph also shows initial steep rise in SC CO_2 density and gradual increase afterwards with increasing pressure.

Meguro *et al.* [11] from equilibrium study observed a continuous decrease in uranium distribution ratio in the 100–400 atm pressure range. Whereas in the present SFE study the decreasing trend is observed in 150–300 atm range only and in the range of 100–150 atm steep rise in extraction efficiency was observed. In SFE, SC CO_2 was continuously purged through aqueous phase which shattered the aqueous phase into small droplets. The SFE can be visualized as small aqueous droplets immersed in flowing SC CO_2 stream thereby continuously renewing the supercritical phase. Hence, SFE can be considered as non-equilibrium process and is not expected to resemble uranium distribution ratio variation trend as observed by Meguro *et al.* However, eventually any non-equilibrium process progresses towards attaining equilibrium. In the present SFE study, equilibrium behavior is reflected only in 150–300 atm pressure range. In this range, the theory corresponding to equilibrium process can be adopted to explain the SFE behavior.

Table 2. Experimental conditions for parameter study of SFE of uranium.

Uranium concentration	500.8 µg/mL
Uranium solution in extraction vessel	5 mL
Molarity of uranium solution	4 M
Extraction time	30 min
Extraction mode	Dynamic
Complexation mode	Online
Collection liquid ($CHCl_3$)	3 mL
CO_2 flow rate	1 mL/min
TBP flow rate	0.1 mL/min

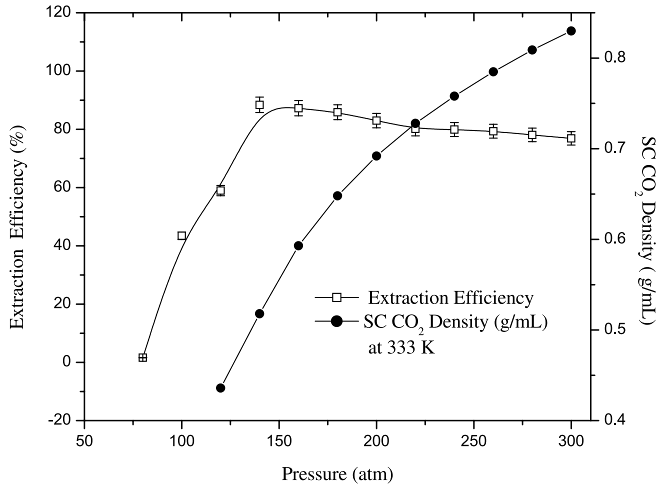

Fig. 2. Graph of pressure *versus* uranium extraction efficiency/SC CO_2 density, {CO_2 flow rate = 1 mL/min, TBP flow rate = 0.1 mL/min, temperature = 333 K, uranium amount = 2504 µg}, (error bar is ±3% of the value).

Substituting the values of phase distribution constants of TBP and U-TBP complex according to Eq. (18) into Eq. (13), the expression for uranium distribution ratio D_U becomes:

$$\begin{aligned}\log D_U = {} & k_{U\text{-}TBP}\log\rho + C_{U\text{-}TBP} - \log S_{U\text{-}TBP,aq} - 2k_{TBP}\log\rho \\ & - 2C_{TBP} + 2\log S_{TBP} + 2\log[NO_3{}^-]_{aq} \\ & + 2\log[TBP]_{SF}\,. \end{aligned} \qquad (19)$$

Eq. (19) can be rearranged to Eq. (20) so that D_U can be related to supercritical CO_2 density by Eq. (20):

$$\log D_U = (k_{U\text{-}TBP} - 2k_{TBP})\log\rho + A + B\,, \qquad (20)$$

where

$$\begin{aligned} A = {} & \log K_{f,U\text{-}TBP} + (C_{U\text{-}TBP} - 2C_{TBP}) \\ & - \log\left(S_{U\text{-}TBP,aq}/S^2_{TBP,aq}\right) \end{aligned} \qquad (21)$$

and

$$B = 2\log[NO_3{}^-]_{aq} + 2\log[TBP]_{SF}\,. \qquad (22)$$

A is a pressure-independent constant and B is a variable determined by the distribution equilibrium of HNO_3. Eq. (20) can be further simplified in the following form

$$\log D_U = \alpha\log\rho + \beta\,, \qquad (23)$$

where $\alpha = k_{U\text{-}TBP} - 2k_{TBP}$ and $\beta = A + B$.

Iso *et al.* [20] studied the pressure dependence on uranium distribution ratio under equilibrium condition and observed linear plots between $\log D_U$ and $\log\rho$. The plots had negative slopes (corresponding to $k_{U\text{-}TBP} - 2k_{TBP}$) implying decrease in D_U with increasing SC CO_2 density. Meguro *et al.* [11] determined the value of k_{TBP} to be 21.8 and that of $k_{U\text{-}TBP}$ to be 40.6 at 333 K. From these values of k_{TBP} and $k_{U\text{-}TBP}$, the α was calculated to be −3. Hence the decrease in extraction efficiency with increasing pressure at constant temperature is due to negative value of slope. For SFE in the pressure range (150–300 atm), the dependence of extraction efficiency on pressure could be fitted into a linear equation; $E = 98.785 - 0.075P$, having correlation coefficient −0.9912. Where E and P represent extraction efficiency and pressure respectively.

In the pressure range of 80–150 atm, the graph resembles SC CO_2 density *versus* pressure graph. The SFE process can be visualized as two step process. First step involves formation of U-TBP complex at the aqueous-supercritical CO_2 interface. Second step consists of dissolution of the U-TBP complex in the SC CO_2 phase.

The dissolved U-TBP complex is immediately carried away by flowing SC CO_2. Thus, a non-equilibrium steady state is established. Uranium is brought to the aqueous–supercritical CO_2 interface at certain rate by a diffusion controlled process. As shown in Fig. 2. higher the pressure higher will be SC CO_2 density. Pressure in extraction vessel was achieved by feeding SCF mixture by pumping liquid CO_2 and TBP while keeping fixed ratio of flow rates. After achieving the desired pressure, extraction was carried out by flowing SCF mixture for fixed time. Hence, during extraction same amount of CO_2 and TBP were flown through the extraction vessel independent of pressure. However, to achieve higher pressure, SCF mixture needs to be fed for larger time period resulting in higher amount of SC CO_2 as well as TBP in the supercritical phase.

As per Eq. (3), according to Le Chatelier's principle a greater amount of TBP in the SC CO_2 phase will result in higher U-TBP complex formation. Similarly, Le Chatelier's principle can be applied for predicting dissolution of U-TBP complex in the SC CO_2, more is the CO_2 (*i.e.* higher SC CO_2 density) higher will be the dissolution of U-TBP in supercritical phase, consequently higher will the extraction efficiency. In addition, solubility data for TBP and U-TBP complex indicate enhanced solvent strength with increasing pressure. Solubility is an indication of solvent strength. Meguro *et al.* [12] observed increase in TBP solubility with rising pressure. At a temperature of 333 K, TBP solubilities were 0.00064, 0.42, 0.71, 1.1 mol/L at pressures of 85, 100, 120,150 atm respectively. Similarly, increase in the solubility of $UO_2(NO_3)\cdot 2TBP$ was observed by Addleman *et al.* [21] at 323 K in the pressure range of 85–160 atm determined by on-line laser induced fluorescence. These studies indicate that solvent strength abates at lower SC CO_2 density. Obviously, dissolution process will be favored by enhanced solvent strength.

Hence in range of 80–150 atm, extraction efficiency resembles the SC CO_2 density *versus* pressure graph. The extraction efficiency (E) dependence on pressure (P) could be fitted into linear relationship $E = -103.618 + 1.379P$ having correlation coefficient 0.9846.

Moreover, extraction kinetics model (Sect. 3.2.6) proposed by Clifford *et al.* [22] predicts increase in uranium diffusion rates with increasing SC CO_2 density. Study by Clifford *et al.* found that diffusion is slow in case of high partition (high D_U), whereas poor partition (low D_U) is associated with rapid diffusion. As per study by Meguro *et al.* [11] at lower pressure D_U is high, implying slower diffusion *i.e.* U-TBP complex is transported to the surface of aqueous phase at slow rate resulting in lower extraction efficiency. As the pressure increases, D_U decreases causing higher diffusion rate leading to further increase in extraction efficiency. Hence, both solubility and extraction kinetics favor higher extraction efficiency. It appears that around 150 atm non-equilibrium process attains the equilibrium. Hence, present study shows that SFE process is combination of many factors which affect the extraction process in a very complicated manner. One has to carefully select and optimize these factors while designing the extraction process. The pressure was optimized at 150 atm.

3.2.2 Effect of extraction temperature

The effect of extraction temperature was evaluated by performing SFE at 150 atm pressure and varying the extraction temperature from 308 to 353 K. The variation in extraction efficiency with temperature is depicted graphically in Fig. 3. along with SC CO_2 density *versus* temperature plot. The graph displays linear decrease in SC CO_2 density with rising temperature. Decrease in density should cause lowering in extraction efficiency. However, observed trend is not in accordance with the expected trend. The extraction efficiency increases in the temperature range of 308–333 K followed by steep fall in the region of 333–353 K. According to Eq. (23) the uranium distribution ratio is influenced by two terms *i.e.* density of SC CO_2 (ρ) and term β. The temperature can affect uranium distribution ratio in Eq. (23) in two ways: (i) influencing SC CO_2 density; the increase in temperature lowers SC CO_2 density (ii) influencing term β by affecting volatility of the U-TBP complex. The volatility of U-TBP complex increases with temperature. Thus, temperature affects the density and volatility factors in opposite manner. On one hand, rising temperature tends to lower the extraction efficiency by decreasing SC CO_2 density. On the other hand, rising temperature tends to enhance the extraction efficiency by increasing volatility. The observed trend in the 308–333 K region indicates that volatility of U-TBP complex increases so sharply that it compensates the effect of decrease in density. While considering the temperature dependence of extraction efficiency, interestingly it is worth considering the increase in k value (No. of CO_2 molecules solvating U-TBP complex) with temperature reported by Meguro *et al.* [11]. They determined the value of k to be 10.4 and 40.6 at 323 and 333 K respectively. The higher k values imply higher heat of solvation and consequently enhanced solubility of U-TBP complex.

In Fig. 3 extraction efficiency falls sharply in the 333–353 K temperature range. Decrease in extraction efficiency indicates that the volatility of the U-TBP complex has reached its maximum value around 333 K and afterwards decrease in density is the dominating factor. The decrease in

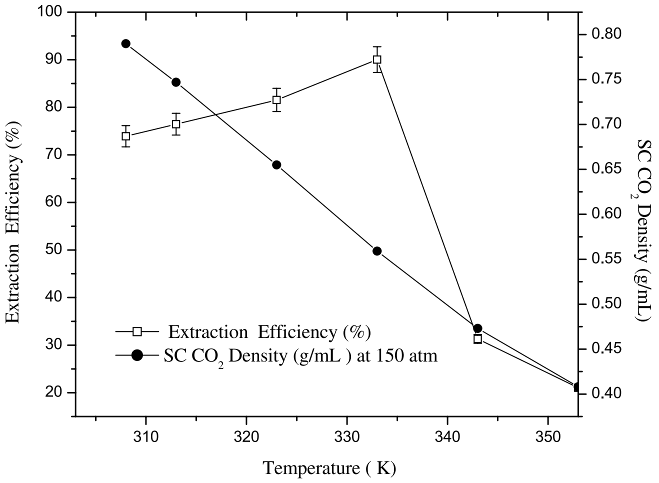

Fig. 3. Graph of temperature *versus* uranium extraction efficiency/SC CO_2 density, {CO_2 flow rate = 1 mL/min, TBP flow rate = 0.1 mL/min, pressure = 150 atm, U amount = 2504 µg}, (error bar is ±3% of the value).

extraction efficiency is very steep and the density decrease factor does not suffice. This steep decrease could probably be attributed to the peculiar behavior of supercritical fluids near the critical point. Solubility behavior is related to thermodynamic properties such as partial molar volume and partial molar enthalpy. These properties diverge near critical point. The divergence is related to isothermal compressibility $K_T = (1/\rho)(\partial\rho/\partial P)_T$. The isothermal compressibility diverges near critical point. As K_T is proportional to the mean squared density fluctuations [23]. K_T is proportional to $\int r^2|g(r)-1|\,\mathrm{d}r$. The pair correlation function $g(r)$ is the ratio of local to bulk density at a distance r away from a molecule. Therefore divergence of K_T is consequence of $g(r)$, a finite quantity becoming long ranged. The quantity ξ called correlation length is a measure of the range of density fluctuations. Near critical point, ξ is abnormally large. For CO_2, $\xi = 55$ at 1 K above T_c and $\xi = 13$ at 10 K above T_c. The average intermolecular distance at critical density is 5.4 Å. Large size cluster formation is peculiar feature of density near critical point. The densities at 343 and 353 K are 0.47 g/mL and 0.41 g/mL respectively, which are very close to critical density of CO_2 *i.e.* 0.47 g/mL. It is expected that at elevated temperature and pressure conditions whenever density approaches that of density near critical point, similar large size cluster formation should occur. Free energy of solvation $\Delta G = \Delta H - T\Delta S$. In solvation process, solute molecule is surrounded by cluster of solvent molecules. In large cluster, the solvation process provides enthalpy gain for solubility enhancement whereas entropy loss due to gathering of solvent molecules disfavor solubility. For large clusters, the entropy loss are very high and net effect is decrease in solubility. The temperature was optimized at 333 K.

Pressure and temperature influence the extraction efficiency by affecting the SC CO_2 density. Hence it is more appropriate to view the variation in extraction efficiency with change in SC CO_2 density. Graph of extraction efficiency *versus* SC CO_2 density under pressure/temperature variation conditions is shown in Fig. 4. The plots exhibit almost similar behavior. It is interesting to note that there is an optimum density (~ 0.58 g/mL) at which maximum extraction efficiency is obtained in both the cases. Beyond this both the plots show a gradual decrease. However, at densities below 0.58 g/mL the extraction efficiencies are significantly different. The temperature has a more profound effect than the pressure. The entropy effects and the larger cluster formation at higher temperatures when the density of the supercritical fluid is very near to that of critical density are more pronounced than when pressure is varied. Thus different physical parameters may be responsible for this difference in the extraction behavior.

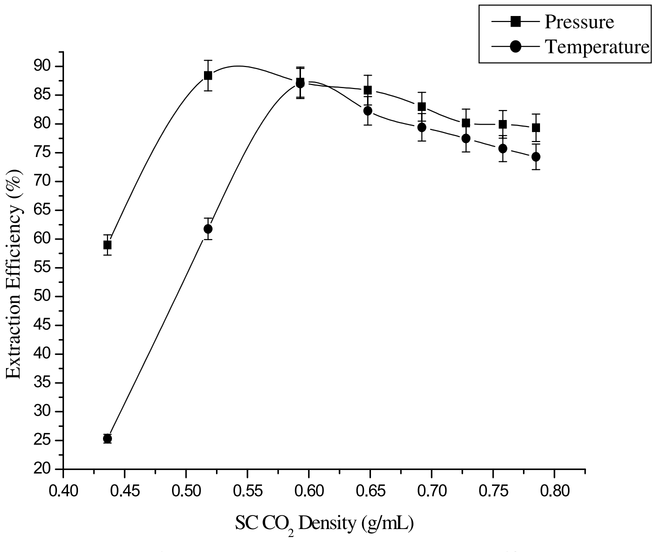

Fig. 4. Graphs of SC CO_2 density *versus* extraction efficiency at various pressure and temperature (error bar is ±3% of the value).

3.2.3 Effect of CO_2 flow rate

Effect of CO_2 flow rate on extraction efficiency was studied for 30 min. dynamic extraction by keeping pressure fixed at 150 atm, temperature at 333 K and varying the flow rate from 0.5 to 3 mL/min. The graph (Fig. 5a) of CO_2 flow rate *versus* extraction efficiency indicates that extraction efficiency increases up to flow rate of 1 mL/min and nearly attains saturation afterwards. As per the model proposed by Clifford *et al.* [23] the over all extraction process consists of partitioning of uranium between aqueous and supercritical CO_2 phase and uranium is brought to the aqueous surface by diffusion process. The model assumes that equilibrium between aqueous and supercritical CO_2 phase is rapidly established whereas diffusion in aqueous phase is a slow process. The extraction process can be visualized as spheres of aqueous phase immersed in flowing supercritical CO_2 phase.

The U-TBP complex from the aqueous phase is carried by flowing supercritical CO_2 into collection vessel. Initial part of the graph (Fig. 5a) indicates that lower flow rates are insufficient in carrying the U-TBP complex into collection vessel. Flow rate of 1 mL/min and above could successfully transport U-TBP complex into the collection vessel, and enhanced flow rates have no significant gain on extraction efficiency. This is due to the fact that at flow rates higher than 1 mL/min extraction process is limited by diffusion rate. Supercritical CO_2 flow rate was optimized at 1 mL/min for 10 ml extraction vessel containing 5 mL solution.

Extraction efficiencies were also compared for various CO_2 flow rates while constant volume of SC CO_2 and TBP was passed through the extraction vessel (Fig. 5b). For flow rate higher than 1 mL/min, the extraction efficiency is nearly constant. At flow rate lesser than 1 mL/min efficiency was low, again indicating lower flow rates are insufficient in carrying the U-TBP complex into collection vessel.

3.2.4 Effect of co-solvent percentage (TBP)

Effect of TBP percentage on extraction efficiency was studied for 30 min dynamic extraction by keeping pressure fixed at 150 atm, temperature at 333 K and CO_2 flow rate at 1 mL/min. The TBP percentage was varied up to 10%. Uranium extraction proceeds according to Eq. (3). Therefore, as per Le Chatelier rule higher amount of TBP in SC CO_2 should result in increase in U-TBP complex in SC CO_2 phase leading to higher extraction efficiency. As shown in Fig. 6, the observed trend is in accordance with the predicted trend. The graph between uranium extraction efficiency *versus* TBP percentage is a straight line having correlation coefficient 0.9829. TBP has a $P_c = 20.08$ atm

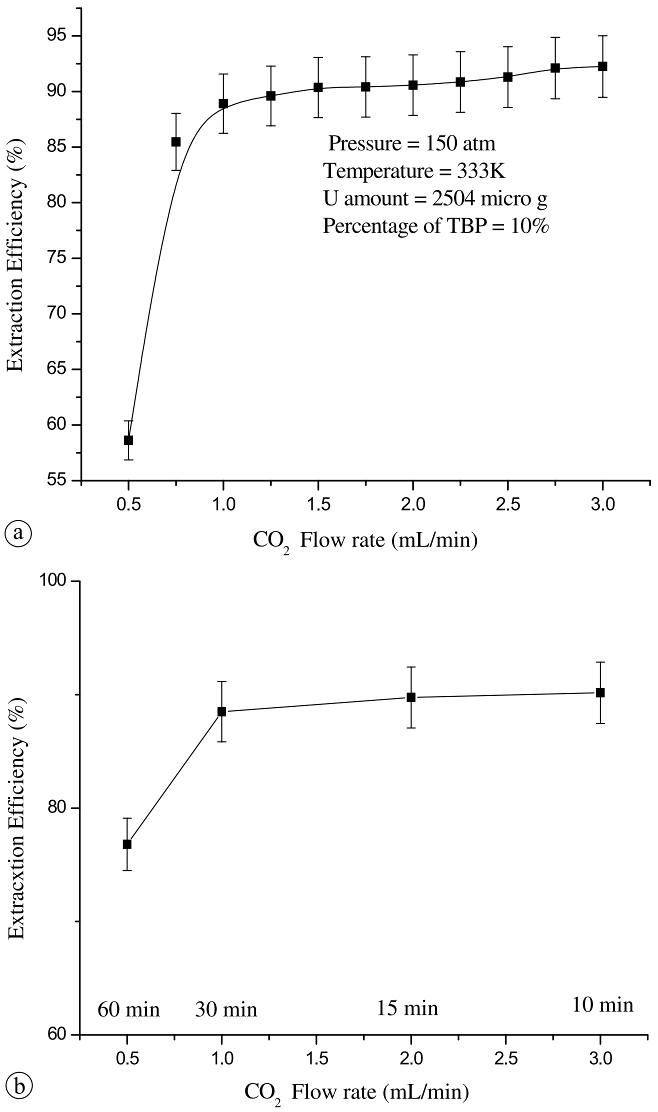

Fig. 5. (**a**) Graph of CO_2 flow rate *versus* uranium extraction efficiency (error bar is ±3% of the value). (**b**) Graph of CO_2 flow rate *versus* extraction efficiency for constant total volume of CO_2 and TBP ($CO_2 = 30$ mL and TBP $= 3$ mL) (error bar is ±3% of the value).

and $T_c = 817$ K. Further enhancement in TBP percentage was avoided in view of the resultant large deviation from the critical parameters of CO_2, which was not desirable. Therefore, the percentage of TBP was fixed at 10% for further studies.

3.2.5 Effect of molarity of nitric acid

The effect of molarity of nitric acid on extraction was investigated under optimized conditions of pressure, temperature, CO_2 flow rate and % of co-solvent. The observed trend is depicted in Fig. 7. Extraction efficiency increases with molarity of nitric acid up to 7 M and slight decrease is observed afterwards. For solvent extraction, the uranium partition coefficient values for 19% v/v TBP in kerosene [24] were converted into extraction efficiency and plotted w.r.t. molarity of nitric acid for comparison. The effect of molarity of nitric acid on extraction is similar to that observed in solvent extraction. Both the graphs merge at ~ 6.3 M and afterwards almost same trend of slight decrease was observed.

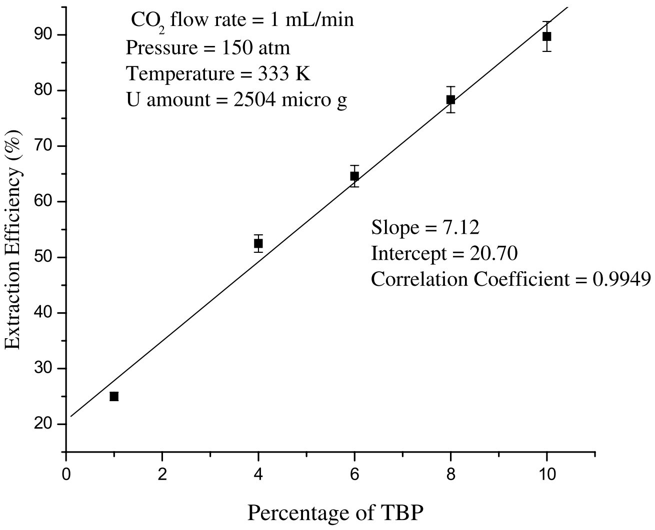

Fig. 6. Graph of TBP percentage *versus* uranium extraction efficiency (error bar is ±3% of the value).

From Eqs. (3) and (20), as per Le Chatelier rule increase in NO_3^- concentration in aqueous phase should increase the concentration of $UO_2(NO_3)_2 \cdot 2(TBP)$ complex in the supercritical fluid phase, resulting in higher uranium distribution ratio and subsequently higher extraction efficiency. The observed trend is as per predicted trend up to 7 M nitric acid. Under equilibrium condition Meguro *et al.* [11] found that $\log D_U$ linearly increases with $\log[HNO_3]_{aq}$ having slope of 2 which is in complete agreement with Eq. (14). However, their study was carried out in the 0.5–3 M HNO_3 range.

The probable explanation for decrease in extraction efficiency after 7 M nitric acid can be attributed to co-extraction of HNO_3 into supercritical CO_2 phase similar to solvent extraction process. In fact, molecular dynamics study on dissolution of nitric acid in supercritical CO_2 by TBP by Schurhammer *et al.* [25] revealed the presence of strong hydrogen bonding interactions of TBP with HNO_3. These interactions were found to be stronger than $TBP \cdots H_2O$, $H_2O \cdots H_2O$, $HNO_3 \cdots HNO_3$ interactions. They

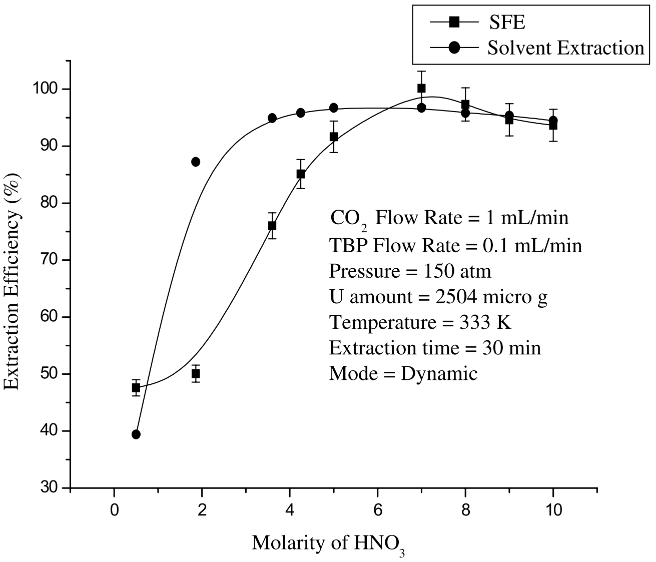

Fig. 7. Graph of molarity of nitric acid *versus* uranium extraction efficiency (error bar is ±3% of the value).

found that in absence of TBP no acid was dissolved in supercritical CO_2. According to study the species dissolved in supercritical CO_2 phase were $TBP(HNO_3)x$, $TBP(H_2O)$, $TBP(HNO_3)(H_2O)x$; where $x = 1$ or 2.

Under equilibrium conditions Meguro *et al.* [11] found that nitric acid gets extracted into supercritical CO_2 phase. They proposed that the extraction proceeds *via* Eq. (24)

$$H^+ + NO_3{}^- + TBP_{SF} \leftrightarrows (HNO_3) \cdot (TBP)_{SF} . \tag{24}$$

On the basis of above equation they arrived at Eq. (25) relating $NO_3{}^-$ concentration to distribution ratio D_H of HNO_3 and initial concentration of HNO_3 (C_{HNO_3})

$$[NO_3{}^-] = \frac{1}{D_H + 1} C_{HNO_3} , \tag{25}$$

$$[TBP]_{SF} = C_{TBP} - \frac{D_H}{D_H + 1} C_{HNO_3} . \tag{26}$$

They determined D_H to be 0.044 ± 0.005. The D_H was found to be independent of pressure and temperature. Hence, Eq. (19) can be written as

$$[NO_3{}^-] = 0.958 C_{HNO_3} , \tag{27}$$

$$[TBP]_{SF} = C_{TBP} - 0.042 C_{HNO_3} . \tag{28}$$

Extraction of nitric acid is a competing reaction for SFE of uranium. As per Eq. (26) higher the molarity of nitric acid, higher the nitric acid extracted into supercritical CO_2 phase decreasing TBP concentration in supercritical CO_2 phase. As per Eq. (26) uranium distribution ratio will be lowered.

3.2.6 Variation of uranium extraction efficiency with extraction time

The effect of extraction time on extraction efficiency was investigated by carrying out SFE of uranium from the acid solution and collecting the extract after every 5 min up to 60 min. The observed trend is depicted graphically in Fig. 8, which is similar to the trend observed by Clifford *et al.* [22]. Equation, $y = 32.235 \ln x - 41.582$ (y = extraction efficiency, x = extraction time) has been found to fit into the graph having correlation coefficient 0.9943. As is evident from Fig. 9, up to 40 min the amount of uranium extracted in 5 min decreases sharply with time. Afterwards the decreases is sluggish indicating that initially the extraction is fast and slows down subsequently. This also indicates that uranium extraction is a diffusion controlled phenomenon. Diffusion rate is controlled by concentration gradient which decreases with the progress of extraction.

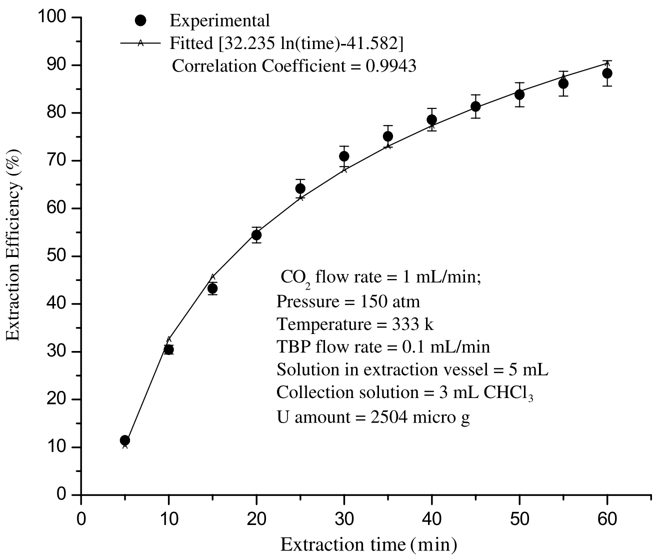

Fig. 8. Variation in extraction efficiency with time (error bar is ±3% of the value).

The graph between logarithm of uranium fraction unextracted and initial uranium amount shows linear decrease with extraction time having correlation coefficient of −0.9948 (Fig. 10). During the SFE, geometry of the liquid system changes in complex and chaotic way. For sake of simplicity in Clifford's extraction model, an approximation has been assumed that aqueous solution is present in the system as spheres of uniform size immersed in flowing SC CO_2. The uranium is transported to aqueous–supercritical fluid interface by diffusion process. The uranium amount in the solution at particular time was obtained by solving the dif-

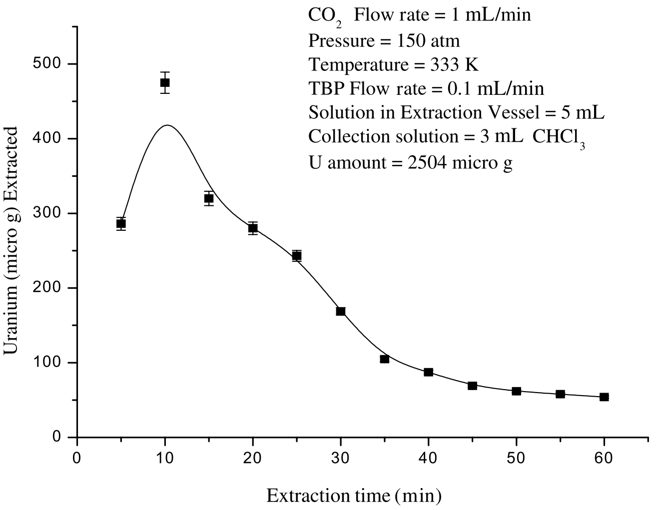

Fig. 9. Uranium (μg) extracted in 5 min interval at different time (error bar is ±3% of the value).

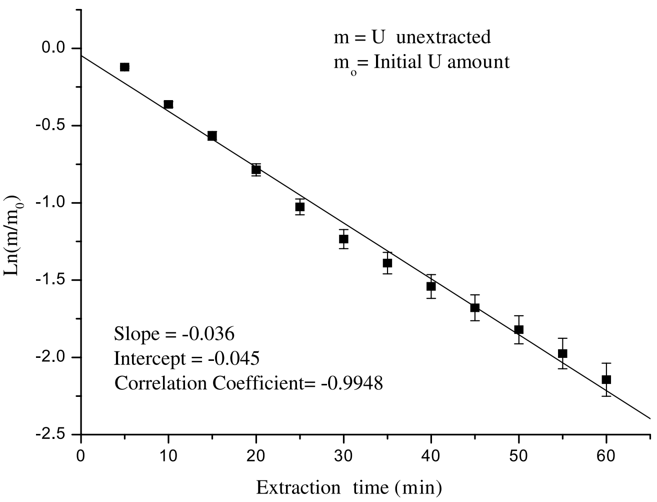

Fig. 10. Graph of extraction time *versus* logarithm of fraction of uranium unextracted (error bar is ±3% of the value).

fusion equation (Fick's second law) within sphere, subject to boundary condition at its surface determined by partition, obtained from Fick's first law. Concentration gradient is initially high, but abates with time. The observed trend in present study is in accordance with the model's prediction.

3.3 Comparison study of modes of extraction

SFE could be carried out in two modes *viz.* static and dynamic. In static mode, pressure and temperature of the extraction vessel was kept constant for 20 min followed by 20 min of extraction under same conditions of pressure and temperature. In dynamic mode, extraction was carried out at a particular pressure and temperature for 30 min. The uranium amount extracted as well as uranium amount unextracted was determined. To know the mass balance, extracted and unextracted amounts were added up. The results are shown in Table 3. In both modes, mass balance of $\sim 100\%$ could be obtained. It is evident from Table 3, 30 min dynamic extraction was equivalent to 40 min extraction in static mode.

3.4 Comparison study of modes of complexation

For SFE of uranium from nitric acid solution, the metal complexation could be performed *via* two modes *viz.* online and *in situ* complexation mode. In online complexation mode, CO_2 and TBP were pumped at desired flow rates into extraction vessel containing uranium solution. In the *in situ* complexation mode, the TBP was directly added to the extraction vessel containing uranium solution. The system was allowed to withstand the pressure and temperature conditions for 20 min followed by 20 min collection. With 1 mL of TBP, 63% uranium extraction efficiency was obtained which further got lowered with 2 and 3 mL of TBP (Table 4). Hence, for uranium extraction from acidic solution with TBP as co-solvent, the online complexation mode is preferable.

3.5 Reproducibility and mass balance study

Reproducibility study of uranium SFE was performed on a set of 5 samples under identical conditions. SFE was carried out under optimized conditions (Table 5) in the online complexation mode for 30 min of dynamic extraction. The amount of uranium left in the extraction vessel was also determined to study the mass balance. The mass balance calculations yielded results acceptable in the range of experimental error (100 ± 1) % giving full credence to the extraction process. From the reproducibility study (Table 6) the uranium extraction efficiency was found to be (98 ± 2) %. Also extraction efficiency could be determined from the knowledge of uranium amount left unextracted in the extraction vessel, defined as

$$\text{Extraction efficiency} = \left(1 - \frac{\text{U amount unextracted}}{\text{U amount taken}}\right) \times 100\,. \tag{29}$$

The extraction efficiency calculated from unextracted uranium was found to be (97 ± 1) %. The extraction efficiencies obtained by both modes *i.e.* by determining uranium back extracted into aqueous phase and uranium left unextracted in extraction vessel are in excellent agreement.

4. Conclusions

In the present study effects of various parameters on SFE of uranium from nitric acid employing TBP as co-solvent have been examined. The parameters influencing SFE were identified as pressure, temperature, molarity of acid, CO_2 flow rate, percentage of TBP, mode of complexation (online/*in situ*), mode of extraction (dynamic/static) and extraction time. This study of interdependence of various parameters provides us an insight for understanding the SFE process which indeed is very helpful in selecting pressure, temperature and other conditions for higher extraction efficiency.

Table 3. Comparison of static and dynamic mode.

Mode	Uranium extracted (μg)	Extraction efficiency	Uranium unextracted (μg)	Extracted + unextracted (μg)	% mass balance
Dynamic	2385	95	95	2480	99
Static	2289	92	214	2503	100

(U amount taken = 2504 μg; molarity of nitric acid = 7 M; CO_2 flow rate = 1 mL/min; TBP flow rate = 0.1 mL/min; temperature = 333 K; pressure = 150 atm; solution in extraction vessel = 5 mL).

Table 4. *In situ* SFE of uranium.

TBP taken (mL)	Uranium extracted (μg)	Extraction efficiency (%)
1	312	62
2	285	57
3	277	55

(U amount taken = 500.8 μg; CO_2 flow rate = 1 mL/min; pressure = 150 atm; temperature = 333 K; volume of uranium solution = 5 mL; molarity = 4 M).

Table 5. Optimsied parameters for uranium SFE.

Parameter	Optimised value
Pressure	150 atm
Temperature	333 K
CO_2 flow rate	1 mL/min
TBP flow rate	0.1 mL/min
HNO_3 molarity	7 M
Extraction time (online, dynamic)	30 min

Table 6. Reproducibility and mass balance study.

Sample No.	Uranium extracted (μg)	Uranium unextracted (μg)	Uranium ext + unext (μg)	% mass balance	Extraction efficiency direct	Extraction efficiency back ext.
1	2435	79	2513	101	97	98
2	2385	95	2480	99	96	96
3	2519	21	2540	101	99	101
4	2428	73	2501	100	97	97
5	2507	38	2545	102	98	100

[Extraction efficiency: direct = (97 ± 1) %; back extraction (98 ± 2) %; mass balance = (100 ± 1) %] (U amount taken = 2504 μg; molarity of nitric acid = 7 M; CO_2 flow rate = 1 mL/min; TBP flow rate = 0.1 mL/min; pressure = 150 atm; temperature = 333 K; solution in extraction vessel = 5 mL; mode = dynamic).

The study has enabled us to understand the extraction mechanism in SFE. The overall extraction process consists of many elementary processes resulting in the formation of $UO_2(NO_3)_2 \cdot 2TBP$ which is carried into SC CO_2 phase. Extraction efficiency is affected by distribution ratio of uranium (D_U), density of SC CO_2, diffusion rate and number of CO_2 molecules solvating TBP/U-TBP complex.

In the 150–300 atm pressure range, variation in extraction efficiency resembled to that of uranium distribution ratio variation under equilibrium conditions. Extraction efficiency was found to decrease gradually. The decrease in extraction efficiency was attributed to the term ($k_{\text{U-TBP}} - 2k_{\text{TBP}}$) which has a negative value. ($k_{\text{U-TBP}} - 2k_{\text{TBP}}$) is the slope of plot of $\log D_U$ *versus* $\log \rho$. Below 150 atm mismatch between uranium distribution ratio under equilibrium conditions and extraction efficiency was observed. Extraction efficiency variation resembled with SC CO_2 density variation with pressure. The behavior in this region could be attributed to non-equilibrium nature persisting in the extraction system. In the non-equilibrium region, SC CO_2 density increased with pressure which favored enhancement in solubility as well as extraction kinetics. The non-equilibrium process eventually progressed towards attaining equilibrium at 150 atm.

Temperature increase was found to affect the efficiency in two ways: (i) enhancement in volatility of solute (ii) decreasing SC CO_2 density. Up to 333 K, extraction efficiency increased linearly indicating the volatility increases to higher extent so that it not only compensates the solubility decrease due to SC CO_2 density decrease but results in overall increase in extraction efficiency. Steep fall in 333–353 K range most probably indicates a saturation in volatility, so that SC CO_2 density decrease governs the extraction process. Steep fall was attributed to the formation of large size cluster formation at densities approaching near critical point density. Molarity of nitric acid has been found to influence efficiency almost in similar fashion as in case of solvent extraction. The extraction efficiency increased up to 7 M nitric acid followed by slight decrease. This behavior was assigned to the fact that increase in molarity leads to the higher formation of U-TBP complex as well as higher co-extraction of HNO_3 *via* formation of $TBP \cdot HNO_3$ complex. CO_2 flow rate of 1 mL/min was found to be sufficient, no significant gain in extraction efficiency was observed at higher flow rates. Extraction efficiency was found to linearly increase with percentage of TBP.

The optimum parameters were 150 atm pressure, 333 K temperature, 1 mL/min CO_2 flow rate, 0.1 mL/min TBP flow rate (10% TBP), 7 M nitric acid and 30 min dynamic extraction time. Under optimized conditions in online complexation mode, nearly complete, (98 ± 2) % uranium extraction efficiency was achievable. A mass balance of (100 ± 1) % was observed giving full credence to the extraction process. 30 min dynamic extraction mode was found equivalent to 40 min static mode. Online complexation mode was more efficient than *in situ* mode.

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