

The Effect of Type and Concentration of Surfactant and Ligand on Uranium(VI) Cloud-Point Extraction (CPE) from Aqueous Solutions

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Abstract: In this article cloud-point extraction (CPE) was used with chelating agent to extract uranium from aqueous solutions. The methodology used is based on the formation of metal complexes soluble in a micellar phase of surfactant. The metal ions complexes are then extracted into the surfactant-rich phase at a temperature above the cloud-point temperature. The effect of type of surfactants and ligands on extraction efficiency at constant condition (pH =6, surfactant concentration of 0.5 % (w/v), chelating agent concentration of 1.5×10^{-3} M, incubation time of 20 min, equilibrium temperature of 50°C, centrifugation time of 10 min) were studied and the best surfactant and ligand was identified. Then optimum concentration of surfactant and ligand and also the other optimal conditions of extraction was determined. By using CPE method and obtained optimal conditions, determination of uranium in water samples with a detection limit of $0.15 \mu\text{g L}^{-1}$ was conducted.

Key words: cloud-point extraction, uranium, Triton X-114, Triton X-100, CTAB, 8-HQ, SDS, PAN, DBM, Br-PADAP

INTRODUCTIONS

Extraction of uranium in aqueous systems is often required for environmental control and geochemical prospecting (Jain, 2006; WHO, 1998; Sheppard, 2005; Kocher, 1989). Uranium has special significance among actinides as nuclear fuel for electricity production in power plants. They are known to cause acute toxicological effects for human and their compounds are potential occupational carcinogens. They are highly toxic which cause progressive or irreversible renal injury that in acute cases may lead to kidney failure and death. In view of the extensive usage of uranium for various industrial purposes and their toxicity, precise extraction and determination of this element in environmental and biological samples is a challenging task (IAEA-TECDOC-1296, 2002; Naftz, 2000; Merritt, 1971). Liquid-liquid extraction, ion exchange and solid phase extraction are commonly used methods (Rao, 2006). There is a trend to replace the solvent extraction procedure with ion exchange and solid phase extraction in order to minimize sample manipulation, analyte losses and use of toxic solvents. However, these methods are time-consuming and the tolerance of adsorbed matrix components is low. Thus alternative methods such as co-precipitation (Chou, 2000), nanofiltration (Favre-Reguillon, 2003) and micellar systems have been developed (Huddleston, 1999). Recent studies have shown the micellar system to be an appropriate substitute for organic solvents in extracting metallic ions from liquid samples of the environment. CPE consist of three simple steps: (1) solubilization of the analytes in the micellar aggregates; (2) clouding; (3) phase separation for analysis. When a surfactant solution is heated over a critical temperature, the solution easily separates into two distinct phases: one contains a surfactant at a concentration below, or equal to, a critical micelle concentration; the other is a surfactant-rich phase. The hydrophobic compounds initially present in the solution and bound to the micelles are extracted to the surfactant-rich phase (Corti, 1984; Komaromy-Hiller, 1996; Garcia-Pinto, 1995; Sirimanne, 1996; Eiguren-Fernández, 1998; Shariati, 2006; Tavakoli, 2008). Metal analysis by spectroanalytical techniques such as flame atomic absorption spectrometry (FAAS), graphite furnace atomic absorption spectrometry (GFAAS), inductively coupled plasma (ICP) optical emission spectrometry (OES), mass spectrometry (MS) and Liquid Scintillation spectrometry (LSS) is well established (Stalikas, 2002; Shemirani, 2005; Martnez, 2000; Pinto,

1996; Oliveros, 1998; Paleologos, 2000). Establishing a simple, quick, low cost, sensitive and selective analytical method to extract and determine pollutants such as uranium in environment is one of the most fundamental lines of research in this article.

2. Experimental:

2.1.Reagents and Materials:

All reagents used were of analytical grade, and all solutions were prepared in deionized doubly distilled water. A stock solution of U(VI) at a concentration of 1000 µg ml⁻¹ was prepared by dissolving the appropriate amounts of UO₂(NO₃)₂·6H₂O in water. Working solutions were obtained by appropriate dilution of the stock solution. The nonionic surfactant Triton X-114, Triton X-100, sodium dodecyl sulfate (SDS), cethyl tri methyl ammonium bromide (CTAB), 8 hydroxyquinoline (8HQ), 2-(5-bromo-2-pyridylazo)-5-(diethylamino)phenol (Br-PADAP), dibenzoylmethane (DMB) and 1-(2-pyridylazo)-2-naphthol (PAN) (obtained from aldrich company) were used without further purification. Buffer solution (0.1M) of pH 6.0 was prepared by dissolving the appropriate amount of sodium acetate (Merck) in water, adjusting pH with nitric acid (Merck).

2.2.Apparatus:

The determination of uranium was carried out by liquid scintillation counting(Perkin-Elmer, model 1220 Quantulus). A thermostated bath (fision-Germany, model D 3006) maintained at the desired temperature, was used for cloud point experiments. A centrifuge with 50 ml calibrated centrifuge tubes (Germany, sigma-2-k-15-c) equipped with an angle rotor (4-place, 5000 rpm) were used to accelerate the phase separation process. A Metrohm pH meter (model 744) with a combined glass electrode was used for pH measurements.

2.3. General Procedure:

50mL of working solution containing uranium 20 mg l⁻¹, an appropriate amount of ligand and surfactant were transferred into a centrifuge tube, and diluted to the mark with buffer solution at pH 6.0. After homogenization of the mixture the solution was left to stand in a thermostatic bath for 30 min at CPT (50 °C) to obtain phase separation of the micellar phase into a surfactant-rich phase and an aqueous solution depleted in surfactant. The phase separation was accelerated by centrifuging for 15 min at 5000 rpm. The upper aqueous phase (i.e., the surfactant-poor phase) was then removed and its U(VI) concentration was determined by liquid scintillation counting. The experimental procedure is illustrated in Fig.1. CPE of U(VI) from micellar solutions was evaluated in terms of extraction efficiency E

$$E = \frac{C_i V_i - C_f V_f}{C_i V_i} \times 100$$

where C_i is the initial concentration of metal ion in the micellar solution, C_f is the concentration of metal ion in aqueous phase after CPE, V_i is the volume of the micellar solution and V_f is the volume of aqueous phase after CPE.

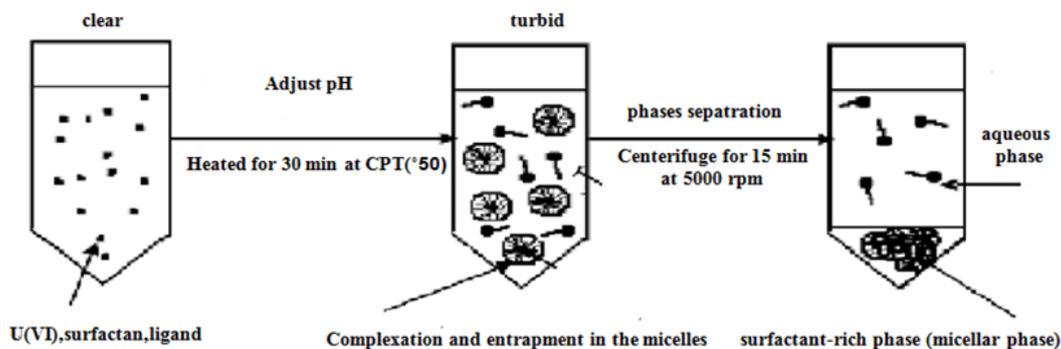


Fig. 1: The experimental procedure steps for implementation of cloud-point extraction

RESULTS AND DISCUSSION

3.1. Effect of Different Types of Surfactant and Their Mixture on Extraction Efficiency:

By investigating uranium (VI) cloud-point extraction efficiency for different types of available surfactant (Triton X-100, CTAB, SDS and Triton X-114) and their mixture, the most effective surfactant was selected for further experiments. Experiment was conducted at constant condition ($[U]=20 \text{ mg l}^{-1}$, $\text{pH}=6$, $[8\text{-HQ}]/[U(\text{VI})]=20$, surfactant concentration of 0.5 % (w/v)) and Triton X-114 was selected as the most effective surfactant. The results obtained are shown in figures 2 to 4 (Shahab Ahariati, 2008; Hadla Sousa Ferreira, 2006; Alain Favre-Re' guillon, 2006).

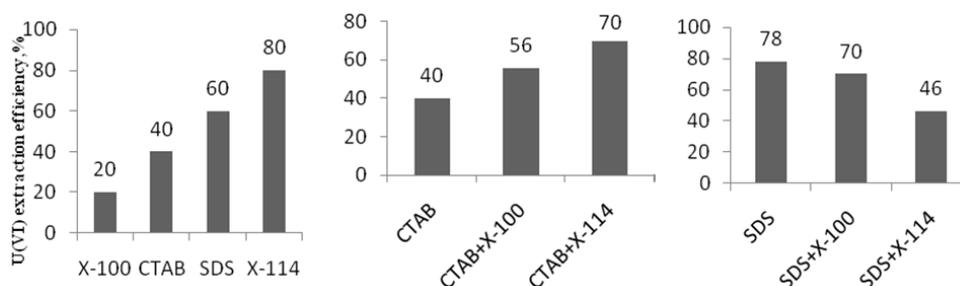


Fig. 2,3,4: Effect of different types of surfactant and their mixture on U(VI) extraction efficiency $[U]=20 \text{ mg l}^{-1}$, $\text{pH}=6$, $[8\text{-HQ}]/[U]=20$, $[\text{surfactants}]=0.5 \text{ \% (w/v)}$, $T_{\text{eq}} = 50^\circ\text{C}$, $t_{\text{eq}} = 20 \text{ min}$, $t_{\text{rot}} = 10 \text{ min}$, $\omega = 5000 \text{ rpm}$

3.2. Effect of Different Types of Ligand on Extraction Efficiency:

By investigating uranium(VI) cloud-point extraction efficiency for different types of available ligand (DBM, Br-PADAP, PAN and 8-HQ) the most effective ligand was selected for further experiments. Study was conducted at constant condition ($[U]=20 \text{ mg l}^{-1}$, $\text{pH}=6$, $[8\text{-HQ}]/[U(\text{VI})]=20$, surfactant concentration of 0.5 % (w/v)) and 8-HQ was selected as the most effective ligand. The results obtained are shown in figure 5 (Shahab Ahariati, 2008; Hadla Sousa Ferreira, 2006; Alain Favre-Re' guillon, 2006).

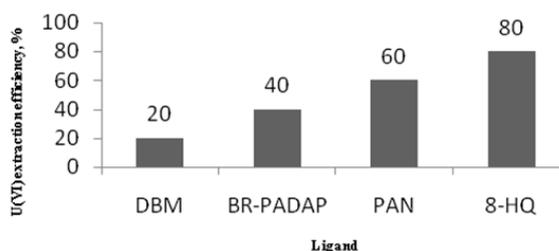


Fig. 5: Effect of different types of ligand on U(VI) extraction efficiency $[U]=20 \text{ mg l}^{-1}$, $\text{pH}=6$, $[\text{ligand}]/[U(\text{VI})]=20$, Triton X-114=0.5(w/v)%, $T_{\text{eq}}=50$, $t_{\text{eq}}=20 \text{ min}$, $t_{\text{rot}}=10 \text{ min}$, $\omega=5000 \text{ rpm}$

3.3. Effect of Triton X-114 Concentration:

Triton X-114 was chosen for the extraction due to reason mentioned (In part 3.1) and also its low cloud-point temperature (CPT) and high density of the surfactant-rich phase, this facilitates phase separation by centrifugation (Shahab Ahariati, 2008). A successful CPE should maximize the extraction efficiency by minimizing the phase volume ratio ($V_{\text{org}}/V_{\text{aqueous}}$), thus improving its concentration ability (Hadla Sousa Ferreira, 2006). The variation of extraction efficiency upon the surfactant concentration was examined within 50 mL of solution containing certain amount U(VI) in the presence of $[8\text{-HQ}]/[U(\text{VI})]=20$ and Triton X-114 range from 0% to 1.25% (w/v). The results are shown in Figure 6. Extraction rate of the analytes increased with the increase of Triton X-114 concentration from 0% to 0.25% (w/v). At lower concentrations of surfactant, the extraction efficiency was low, probably due to inadequacy of the assemblies to entrap the hydrophobic complex quantitatively. Further increase in the concentration of Triton X-114 (higher concentrations than 0.25% (w/v)) decrease extraction efficiency because of the increment in the volumes and the viscosity of the surfactant phase. So a concentration of 0.25% (w/v) was chosen as the optimum surfactant concentration in order to achieve the highest possible extraction efficiency and preconcentration factor (Dongsheng Zhao, 2009).

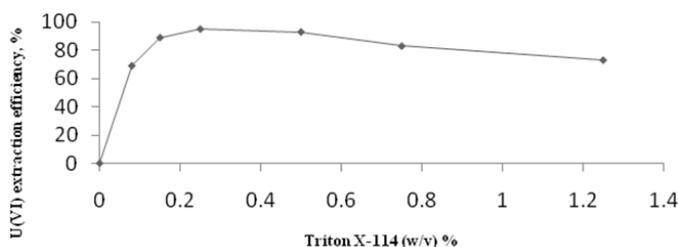


Fig. 6: U(VI) extraction efficiency (%) as a function of Triton X-114 concentration (weight %). [U]=20 mgL⁻¹, pH=6, [8-HQ] / [U]=20, T_{eq}=50, t_{eq}=30 min, t_{rot}=15 min, ω=5000rpm

3.4. Effect of 8-HQ Concentration:

Metal ion separation could be improved by the formation of hydrophobic complexes. Since Watanabe and Tanaka's pioneering work on nickel and zinc cation extraction, many chelating agents have been used to extract metal ions. The nature of the chelating agent and its concentration are important factors that should be considered. CPE efficiency depends on the hydrophobicity of the ligand and the formed complex, the apparent equilibrium constants in the micellar medium, the kinetics of the complex formation and the transference between the phases. In the present study, 8-hydroxyquinoline was used as a reagent due to reason mentioned (In part 3.2) that forms 1:2 complexes (metal:ligand) with target ions (Alain Favre-Re' guillon, 2006). The variation of the extractin efficiency as a function of the ligand concentration was evaluated for uranium complex formation during the CPE procedure. Figure7 . shows the variation of extraction efficiency over the 8-HQ concentration when 50 mL of solution containing certain amount U(VI) in the presence of 0.25% (w/v) Triton X-114 concentration , is subjected to the cloud point extraction. molar ratio of [8-HQ]/[U(VI)] was varied in the range of 0 to 50. The results revealed that at the molar ratio of 30 to 40, more extraction occurred. Therefore molar ratio 30 was selected as the optimal chelating agent concentration value. The decreasing extraction of uranium with the increasing 8-HQ concentration might be due to more hydrophilic metal-complexes formed when the 8-HQ concentration exceeds a certain value (Farshid Ahmadi,).

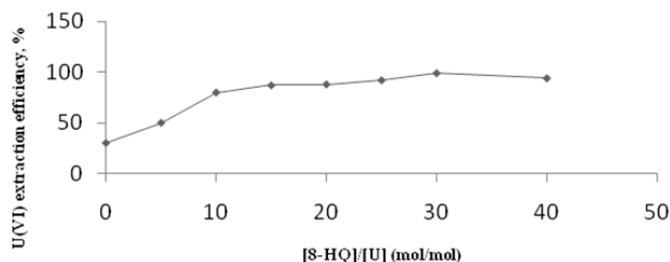


Fig. 7: U(VI) extraction efficiency (%) as a function of 8-HQ concentration [U]=20 mgL⁻¹, pH=6, Triton X-114=0.25(w/v)%, T_{eq}=50, t_{eq}=30 min, t_{rot}=15 min, ω=5000rpm

4. Conclusions:

The use of micellar systems as an alternative to other methods of separation and preconcentration offers several advantages including experimental convenience, safety and being an inexpensive method. Further, in comparison to solvent extraction methods, it is much safer, since only a small amount of the surfactant, which has a low toxicity, is used.

In this study we selected the most effective surfactant and ligand and optimized their concentration and the other parameters to achieve high U(VI) cloud-point extraction efficiency. The low detection limit of real sample analysis is an indication of methods versatility for real sample.

ACKNOWLEDGMENTS

The authors wish to thank the LSS laboratory of Jaber-Ibn-Hayan research laboratory and Dr. R. Davarkhah and Mr Salimi for their encouragement and their fruitful discussion.

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