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

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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 together with 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 0.15μg L^{-1} was conducted.

Introduction

Extraction of uranium in aqueous systems is often required for environmental control and geochemical prospecting [1-4]. Uranium has special significance among actinides as nuclear fuel for electricity production in power plants. It is known to cause acute toxicological effects for human and its compounds are potential occupational carcinogens. Uranium is highly toxic which causes 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 [5-7].Liquid–liquid extraction, ion exchange and solid phase extraction are commonly used methods [8].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 [9], nanofiltration [10] and micellar systems have been developed [11]. Recent studies have shown the miceller system to be an appropriate substitute for organic solvents in extracting metallic ions from liquid samples of the environment. CPE consists 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 one is a surfactant-rich phase. The hydrophobic compounds initially present in the solution and bound to the micelles are extracted to the surfactant-

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rich phase [12-18]. Metal analysis by spectro-analytical 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 [19-24]. 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 $UO_2(NO_3)_2 \cdot 6H_2O$ in water. Applied 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) with pH 6.0 was prepared by dissolving the appropriate amount of sodium acetate (Merck) in water and pH was adjusted 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 mgl^{-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 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.

3. 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 mgl^{-1}, pH=6, [8-HQ]/[U(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 [25-27].
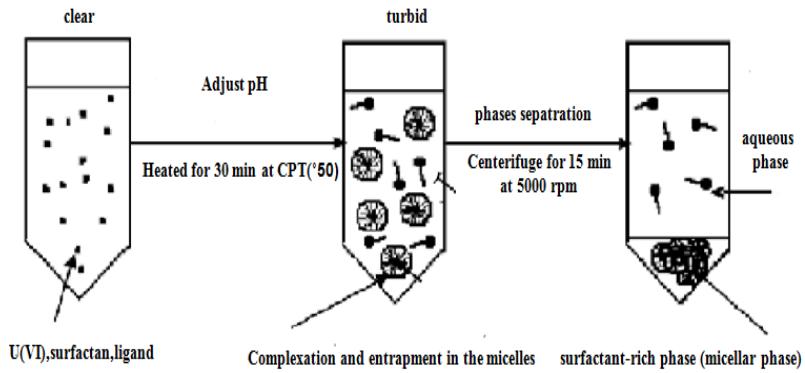
**Figure 1: The experimental procedure steps for implementation of cloud-point extraction**
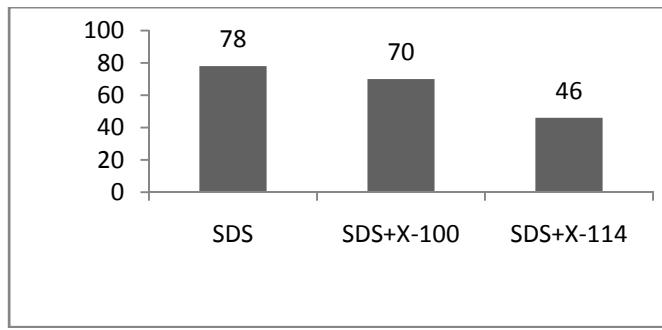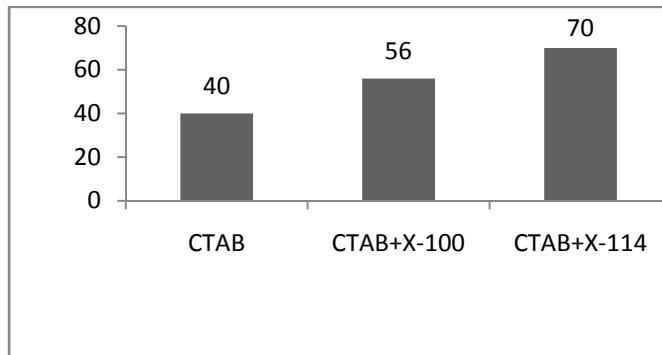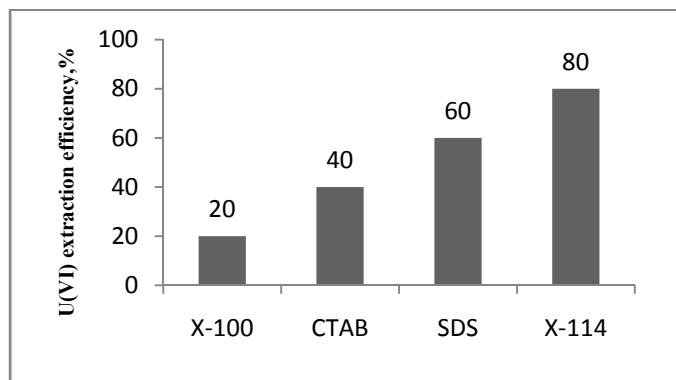
Figure 2,3,4: Effect of different types of surfactant and their mixture on U(VI) extraction efficiency [U]=20 mgl⁻¹,pH=6, [8- HQ] / [U]=20,[surfactants]= 0. 5 % (w/v), T_{eq}= 50˚C, t_{eq}=20 min , t_{rot} =10 min,ω=5000rpm
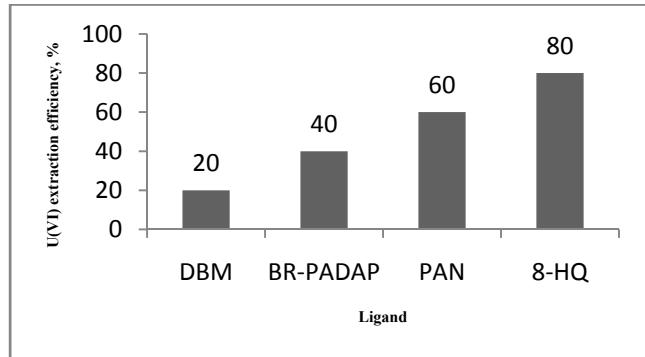
**Figure 5: Effect of different types of ligand on U(VI) extraction efficiency
[U]=20 mgl-1 , pH=6, [ligand]/[U(VI)]=20, Triton X-114=0. 5(w/v)%,
Teq=50, teq=20 min,t rot=10 min, ω=5000rpm**
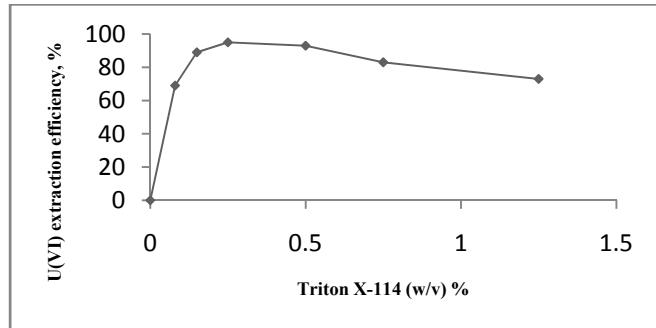
**Figure 6:U(VI) extraction efficiency(%) as a function of TritonX-114
concentration (weight %).[U]=20 mgl-1, pH=6,
[8-HQ] / [U]=20,Teq=50,t eq=30 min,t rot=15 min, ω=5000rpm**
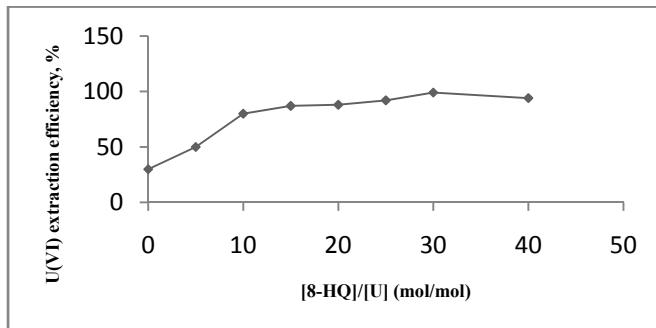
**Figure 7:U(VI) extraction efficiency (%) as a function of
8-HQ concentration [U]=20 mgl-1, pH=6, Triton X 114=0.25(w/v)%,
Teq=50,teq=30 min,t rot=15 min, ω=5000rpm**

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 studies. Experiment was conducted at constant condition ([U]=20mgl^{-1}, pH=6, [8-HQ] /[U(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 [25-27].

3.3. Effect of Triton X-114 concentration

Triton X-114 was chosen for the extraction due to the reason mentioned in part 3, together with its low cloud-point temperature (CPT) and high density of the surfactant-rich phase which facilitates phase separation by centrifugation [25]. A successful CPE should maximize the extraction efficiency by minimizing the phase volume ratio (Vorg/Vaqueous), thus improving its concentration ability [26]. The variation of extraction efficiency upon the surfactant concentration was examined with 50 mL of solution containing certain amount of U(VI) in the presence of [8-HQ]/[U(VI)]=20 and Triton X-114 ranging 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 the 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[28].

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 the reason mentioned in part 3.2 that forms 1:2 complexes (metal:ligand) with target ions [27]. The variation of the extracting 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 [29].

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. Furthermore, 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.

Acknowledgements

References:

1- Jain, V.K., Pandya, R.A., Pillai, S.G. and Shrivastav, P.S. (2006). "Simultaneous preconcentration of uranium (VI) and thorium (IV) from aqueous solutions using a chelating calyx arene anchored chloromethylated polystyrene solid phase."*J. Talanta*, Vol. 70, pp. 257–266.

2- WHO (1998). Guidelines for Drinking Water Quality. 2nd Ed., Chapter. 2, WHO/EOS Pub., Geneva

3- Sheppard, S.C., Sheppard, M.I., Gallerand, M.O. and Sanipelli, B. (2005). "Derivation of ecotoxicity thresholds for uranium." *J. Environ Radioactiv,* Vol. 79, pp. 55–83

4- Kocher, D.C. (1989). "Relationship between kidney burden and radiation dose from chronic ingestion of U: implications for radiation standards for the public." *J. Health Phys.*, Vol. 57, pp. 9–15.

5- IAEA-TECDOC, (2002). Technologies for the Treatment of Effluents from Uranium Mines, Mills and Tailings. DOC-1296, Chapter. 5, International Atomic Energy Agency, Vienna.

6- Naftz, D., Feltcorn, E., Fuller, C.,Wilhelm, R., Davis, J.,Morrison, S, et al, (2000) .Filed demonstration of permeable reactive barriers to remove dissolved uranium from groundwater. Interim Report. Chapter: 1, Environmental Protection Agency, Washington, DC.

7- Merritt, R.C. (1971). The Extractive Metallurgy of Uranium. 5^{td}.Ed., Chapter. 4, Johnson, Boulder Pub. CO., Colorado School of Mines Research Institute.

8- Rao, T.P., Metilda, P. and Gladis, J, M. (2006). Preconcentration techniques for uranium (VI) and thorium (IV) prior to analytical determination: an overview. *J. Talanta*, Vol. 68, pp. 1047–1064.

9- Chou, C.L. and Moffatt, J.D. (2000). "A simple co-precipitation inductively coupled plasma mass spectrometric method for the determination of uranium in seawater. Fresen." *J. Anal Chem.*, Vol. 68, pp. 59–61.

10- Favre-Reguillon, A., Lebuzit, G., Foos, J., Guy, A., Draye, M. and Lemaire, M. (2003). "Selective concentration of uranium from seawater by nano filtration." *Ind. Eng. Chem. Res.*, Vol. 42, pp. 5900–5904

11- Huddleston, J.G., Willauer, H.D., Griffin, S.T. and Rogers, R.D. (1999)."Aqueous polymeric solutions as environmentally benign liquid/liquid extraction media." *Ind. Eng. Chem. Res. J.*, Vol.38, pp. 2523–2529.

12- Corti, M., Minero, C. and Degiorgio, V. (1984). "Cloud point transition in nonionic micellar solutions." *J. Phys. Chem.* Vol. 88, pp. 309–317.

13- Komaromy-Hiller, G. and Von Wandruszka, R. (1996). "Anisotropy changes of a fluorescent probe during the micellar growth and clouding of a non-ionic detergent." *J. Colloid Interface Sci.* Vol. 177, pp. 156–161.

14- Garc̆ıa-Pinto, C., P´erez-Pav´on, J.L. and Moreno-Cordero, B. (1995). "Cloud point preconcentration and high-performance liquid chromatographic determination of organophosphorus pesticides with dual electrochemical detection." *Anal. Chem.,* Vol. 67, pp. 2606–2612.

15- Sirimanne, S.R., Barr, J.R., Patterson, D.G. and Ma, L. (1996). "Quantification of polycyclic aromatic hydrocarbons and polychlorinated dibenzo-*p*-dioxins in human serum by combined micelle-mediated extraction (cloud-point extraction) and HPLC." *Anal. Chem.,* Vol. 68, pp. 1556–1560.

16- Eiguren, A., Sosa- Ferrera, Z. and Santana-Rodr̆ıguez, J.J. (1998). Determination of polychlorinated biphenyls by liquid chromatography following cloud point extraction, *Anal. Chim. Acta*, Vol. 358, pp. 145–155.

17- Shariati, S. and Yamini, Y. (2006). "Cloud point extraction and simultaneous determination of zirconium and hafnium using ICP-OES." *J. Colloid Interface Sci.* Vol. 298, pp. 419–425.

18- Tavakoli, L., Yamini, Y., Ebrahimzadeh, H., Nezhadali, A., Shariati, S. and Noormohamadian, F. (2008). "Development of cloud point extraction for simultaneous extraction and determination of gold and palladium using ICP-OES." *J. Hazard. Mater*, Vol. 152, pp. 737–743.

19- Stalikas, C.D. (2002). "Micelle-mediated extraction as a tool for separation and preconcentration in metal analysis." *TrAC Trends Anal. Chem*, Vol. 21, pp. 343–355.

20- Shemirani, F., Baghdadi, M. and Ramezani, M. (2005). "Preconcentration and determination of ultra trace amounts of arsenic (III) and arsenic (V) in tap water and total

arsenic in biological samples by cloud point extraction and electrothermal atomic absorption spectrometry." *J. Talanta,* Vol. 65, pp. 882–887.

21- Martnez, R.C., Gonzalo, E.R., Cordero, B.M., Pavon, J.L.P., Pinto, C.G. and Laespada, E.F. (2000). "Surfactant cloud point extraction and preconcentration of organic compounds prior to chromatography and capillary electrophoresis." *J. Chromatogr*, Vol. 902, pp.251–265.

22- Pinto, C.G., Pavon, J.L.P., Cordero, B.M., Beato, E.R. and Sanchez, S.S. (1996)."Cloud point preconcentration and flame atomic absorption spectrometry: application to the determination of cadmium." *J. Anal. At. Spectrom*, Vol. 11, pp. 37–41.

23- Oliveros, M.C.C., de Blas, O.J. J., Pavon, L.P. and Cordero, B.M. (1998). "Cloud point preconcentration and flame atomic absorption spectrometry: application to the determination of nickel and zinc." *J. Anal. At. Spectrom*, Vol. 13, pp. 547–550.

24- Paleologos, E.K., Stalikas, C.D., Tzouwara-Karayanni, S.M., Pilidis, G.A. and Karayannis, M.I. (2000). "Micelle-mediated methodology for speciation of chromium by flame atomic absorption spectrometry." *J. Anal. At. Spectrom*, Vol. 15, pp. 287–291.

25- Ahariati, S., Yamini, Y. and Khalili Zanjani, M. (2008). "Simulation preconcentration and determination of U (Vi), Th (IV), Zr (IV) and Hf (IV) ions in aqueous samples using micelle- mediated extraction coupled to inductively coupled plasma-optical emission spectroscopy." *Journal of Hazardious Materials*, Vol. 156, pp. 583-590.

26- Ferreira, H.S., Bezerra1, M.d.A. and Ferreira, S.L. (2006). "A Pre-Concentration Procedure Using Cloud Point Extraction for the Determination of Uranium in Natural Water." *Journal of Springer-Verlag*, Vol. 45, pp. 567-578.

27- Guillon, A.F., Murat, D., Cote, G.R., Foos, J. and Draye, M. (2006). "Temperature-induced surfactantmediated pre-concentration of uranium assisted by complexation." *J. Chem. Technol. Biotechnol.*, Vol. 96, pp. 1872–1876.

28- Zhao, D., Bian, R. and Ding, Y. (2009)."Determination of lead and cadmium in water samples by cloud point extraction prior to flame atomic absorption spectrometry determination." *Journal of J. Iranian Chem. Res.*, Vol. 2, PP. 87-94.

29- Ahmadi, F., Khanmohammadi, A., Heydari, S., Mirzazadeh, M., Malekpour, E., Micelle Mediated Methodology for the Determination of Heavy Metals in Real Samples by Flame Atomic." *Journal of Hazardious Materials*, Vol. 136,PP. 523-540.