Development of Methodology for Separation and Recovery of Uranium from Nuclear Wastewater

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Abstract:

Uranium plays a key role in nuclear power supply, demand of which is growing up with time because of its prospective features. Persistent increase in different nuclear activities leads to increase generation of nuclear wastewater containing uranium. Separation and recovery of the uranium from its unconventional source like nuclear wastewater is worth to explore for addressing the reutilisation of the uranium source. It is also necessary to improve remediation technology of nuclear industries for environmental protection. Development of a suitable process methodology is essential for the purpose to supersede the conventional methodology. In the article, recent developments in several possible methodologies for separation of uranium from dilute solution have been discussed with their merits and demerits. Sorption technique as solid phase extraction methodology has been chosen with suitable polymer matrix and functional moiety based on wastewater characteristics. Polyhydroxamic Acid, PHOA sorbent synthesized following eco-friendly procedure is a promising polymeric chelating sorbents for remediation of nuclear wastewaters and recovery of uranium. Sorption and elution characteristics of the PHOA have been evaluated and illustrated for separation and recovery of uranium from a sample nuclear wastewater. For the remediation of nuclear wastewater SPE technique applying the PHOA, a polymeric sorbent is found to be a potentially suitable methodology.

Introduction

Unhindered growth of a nation depends on energy security which is the availability of natural resources for energy consumption. There is an acute demand for more and more reliable power supplies. Nuclear power will be playing a key role in near future for reliable power supply of India and about 25% nuclear contribution in the power supply is the ambition for year 2050 [1]. Uranium has been projected as the main workhorse of future fuel and it gives large amount of power using a small amount of fuel and space. Due to limited reserve of natural uranium in India it is required to explore various other resources of uranium including secondary resources and unconventional sources to meet the long term energy sustainability of Indian nuclear programme [2]. It is important and necessary to recognize the concern over the environmental and health impacts in parallel to ensure a long term supply of uranium to sustain any country’s nuclear power program. As a result of the developments that have taken place world wise in the areas of uranium recovery from unconventional sources or from its lean solution, the philosophy and the concept of the processing of the plant effluent have changed from the traditional methodology. Thus, the uranium recovery technique or separation methodology should be recognized as having a bright future.

The amount of uranium in the environment has exceeded due to activities of nuclear industry, mineral extraction, uranium combustion, mining processes and use of phosphate fertilizer that contains uranium. As per the World Health Organization (WHO) standards, the maximum acceptable concentration of U(VI) in water is 50 mg L\(^{-1}\) [3]. Toxicity of uranium is closely associated with its solubility. In regions of radioactive
contamination of local soil and groundwater, the chemical toxicity of uranium has aggravated health concerns. Water and soil contamination with uranium ions has become a global environmental problem. Even at low concentrations, because of their persistent and accumulative nature these are toxic. Therefore, separation and recovery of uranium are of great practical significance.

**Uranium separation techniques**

Toxic metals like uranium can be removed from wastewaters, for the clean-up process, by a number of separation technologies, such as chemical precipitation, membrane process, solvent extraction, floatation, coagulation and sorption process. Despite different techniques applied for the remediation of uranium removal from wastewater, it is important to mention that the selection of the most apposite treatment techniques depends on the composition of the wastewater, initial metal concentration, principal investment and operational cost, plant tractability and reliability and environmental impact. Chemical precipitation is applicable for relatively concentrated solution. Floatation process requires addition of uranium specific surfactant or flocculent which is rarely available. Chemical precipitation, coagulation and floatation processes add contamination (organic / inorganic) to the wastewater and recovery of the uranium is difficult. Solvent extraction is recognized as a versatile for laboratory as well as for large scale separation of uranium from different streams. However, separation and recovery of uranium by conventional solvent extraction has some short coming with respect to third phase formation, crude oil formation as well as solvent loss. Moreover, this method cannot be used for effective separation and recovery of metal ions from dilute solutions of alkaline medium. Thus, the development of more efficient techniques has lead to development of liquid-membrane based separation which holds promise for recovery of uranium ions from dilute resources and has received a considerable attention in separation science and technology. Liquid membrane processes are finding increasing application in chemical industry for achieving energy efficient (with respect to conventional membrane process) and selective separations from very dilute medium. In general two types of liquid membranes - bulk / supported liquid membrane (BLM / SLM) and emulsion liquid membrane (ELM) have been reported widely are being extensively studied, for their application in extraction and concentration of dissolved metals from effluents using various extractants. The problem of low flux rate due to high diffusion resistances, inefficient operation and exorbitant costs encountered in bulk and supported liquid membranes (BLM/SLM) are overcome in an ELM. In the ELM process, an emulsion of organic membrane phase and aqueous inner phase is dispersed in the continuous aqueous feed phase. This gives a highly selective and ultra thin liquid film generating a large mass transfer area for separation. ELM technique has been tried by various workers for recovery of uranium, plutonium and lanthanides from dilute solutions using various carriers. But main disadvantages are the leakage and swelling problems and difficulties in de-emulsification step for which the technology yet to be brought up to industrial scale with full confidence. Hence, solid phase extraction for separation and removal of uranium ions is the method of choice due to its high separation efficiency, good reproducibility of retention parameters, and simplicity and is a popular method owing to its applicability to both pre-concentration and separation [4].

**Solid Phase Extraction (SPE)**

SPE has additional advantages over other separation techniques such as (i) reduced solvent usage (ii) low disposal costs, (iii) short extraction times, (iv) high efficiency, (v) ecologically-safe, (vi) elimination of some of the glassware, (vii) reduced exposure of analysts to organic solvents (viii) more reproducible results (ix) remote operation etc. In recent years, SPE is the most often used method in trace metal analysis in environment for the separation and/or pre-concentration purposes. Sorption process, a SPE technique, is defined as a surface phenomenon; sorption is the adhesion of a molecule onto the sorbent surface. The sorption proceeds by complex
process affected by several mechanisms involving adsorption by physical forces on surface and pores, chemisorptions, ion exchange, complexation, chelation, and entrapment in capillaries. Due to high affinity of the sorbent for the uranium(VI) ion species, the latter is attracted and bound by the sorbent via these mechanisms.

A solid phase extractant, adsorbent/sorbent consists of two parts: a matrix and functional components. An inert host structure which allows diffusion of hydrated ions i.e. a hydrophilic matrix is an essential part of any sorbent. The selection of the matrix depends on several important criteria of application like regular and reproducible form of its structure, stability in conditions of application medium, option on the type of exchanger etc. The functional group represents the ligand required for metal complexation. The most common coordinating atoms present in the main or side chain are N, O, P and S. It is possible to make chelating sorbent that have a selective adsorption capacity for specific metal ions by fixing the desired ligand groups on the sorbent matrix. Commonly used materials for the matrix can be broadly divided into four groups: (i) Minerals and Inorganic oxides: clay, diatomite, zeolite, alumina, silica, ceramic, tin oxide, iron oxide etc. (ii) Carbonaceous materials: activated carbon (AC), mesoporous carbon, carbon nano-tubes (CNTs), graphite and its derivatives/grapheme etc. (iii) Biosorbent: Chitosan, yeast, alga, agro-waste etc. and (iv) Polymers/copolymers: resins, hybrid materials/composites, gels and related materials. For each type of matrix have advantages and disadvantages based on its application. Based on nuclear wastewater characterisation, case specific suitable SPE matrix material is chosen for uranium separation and recovery from nuclear wastewater.

Promising chelating sorbent for uranium extraction

Chelating agents are compounds containing donor atoms (ligands) that can combine by coordinate bonding with metal ion to form an organised structure called as a chelate. Co-ordination between metal – ligand is a Lewis acid – Lewis base neutralization process. Complexing sorbents of new types are developed deliberately; possessing a tailor made structure that would bind the element with the ligand. Ability of a ligand to complex with a target metal ion is also a function of the solution pH and the presence of competing anions. The removal of desirable metal ions from wastewaters and process effluent stream has led to the development of several

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<th>Chemical form</th>
<th>Suitability</th>
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<tr>
<td>Hydrous titanium oxide (developed before 90’s)</td>
<td>Difficulty in large scale in submerged mode for seawater application. Low kinetics and capacity.</td>
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<tr>
<td>Macroyclic hexacarboxylic acid (developed before 90’s)</td>
<td>Difficulty in production of polymer-bound hexacarboxylic acid.</td>
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<td>Amidoxime (developed before 1995)</td>
<td>Most extensively studied, suitable for large scale production in the form of fibres, resin, or grafted fibrous sheet, slow kinetics and limited selectivity. Have advantages of Amidoxime group and show better uranium sorption kinetics. Hazardous synthesis process.</td>
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<td>Amidoxime + Methacrylic acid [5]</td>
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<tr>
<td>Calixarene-based uranophiles and others</td>
<td>Highly selective towards uranium, slow sorption kinetics, difficulty in anchoring in polymer matrix, synthetic chemistry involved is not suitable for large scale production. Very costly.</td>
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<tr>
<td>2,2’-dihydroxy azobenzene and related chemical groups [6]</td>
<td>Involve synthetic chemistry, not evaluated for real application.</td>
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<tr>
<td>Poly(Hydroxamic Acid) Resin (developed before 90’s and recently [7])</td>
<td>Have all advantages of hydroxamic acid group for recovery heavy metals including uranium along with iron. Cheaper, safe synthesis process &amp; easy to dispose.</td>
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types of chelating sorbents. Few reportedly important inorganic and potential sorbents for uranium recovery from dilute solutions are mentioned in Table – 1. The diffusion mobility of U(VI), either in [UO2(CO3)3]4- form or UO22+ form, in the sorbent would be dependent on the physical as well as chemical interactions (electrostatic and covalent) with the ligand-sites in sorbent matrix. As de-complexation of [UO2(CO3)3]4- can be catalyzed by H+-ions, the presence of acidic monomer or co-monomer with appropriate pKa value may enhance the sorption kinetics of U(VI) in the sorbent from the wastewaters. Considering these parameters, a new sorbent Poly – hydroxamic Acid, PHOA has been evaluated for uranium recovery from a nuclear wastewater.

**Evaluation study:**

Materials/chemicals such as acrylamide, N, N’ methylene bis acrylamide, hydroxyl amine hydrochloride, methanol, acetone, sodium hydroxide, HCl were procured from local market and were used in the synthesis process without further purification. Synthesis route of the sorbent has been chosen carefully to follow safe and economic process. The sorbent has been synthesised by a two-step method: (a) by addition polymerisation of homogeneously mixed acrylamide with a cross-linking agent and in situ gelling of the whole mass followed by precipitation and (b) the crumbled, washed and dried gel was converted into a macro-porous chelating agent by treatment with hydroxylamine hydrochloride. Photograph of the sorbent preparation scheme has been shown in Fig.1.

Sorbent’s surface pores are opened up in the water (swelling) because of hydrophilic nature of the sorbent, as designed for the purpose. Suitability tests with synthetic solution indicated that the sorbent can be used for sorption process in alkaline medium and for elution process in HCl medium. Equilibrium capacity was found to be 1.1 mg/g of sorbent with distribution coefficient 2500 mL/g of sorbent. Treated raffinate filtrate of uranium processing plant, wastewater was characterized and composition analysis shows that it contents uranium 5 – 10 mg/L and Mg, Ca and nitrate ions (all g/L level) along with low concentration of Fe, Cu, Mn (<5 mg/L) and the wastewater is alkaline in nature (pH>7). An Inductively Coupled Plasma Emission Spectrophotometer (ICPAES), Jobinyvon Emission, Model No. JY 328 was used to determine uranium and other metal ions’ concentrations in solutions. Batch experiments were carried out in laboratory scale at room temperature (RT).
Appearance of virgin PHOA and PHOA loaded with uranium from the wastewater along with envisaged sorption process has been shown in Fig. 2. Uranium sorption onto PHOA has been established by energy-dispersive X-ray spectroscopy (EDS) analysis as well as Fourier transform infrared spectroscopy (FTIR) analysis of the uranium sorbed PHOA which is depicted in Fig. 3. The sorption reaction between PHOA and U(VI) was investigated for its kinetics and mechanism. As shown in Fig. 4, the process follows the monolayer molecule sorption procedure. It also reflects that chemical sorption may be the pathway for the chelating reaction between U(VI) and PHOA. The Boyd plot indicates that external mass transfer is not the rate limiting step in the process and the rate is controlled by both, intra-particle diffusion or metal-ligands interaction.

The results of efficiency of different chemical agents as eluents are shown in Fig. 5 which has been articulated in the mechanism of sorption process in Fig. 2. Inorganic acids are found to be more efficient eluent than others. To avoid damages of sorbent structure application of oxidising acids has been
avoided. Hence, HCl has been chosen as effective eluent and more than 97% uranium recovery is achieved within 3h time.

Fig. 6 describes the uranium recovery methodology from nuclear wastewater using PHOA as solid phase extractant with six times regeneration capacity. The experimental studies are indicative of the fact that Uranium recovery from wastewater generated in nuclear establishment using novel sorbent, PHOA is viable and technologically implementable.
Conclusion

Uranium although present in low level (<10 mg/L) in nuclear wastewater, can be separated and recovered by the developed SPE methodology, which is better in choices. The process envisages deploying the possibility of harnessing uranium from nuclear wastewater. This also indicates that the methodology is available well in hand to polish the wastewater if required in future. As a matter of case study, a wastewater of uranium processing plant has been adopted for the evaluation of methodology which has been successfully demonstrated for separation and recovery of uranium.

References