

TREATMENT OF URANIUM CONTAMINATED WASTEWATER – A REVIEW

M. DULAMA, M. IORDACHE, N. DENEANU

Institute for Nuclear Research Pitesti, Romania, mirela.dulama@nuclear.ro

ABSTRACT

The paper presents a study of the treatment techniques used for uranium recovery from aqueous solutions, such as: precipitation, ion exchange processes, sorption processes, solvent extractions, separation by liquid membrane, nanofiltration and reverse osmosis.

The necessary elements for rigorous treatment experiments that can be used to define innovative procedure for uranium contaminated wastewater treatment are described in this review. The published data were summarized and the areas for further research were identified in order to be able to propose an environmental friendly technology in the field of uranium production and recovery cycle.

Key words: uranium, wastewater, recovery

Introduction

The selection of radioactive wastewater treatment methods is determined by the flow, the radioactive composition, the release procedure, etc. By comparison with the treatment of conventional wastewater, the radioactive wastewater decontamination is more difficult due to the following: the chemical composition which conducts to radioactive complex, the very low radionuclides concentrations with high radiotoxicity and with other behavior than non-radioactive contaminants.

The literature in the field of wastewater contaminated with uranium is address, predominantly radioactive waste issues in uranium ore and uranium extraction from seawater. During the present research we found just few published data on the recovery of uranium from wastewaters originating in the final stages of the nuclear fuel fabrication, powder sintering UO_2 and fuel elements preparation, respectively.

A treatment plant for liquid radioactive waste contaminated with natural uranium, from the manufacturing of CANDU nuclear fuel is in operation, since 1983, at Institute for Nuclear Research Pitesti (SCN Pitesti). Recovery of uranium is performed by precipitation with trisodium phosphate in a treatment process which uses significant amounts of ammonia, nitric acid and trisodium phosphate. The aim of the literature data

study presented in the paper is to identify technologies based on environmental friendly treatment methods, which follow the principles of sustainable development and green chemistry.

Uranium speciation

Into aqueous solution, the uranium oxidation states are +3 (red), +4 (green), +5 (unstable), and +6 (yellow). Uranium ions are water-soluble, but the degree of solubility is highly dependent on the presence of inorganic ligands (mainly $[\text{OH}]^-$, $[\text{HCO}_3]^-$, $[\text{CO}_3]^{2-}$, $[\text{H}_2\text{PO}_4]^-$, $[\text{HPO}_4]^{2-}$, $[\text{PO}_4]^{3-}$ and $[\text{SO}_4]^{2-}$) [1-3]. In the case of an ion complex formation (hydrolysis is a special case) anion "basicity" will play an important role, such ions ClO_4^- , Cl^- , NO_3^- , SO_4^{2-} are weak anion complexing and acetate, carbonate and bicarbonate are strong anion complexing.

Uranium recovery methods

There have been several methods of uranium extraction explored during the past four decades. These include, in particular, solvent extraction, co-precipitation, ion-exchange, evaporation, sorption processes, foam separation, separation by liquid membrane, nanofiltration, reverse osmosis and biological separation [4].

Solvent extraction

Solvent extraction is not a novel method for uranium processing, being used successfully in the purification stage and also in the processing of spent nuclear fuel. Extraction processes originate in the discovery of the property of uranium nitrate to be readily soluble in diethyl ether (Bucholz, 1805) and extraction of uranium with ether was used as a method for the purification of uranium nitrate samples (Péligot, 1812).

Among several hundreds of organic compounds examined, the best extraction was obtained with of certain classes of alkylamine and organophosphorus compounds. Compounds like quaternary ammonium salts are also important for the extraction of high pH, but the problem of the organic phase solubility, is more severe than in the case of the most simple amine salts.

Co-precipitation

For the treatment by precipitation, it is very important that the solubility product to be achieved and the radionuclides to be removed as insoluble compounds. *Gorman-Lewis et al, 2008* [5] present a review of published solubility data for environmentally relevant uranyl phases.

In the case of acid solution, precipitation can be achieved with alkali metal hydroxides, ammonia, reduction to U (IV) followed by phosphate precipitation or through addition of hydrogen peroxide and precipitation. In the case of alkaline solution, precipitation can be achieved by acidification and heat decomposition of the carbonate or by subsequent addition of alkali hydroxides or ammonia.

Coagulation and co-precipitation methods are reported in the literature by using precipitation agents, $\text{Fe}(\text{OH})_3$, $\text{Al}(\text{OH})_3$, $\text{Ti}(\text{OH})_4$ and $\text{Ca}_3(\text{PO}_4)_2$ [4,6]. However, the long precipitation time that is required makes the process impractical with large volumes of wastewater.

Ion exchange is one of the earliest methods investigated. The separation of uranium can be carried out with higher yields by the ion exchange resins, such as methods like solvent extraction and precipitation have been replaced. The use of ion exchange for radioactive clean-up is recommended for aqueous solutions with low TDS (Total Dissolved Salts) and particulates and colloids free.

An effective decontamination is obtained using organic ion exchange resins, strong acid or strong base. However, the presence of increased concentrations of stable isotopes leads to rapid saturation of the ion exchanger. In sulfuric acid solutions, uranium tends to find as anionic complex form. In this case strong base anionic resins are very efficient for retention of uranium. The advantage of these resins compared to the cationic form consists in their selectivity because the dissolved impurities will not be retained, being mostly cationic species. *Bunus, 1976* [7] show that Amberlite IRA 400 has an exchange capacity of approx. 300 g/l, and that the environmental acidity reduces the capacity to 50 g/l. In the case of alkaline attack, uranyl ion is in the anionic form of $[\text{UO}_2(\text{CO}_3)_3]^{4-}$ at low concentrations, when it will use anionic resin, too. The use of cationic resin is possible in acidic medium, at low acidity, pH 2.5-3, when prevail UO_2^{2+} .

Sodaye et al., 2009 [4] reported that resins having complexing reagents, such as 8-hydroxyquinoline or resorcinol arsenic acid formaldehyde, show a very good uptake of uranium.

Sorption processes

There are many adsorbents explored for the extraction of uranium. Natural and synthetic zeolites represent good ion-exchange materials for removal of uranium from the aqueous solutions. Beside other, a group of microporous materials, which was found to have a high potential for these decontaminations, is constituted by crystalline microporous titanosilicates.

Titanium oxide (TiO_2) is one of the earliest adsorbent explored for uranium extraction. The various kinds of preparations of hydrous titanium oxide can be roughly classified into three types.

- i) Neutralization method: a titanium solution is neutralized by alkali
- ii) Urea method: urea is added to a titanium solution and then heated
- iii) Thermal decomposition method: a titanium solution is heated and hydrolyzed.

For the elution of the adsorbed uranium, acids such as hydrochloric acid and sulfuric acid and solutions of carbonates as ammonium carbonate, sodium carbonate and sodium bicarbonate can be used. The rate of elution by acid (e.g., 0.2 N HCl) is slower than that by using carbonate. With 1 N ammonium carbonate it needs 48 h for eluting more than 90% of the adsorbed uranium at room temperature. The crystalline microporous titanosilicates have a high potential for these decontaminations.

Zhijun et al., 2004 was studied the sorption of UO_2^{2+} on TiO_2 as a function of pH at moderate concentration (10^{-4} - 10^{-5} mol/l). It was found that the sorption rates increased with increasing pH from 2 to 10. The sorption at constant pH followed the linear sorption isotherm, and the distribution coefficients found are of the order of 10 to 10^3 ml/g. [8]

Activated carbon

Activated carbon has been reported to be very effective in adsorbing uranium from water. However, the adsorption rate of a particular activated carbon can vary dramatically, depending upon the original carbon source material used: the pyrolysis method and the activation method [9].

The advantage of activated carbon is in the elution process, where carbon will not dissolve in the more concentrated eluents. The second method of recovery would be to burn the carbon in a conventional coal fired turbine or gasify, leaving an ash which is highly concentrated uranium ore.

In 2012, *Foo et al.* [1] shown that the feasibility of activated carbon adsorption processes for the remediation of uranium contaminated water has been well proven by a number of laboratory and pilot-scale studies, but a great progress in this area can be expected in the future.

Galena (PbS)

C.-K. Yun, 1982 [10] reported that galena is a better adsorbent than hydrous titanium oxide. The adsorption capacity of reagent grade galena is around $1100\mu\text{g/g}$ PbS as compared to adsorption capacity of hydrated titanium oxide of $600\mu\text{g/g}$ of TiO_2 . The adsorption performance of the galena is not affected by repeated use as it is regenerated by use of dilute hydrochloric acid [4].

Use of polymers

Micro and macroporous polymers having dihydroxamic acid groups are studied for uranium uptake. The separation of uranium after elution from transition metal ions is thus a possibility. Also, the incorporation of amino acids and/or polyamino acid into a polymer matrix has certain advantages since the amino acids are very reactive with different substances including metal ions and bio-molecules. The high affinity of the uranyl-carbonate complex towards the polyamidoxime drew attention for the possible recovery of uranium from seawater in the 70's and has gained importance in recent years [4, 11–15].

Evaporation

This treatment method leads to decontamination factors in the range $10^4 - 10^6$. The main difficulties encountered in evaporation of radioactive solutions with unknown composition are foaming, crust formation and evaporation of volatile compounds. It is necessary to remove from the effluent materials like ammonium nitrate, which can thermally decay with explosion. The foaming can be somehow controlled through addition of anti-foaming agents and the use of chemical treatment with anti-scaling agent is recommended to prevent the scale formation.

In spite of high decontamination efficiency and the wastewater volume reducing obtained by evaporation, until now this treatment process remains an expensive method, because its high energy consumption [16].

Foam separation

Surface-active agents can be used in collecting metal ions by foam separation. Kim *et al.* 1971 shown that the average recovery of uranium by this method is around 82%. They recommend flotation made with coagulants such positively charged ferric hydroxide with an anionic surfactant as, sodium dodecyl sulfate. However, it is difficult to recover the surface-active agents after use. [17]

Separation by liquid membranes (LM)

The study of uranium separation by liquid membranes was carried on uranium recovery from seawater, in particular. In this case, the uranyl ions are transferred across the membrane and released into a aqueous phase by dissociation process. In order to obtain an effective concentration of uranyl ions is necessary to carry UO_2^{2+} ions against their concentration gradient, across the membrane, by the application of other chemical potential difference, in the opposite direction, across the membrane. Uranyl species accumulate in the receiving phase. In literature there are many data on uranium recovery through liquid membranes by using as carrier TOPO (trioctylphosphine oxide), TBP (tributyl phosphate), KELEX 100 (7-dodeceny-8-quinolinol), D2EHPA (di-(2-ethylhexyl) phosphoric), Cyanex 272 (bis-(2,4,4-trimethylpentyl) phosphinic acid) and crown ethers like DCH18C6 (dicyclohexano-18-crown-6). Recently, considering uranophile properties of calixarenes, their derivatives were synthesized and the use of them as carrier in LM separation was studied with success. By comparing the solvent extraction process with ML technique it was observed that ML requires very low concentrations of carrier, but it needs an emulsifier and, in addition, an emulsion breaking step [18-23].

Nanofiltration (NF) and reverse osmosis (RO)

Hsiue *et al.*, 1989 [24] reported on the use of RO membranes to treat uranium conversion process effluent containing toxic, corrosive, and radioactive compounds. The FT30 (*Filmtec*TM) membranes studied had

rejections of uranium $\geq 99.5\%$ for water recoveries up to 70%, and the results indicated that the treated effluent would meet regulatory discharge standards. *Chu et al., 1990 [25]* used a three stage process consisting of nanofiltration, reverse osmosis, and precipitation to treat uranium effluents. The process removed both soluble and suspended uranium species; it was found that 95% uranium recovery was possible, and the treated effluent met environmental standards.

Raff et Wilken, 1999 [26] was determined the rejection of the most important uranium species for the mobilization of uranium generated in different model waters, using a broad spectrum of commercially available NF membranes. They showed that the most important uranium species in natural water can be removed to about 95% over a wide range of pH and hydrochemical setting. Since even the molecular weight of the uranyl cation, which is the lightest uranium compound in water is above the typical molecular weight cut-off of NF membranes, it can be expected, that the rejection of other uranium compounds, not investigated, would also be above 90 or 95%.

Biological separation

Radioisotopes recovery from wastewater by microorganisms is performed by adsorption on the surface and intracellular accumulation. The accumulation ability depends on many physicochemical and biological factors. The uranium recovery methods by biological separation, tested at pilot scale, use microorganisms like *Leptospirillum thiooxidans*, *Thiobacillus ferrooxidans*, *Thiobacillus thiooxidans*, separate or admixture, and Thermophile or Heterotrophic bacteria [27,28].

The maximum loading obtained in the case of *Pseudomonas* sp. is 24.5% g (245 mg-U/g dry biomass) dry wt of the biomass at pH 3.5 and for *Talaromyces mersonii* CBS 814.70 it is 323 mg-U/g dry biomass. The adsorption process follows Langmuir adsorption and the equilibrium reaches in 2 min [4,29].

Innovation or improving of developed methods

Between the innovative or improved methods tested for uranium extraction we can notice the next procedures: resin grafted with calixarene, magnetic separations and canal system with braid adsorbents [4].

The innovative procedures for uranium contaminated wastewater treatment must aim, beside the economic aspects, the implementation of sustainable development and green chemistry/technology principles. The term “green chemistry/technology” is becoming the world-wide term used to describe the development of eco-friendly, sustainable chemical products and processes. The principles of sustainable development and green chemistry can be summarized with ensuring that:

- Zero emission technology if possible; and the maximum amounts of raw materials are converted to useful product (atom economy)
- Production of wastes is minimized (solvent recovery; waste/process water treatment with so-called clean technologies)
- Recovery and recycling of used natural resources, raw material or processed raw material
- Production of renewable raw materials and energy, and use of renewable feedstock
- Processes are designed to be inherently safe [30].

Several improved uranium recovery methods are in testing at SCN Pitesti, aiming to decrease the level of chemical contaminants in effluents from the treatment of liquid radioactive waste, contaminated with natural uranium from the manufacturing of CANDU nuclear fuel. One of the approached research direction is the replacement of phosphate precipitation with hybrid separation processes including precipitation achieved with chemical compounds free of phosphorus and nitrogen.

Conclusions

The uranium recovery methods have both advantages and disadvantages. The balance between them will lead to the selection of the optimal method for a specific application.

- For the precipitation technique it is very important that the solubility product to be achieved and the radionuclides to be removed as insoluble compounds, but the degree of solubility for uranium ions is highly dependent on the presence of inorganic ligands.
- Natural and synthetic ion-exchangers represent good materials for removal of uranium, but they are recommended for aqueous solutions with low TDS (Total Dissolved Salts), free of particulates and colloids.
- Ion exchange resins, having complexing reagents, show a very good uptake of uranium, nevertheless, practical application of these materials is restricted by their fairly rapid deterioration with aging.
- The major problem with uranium solvent extractions on large scale is either that it involves complicated procedure, requirement for large amount of chemical and volatile solvent or the solvent loss by entrainment and solubility.
- Nanofiltration is an environmental friendly technique which may be used in fuel fabrication facilities to remove dissolved uranium ions from wash solutions, permitting their discharge with no further treatment.

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II.3 AIR, WATER & SOIL PROTECTION