Enrichment and removal of uranyl ions by using polymeric supports: A review

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ABSTRACT

At one hand uranium is an element of considerable technological importance. In nuclear power plants uranium is used as fuel. Other than this, uranium has no significant commercial use. On the other hand uranium is highly toxic and radioactive heavy metal that mainly originates from nuclear-related activities and causes significant environmental and public health problems by its presence in terrestrial and aquatic ecosystems. There is 4.5 billion tons of uranium in seawater, which can solve global energy crisis by acting as long lasting fuel for atomic power plants. Concentration of uranium in seawater is approximately 2.8–3.3 mg/m$^3$ in the ionic form of uranyl tricarbonate ions ($\text{UO}_2(\text{CO}_3)_3^{4-}$). In the recent past much attention has been paid in the direction of recovering uranium from nonconventional sources such as coal and natural waters (0.1–10 mg/m$^3$), especially from seawater. The recovery of uranium from contaminated water of flooded mines (0.1–15 mg U/m$^3$) also presents a very important environmental problem to be solved. In the recent past use of hydrogels or hydrophilic crosslinked polymers or copolymers as adsorbents for the removal of uranium from sea water, coal, various effluents, and natural waters for both environment management as well as to be used as fuel in nuclear plants has tremendously increased. The aim of this article is to review the use of polymeric supports those have been reported in uranium enrichment and removal. The technical feasibility of various low-cost polymeric adsorbents for uranyl ions enrichment and removal from various sources has been reviewed.

Key words: adsorption; hydrogel; polymeric support; uranium; uranyl ion.

INTRODUCTION

Natural uranium occurs in minor amounts in many soil and rock types. Besides this, uranium accumulation is a normal geological process. Widespread occurring rocks namely granites and sedimentary rocks, are most common hosts for uranium accumulations. Uranium also has a high mobility in natural water. When ground water passes through uranium-containing rocks, the uranium salts get dissolved in water, especially under oxidized conditions. Uranium occurs in ground water mainly in areas which are dominated by basement rocks, especially by granites. In addition to this uranium originates from nuclear-related activities, especially nuclear power plants and poses a serious threat for environment and public health by its presence in terrestrial and aquatic ecosystems [1-3]. Uranium exists mainly as the uranyl tricarbonate ion [UO$_2$(CO$_3$)$_3^{4+}$] in seawater where its concentration is approximately 2.8–3.3 mg/m$^3$. Seawater contains about 0.55 M NaCl and 2.5 mM bicarbonate ion and its pH is 7.8 to 8.2 [4]. Uranium concentration in waste streams is too low for a classical treatment and too high to allow its discharge into the environment [5]. The possibility of coexisting UO$_2^{2+}$, Pb(II) and Cd(II) ions in various industrial wastes and sea water has great probability, and therefore their selective removal is necessary [6].

For last many years, a variety of methods have been used in enrichment and wastewater treatment processes. These methods include chemical precipitation, coagulation, membrane extraction, ion exchange, complexing, solvent extraction and adsorption. All these methods have their own advantages and disadvantages in applications. Solvent
extraction, adsorption and ion-exchange techniques have been extensively used for enrichment, separation and removal of some metal ions including uranyl ions [7-11].

Adsorption/sorption by using water insoluble crosslinked polymers or copolymers is one of the most widely investigated and researched techniques. This technique involves direct adsorption of the heavy metal ions into macroporous polymeric supports. Many studies have been reported on the use of hydrogels or hydrophilic crosslinked polymers as adsorbents for the removal of heavy metals, for removal of toxic and radioactive elements from various effluents, for metal preconcentration, for metal enrichment and for environmental sample analysis from aqueous solutions [12-18].

Crosslinked polymeric hydrogels are extensively being used as potential adsorbing materials for recovery of uranium ions from seawater, waste water, industrial effluents and nuclear power plant wastes. Hydrogels are crosslinked hydrophilic polymers those act as supports for metal ions including uranyl ions either by complexation with metal ions, by acting as ion exchange resins or by acting as selective adsorbents. These polymeric ligands are specifically tailor-synthesized for better selectivity and efficiency. Due to a number of advantages associated with these hydrogels, they have attracted considerable attention for the removal of uranyl ions from seawater and wastewater in recent years. The most remarkable advantages associated with the hydrogels include their selective nature, reusability, high efficiency, low cost, the ease of handling, eco friendly nature, easy availability and easy syntheses.

For the separation and enrichment of uranyl ions, variety of polymeric supports with diverse chelating groups have been developed [19-22]. In the design of chelating polymers with substantial stability for the selective removal or recovery of uranyl ions, many criteria are important. There are a large number of factors which affect specific and fast complexation of the uranyl ions as well as the reusability of the chelating polymeric supports. The design of effective host molecules for uranyl ion is connected with the economic importance of selective extraction of uranium from seawater [23-26].

Most of the polymeric supports involve carboxylates [27,28], EDTA analogues [29-30] phenols [31] amidoximes [32] and β-ketones [33] iminodiacetate, phosphoric acid, amine, dithiocarbamate and oxime as chelating groups [34-36]. Diethyl ester of vinyl phosphoric acid and acrylic acid and crosslinked copolymers of some natural polymers have also been used for the adsorption of some heavy metals ions [37-40]. Besides this, amidoxime derivatives of copolymeric hydrogels prepared from acrylonitrile and divinyl benzene has been used in the recovery of uranium from seawater [41-44].

In this review an attempt has been made to cover some recent developments and advances in the field of removal, separation and enrichment of uranium using polymeric supports from both technology as well as environmental management view point. Different methods for the synthesis of polymeric supports and methods for the enrichment/separation of uranyl ions are also discussed in detail.

SYNTHESES OF POLYMERIC SUPPORTS AND TECHNIQUES FOR URANYL ION UPTAKE/SORPTION

Many reports regarding syntheses of polymeric supports for uranyl ion uptake and methods/techniques for uranyl ion uptake are available in literature. Most widely used polymeric supports are hydrogels containing amidoxime, carboxyl, hydroxyl, amide, nitrile, ester, anhydride, amine, sulphonic acid, pyrrolidone and imidazole groups. Most of these hydrogels are prepared by free radical polymerization reactions involving persulphate (ammonium persulphate or potassium persulphate) initiator and ethylene glycoldimethacrylate (EGDMA) or N,N-methylenebisacrylamide (MBAAm) as crosslinking agents. Most commonly used method for uranyl ion uptake is spectrophotometry involving UV-visible spectrophotometer using sodium salicylate as complexing agent. In the present review, syntheses of some hydrogels and methods/techniques for uranyl ion uptake using these hydrogels/polymeric supports are discussed.

Amidoximated Poly(N,N-dipropionitrile acrylamide)

Amidoximated poly(N,N-dipropionitrile acrylamide) [poly(DPAAm)] containing double amidoxime groups per repeating unit was synthesized first by reaction of 3,3-iminodipropionitrile and acryloyl chloride to get N,N-dipropionitrile acrylamide (DPAAm) monomer. The monomer was polymerized by free radical polymerization reaction using azobisisobutynitrile (AIBN) as the initiator to get poly (DPAAm) and then synthesized polymer was reacted with hydroxylamine to obtain a polymer containing two amidoxime groups per repeating unit.

Uranyl ion uptake by using amidoximated poly(DPAAm) was carried out in batch mode from 100 ppb standard solutions at pH 5 and 25°C at 30 min, 1 h, 3 h, 6 h, 12 h and 24 h time intervals. Metal ion concentrations remaining
in the solution after every adsorption stage were determined by using Hewlett Packard 4500 series Inductively Coupled Plasma analyser (ICP). Similarly, adsorption of uranyl ions from seawater was evaluated in flow-through mode by circulating seawater upward through the amidoximated poly(DPAAm) loaded column at a flowrate of 6 mL/min at 25°C. After 1 hour, 1 day and 1 week contact time, the adsorbent was taken out from the column and immersed in 1 M HCl to elute the adsorbed uranyl ions. Amounts of adsorbed uranyl ions from eluted solutions were determined by ICP [45].

**Amidoximated Poly(N-vinyl 2-pyrrolidone/acrylonitrile) Hydrogel**

Amidoximation of hydrogels prepared from N-vinyl 2-pyrrolidone (VP) and acrylonitrile (AN) was carried out by Sahiner et al. VP and AN mixtures in different mole ratios (AN:VP, 0.67:1.00, 1.00:1.00, 1.50:1.00, and 2.00:1.00) placed in PVC straws of 3mm diameter were irradiated in air at room temperature in a 60Co Gammacell 220 irradiator at a fixed dose rate of 0.45 kGy/h. Poly(N-vinyl 2-pyrrolidone/acrylonitrile) copolymeric hydrogels obtained in long cylindrical shapes were cut into pieces of 4-5 mm in length, swollen in aqueous medium and reacted with 0.05M hydroxylamine hydrochloride solution (1:1 in NH₂OH.HCl: NaOH) at various temperatures to convert –CN groups to –C=N-OH (amidoxime) groups. Optimum amidoximation conditions were determined by following the uranyl ion adsorption capacity of the amidoximated copolymers (g UO₂²⁺/g dry resin) as a function of amidoximation reaction parameters [46].

**Amidoximated Poly(N,N-dipropionitrile acrylamide)**

Particulate and fibrous adsorbents with enriched amidoxime groups were synthesized by using a novel monomer N,N-dipropionitrile acrylamide (DPAAm). DPAAm monomer was first synthesized by the reaction of 3,3-iminodipropionitrile and acryloyl chloride. The poly-(DPAAm) was synthesized from this monomer by free-radical polymerization by using AIBN as the initiator at 70°C with a conversion efficiency of 77%. The polymer synthesized was reacted with hydroxylamine to convert the nitrile groups into amidoxime groups and 99% conversion was reached.

Uranyl ion adsorption capacities of amidoximated poly(DPAAm) were determined from different initial concentrations (100–1500 ppm) by a batch process. Approximately 0.05 g dry amidoximated poly(DPAAm) was placed into 40 mL metal ion solution buffered at pH 5 in a vial agitated magnetically at moderate rpm for a sufficient time. To determine the amount of metal ions adsorbed onto amidoximated poly(DPAAm), uranyl ion concentrations remaining in the solutions were determined by using Philips 8710 UV–Vis spectrophotometer by using sodium salicylate as a complexing agent [47].

**Amidoximated Polyethylene glycol-Acrylonitrile IPNs**

A new polymeric adsorbent bearing both hydrophilic groups and amidoxime groups for chelating with uranyl ions has been developed. Synthesis of this adsorbent involves two steps. The first step is synthesis of IPNs by dissolving polyethylene glycol (PEG, 35,000) in AN and then irradiating this solution by a 60Co-gamma irradiator with 5.0 kGy h⁻¹ dose rate. These IPNs were immersed into dimethyl formamide (DMF) for 48 h and then into deionized water for 24 h, and finally drying at 40°C to constant mass. The -CN) groups of the IPNs were changed into an amidoxime group by reacting with hydroxylamine solution at a molar ratio of NH₂OH/CN =1.25 in aqueous medium at three different temperatures, 30, 40, and 50°C, for 3–4 days.

The absorption of uranyl ions was performed with a Philips 8715 model PU UV–vis spectrophotometer at the wavelength 430 nm using UO₂(NO₃)₂·6H₂O solution in a concentration range of 100–500 ppm taking sodium salicylate as a complexing agent [48].

**Acrylamide–Maleic acid Hydrogels**

Acrylamide–maleic acid (AAm–MA) hydrogels were prepared by taking 1 g AAm and 20, 40, 60, and 80 mg MA in 1 mL of pure water at different compositions (AAm–MA mole ratios: 98.8: 1.2, 97.6:2.4, 96.5:3.5, 95.3:4.7). These solutions were irradiated in PVC straws 3 mm in diameter in a Gammacel 220–type irradiator at different doses between 0.45 and 18.00 kGy, followed by Soxhlet extraction with water as a solvent to remove uncrosslinked polymer and/or residual monomers.

Adsorption of UO₂²⁺ ions from uranyl acetate solution at time intervals was determined with Philips a 8715 UV–vis spectrophotometer taking sodium salicylate as a complexing agent, giving an absorption maximum at 430 nm [49].

**Poly(2-hydroxyethyl methacrylate/itaconic acid) Hydrogels**

Poly(2-hydroxyethyl methacrylate/itaconic acid) [P(HEMA/IA)] hydrogels were prepared and used for uranyl ion uptake in the presence of lead and cadmium ions. Aqueous solutions of monomers were prepared in pure water in different compositions. These monomer solutions were irradiated in poly(vinyl chloride) straws 4 mm in diameter
The absorption of uranyl ions was performed with a Jenway 5105 UV-visible spectrophotometer using UO$_2$$^{2+}$ and residual monomer from the gel.

The second part of this study explored the uptake of UO$_2$$^{2+}$ ions by hydrogels. To increase the capacity of UO$_2$$^{2+}$ ion uptake while preparing HEMA–IA solutions, 26.5 mM uranyl nitrate solutions was used instead of pure water, remaining preparation being the same. The UO$_2$$^{2+}$ ions held by the crosslinked hydrogels were desorbed into 0.1M NaOH for 30 days (until approximately 100% of the uranyl ions desorbed), and these prestructured hydrogels were dried for further use.

The UO$_2$$^{2+}$ ion uptake of hydrogels prepared in distilled water and prestructured with uranyl nitrate solutions were investigated in the presence of lead and cadmium ions. For this purpose, approximately 0.04 g of each type of dry P(HEMA/IA) hydrogel was immersed in a 20.0-mL solution in the concentration range of 1.85–18.50 µM (pH = 5.54) and allowed to stand for 4 days. The equilibrium concentrations of UO$_2$$^{2+}$ in the solution was determined with a differential pulse polarographic technique [50].

**Poly(N-vinyl 2-pyrrolidone-g-citric acid) Hydrogels**

Poly(N-vinyl 2-pyrrolidone-g-citric acid) hydrogels with varying compositions were prepared from ternary mixtures of N-vinyl 2-pyrrolidone–citric acid–water. Aqueous solutions of N-vinyl 2-pyrrolidone and citric acid were prepared in 1 mL of pure water in different compositions. These solutions were irradiated in the PVC straws of 4 mm diameter to 25 kGy in air at an ambient temperature in a PX-g-30 Isslodovateji irradiator at a fixed dose rate of 3.87 kGy h$^{-1}$. The hydrogels, obtained in long cylindrical shapes, were cut into pieces of 4–5 mm length. The uncrosslinked polymer and ungrafted citric acid were removed from the gels by extraction with distilled water.

Uranyl ions adsorption was studied by spectrophotometric measurements using a Jenway 5105 UV–vis spectrophotometer with sodium salicylate as complexing agent and distilled water as reference. Hydrogels separated from aqueous solutions of uranyl ions were left for 3 days in distilled water at 25°C to investigate the desorption [51].

**Poly(2-hydroxyethyl methacrylate/maleic acid) Hydrogels**

Poly(2-hydroxyethyl methacrylate/maleic acid) hydrogels were prepared by using 2-hydroxyethyl methacrylate, maleic acid and water. Aqueous solutions of monomers were prepared in 1 mL of pure water in different compositions (HEMA/MA molar ratios). These solutions were placed in PVC straws, 4 mm in diameter and were irradiated by 2.8 kGy in air in a PX-g-30 Isslodovateji irradiator at a fixed dose rate of 3.36 kGy h$^{-1}$. The hydrogels, obtained in long cylindrical shapes, were cut into pieces 3–4 mm long and were extracted with water and dried to a constant weight. The uncrosslinked polymer and unreacted MA were removed from the gels by extraction with a 0.1 M HCl solution.

Uranyl adsorption by hydrogel was determined via differential pulse polarography, using UO$_2$($\text{NO}_3$)$_2$ · 6H$_2$O solution (pH = 1–7) in a concentration range of 5–50 ppm [52].

**Poly(N-vinyl 2-pyrrolidone-g-tartaric acid) Hydrogels**

Poly(N-vinyl 2-pyrrolidone-g-tartaric acid) (PVP-g-TA) hydrogels with varying compositions were prepared in the form of rods from ternary mixtures of N-vinyl 2-pyrrolidone-tartaric acid/water. Aqueous solutions of VP and TA were prepared in 1.0 mL of water at different compositions (VP/TA mole ratios of 98.4/1.6, 97.6/2.4, 96.8/3.2). The solutions were irradiated in PVC straws (4-mm diameter) to 25 kGy in air in a PX-g-30 Isslodovateji irradiator at a fixed dose rate of 3.87 kGy h$^{-1}$. The hydrogels were subjected to Soxhlet extraction with water to remove ungrafted TA and residual monomer from the gel.

The absorption of uranyl ions was performed with a Jenway 5105 UV visible spectrophotometer using UO$_2$($\text{NO}_3$)$_2$ · 6H$_2$O solution (pH = 4) in a concentration range of 50–500 ppm and sodium salicylate (10% w/w) with an absorption maximum at 466 nm wavelength as a complexing agent against [53].

**Poly(2-hydroxyethyl methacrylate–methacryloylamidoglutamic acid) Beads**

In order to obtain high uranium adsorption capacity, Poly(2-hydroxyethyl methacrylate–methacryloylamidoglutamic acid) [p(HEMA–MAGA)] beads were synthesised in two steps. First step involves the synthesis of 2-methacryloylamidoglutamic acid by reacting 5.0 g of L-glutamic acid and 0.2 g of hydroquinone in 100 mL of dichloromethane solution. This solution was cooled down to 0°C. Then, 13.0 g triethylamine was added to the solution and 4.0 mL of methacryloyl chloride was poured slowly into this solution under nitrogen atmosphere. This solution was stirred magnetically at room temperature for 2 h. At the end of this chemical reaction period, unreacted methacryloyl chloride was extracted with 10% NaOH. The aqueous phase was evaporated in a rotary evaporator and...
was performed at pH 7.0 where the MAAc is in ionized state. Prepared solutions were irradiated on used as the reaction medium. In order to prevent the complexation between MAAc and PEG the copolymerization copolymerization in the presence of EGDMA as a cross-linker. A mixture of water and ethanol (50:50 vol.%) was placed in PVC straws of 3-mm diameter for polymerization. Polymerization and crosslinking took 1 h in gelation of CASA hydrogels. However, for all hydrogel systems, a waiting period of 24 h has good gelation.

Hydrogels based on polyethylene glycol (PEG) and methacrylic acid (MAAc) were obtained by chemically crosslinked acrylamide/sodium acrylate hydrogels were prepared by free radical crosslinking copolymerization of acrylamide with an anionic co-monomer sodium acrylate (10–80 mg sodium acrylate per gram of acrylamide) and a multifunctional crosslinker EGDMA. 1 g acrylamide was dissolved in 1 mL aqueous solutions containing 0 or 10 mg, (or 20, 30, 40, 50, 60, 70, and 80 mg) sodium acrylate. 0.25 mL of 1% EGDMA solution was added to this aqueous solution followed by addition of 0.20 mL of APS (5 g/dL water) and 0.25 mL of N,N,N’,N’-tetramethylethylenediamine (TEMED) (1 mL/dL water) were added to the solution. The solutions were placed in PVC straws of 3-mm diameter for polymerization. Polymerization and crosslinking took 1 h in gelation of CASA hydrogels. However, for all hydrogel systems, a waiting period of 24 h has good gelation.

Adsorption of UO$_2^{2+}$ from aqueous solutions was investigated in batch experiments. Effects of UO$_2^{2+}$ concentration and pH of the medium on the adsorption rate and capacity were studied. The polymer beads (100 mg) were stirred with a uranium nitrate salt solution at room temperature for 2 h. Elution of UO$_2^{2+}$ was studied in 0.1 M NaHCO$_3$ solution [54].

**Acrylamide/Sodium acrylate Hydrogels**

Chemically crosslinked acrylamide/sodium acrylate hydrogels were prepared by free radical crosslinking copolymerization of acrylamide with an anionic co-monomer sodium acrylate (10–80 mg sodium acrylate per gram of acrylamide) and a multifunctional crosslinker EGDMA. 1 g acrylamide was dissolved in 1 mL aqueous solutions containing 0 or 10 mg, (or 20, 30, 40, 50, 60, 70, and 80 mg) sodium acrylate. 0.25 mL of 1% EGDMA solution was added to this aqueous solution followed by addition of 0.20 mL of APS (5 g/dL water) and 0.25 mL of N,N,N’,N’-tetramethylethylenediamine (TEMED) (1 mL/dL water) were added to the solution. The solutions were placed in PVC straws of 3-mm diameter for polymerization. Polymerization and crosslinking took 1 h in gelation of CASA hydrogels. However, for all hydrogel systems, a waiting period of 24 h has good gelation.

Sorption of uranyl ions was studied by spectrophotometric measurements using Shimadzu UV 1601 model UV-Vis spectrophotometer with uranyl acetate solution and sodium salicylate as complexing agent [55].

**Polyethylene glycol /Methacrylic acid Hydrogels**

Hydrogels based on polyethylene glycol (PEG) and methacrylic acid (MAAc) were obtained by chemically crosslinked acrylamide/sodium acrylate hydrogels were prepared by free radical crosslinking copolymerization of acrylamide with an anionic co-monomer sodium acrylate (10–80 mg sodium acrylate per gram of acrylamide) and a multifunctional crosslinker EGDMA. 1 g acrylamide was dissolved in 1 mL aqueous solutions containing 0 or 10 mg, (or 20, 30, 40, 50, 60, 70, and 80 mg) sodium acrylate. 0.25 mL of 1% EGDMA solution was added to this aqueous solution followed by addition of 0.20 mL of APS (5 g/dL water) and 0.25 mL of N,N,N’,N’-tetramethylethylenediamine (TEMED) (1 mL/dL water) were added to the solution. The solutions were placed in PVC straws of 3-mm diameter for polymerization. Polymerization and crosslinking took 1 h in gelation of CASA hydrogels. However, for all hydrogel systems, a waiting period of 24 h has good gelation.

Sorption of uranyl ions was studied by spectrophotometric measurements using Shimadzu UV 1601 model UV-Vis spectrophotometer with uranyl acetate solution and sodium salicylate as complexing agent [55].

**Poly(1-vinyl imidazole-co-acrylic acid) Hydrogels**

Crosslinked poly(1-vinyl imidazole-co-acrylic acid) and crosslinked poly(1-vinylimidazole-co-2-acrylamido-2-methyl-1-propanesulfonic acid) were synthesized by radical polymerization by Rivas et al. Synthesis of crosslinked poly(1-vinyl imidazole-co-acrylic acid) was carried out by mixing 0.03 mol (2.7 mL) of 1-vinyl imidazole, 0.03 mol (2.5 mL) of acrylic acid, 2.0 mol % of MBAAm as crosslinker, and 1.0 mol % of ammonium persulfate as initiator. Similarly, crosslinked poly(1-vinylimidazole-co-2-acrylamido-2-methyl-1-propanesulfonic acid) was synthesized by mixing 0.016 mol (1.44 mL) of 1-vinyl imidazole, 0.016 mol (3.4 g) of 2-acrylamido-2-methyl-1-propanesulfonic acid, 0.00064 mol (2.0 mol %) of N,N-methylene-bisacrylamide, and 0.00032 mol (1.0 mol %) of ammonium persulfate. Both the reaction mixtures were kept under nitrogen at 70°C for 24 h. The resins were filtered and washed with abundant water and dried up to constant weight.

Batch metal uptake experiments were performed using standard metal salt Cu(NO$_3$)$_2$ . 6H$_2$O solution in a concentration range of 100–500 ppm and sodium salicylate as a complexing agent [56].

**Poly(1-vinyl imidazole-co-acrylic acid) and Poly(1-vinylmidazole-co-2-acrylamido-2-methyl-1-propanesulfonic acid) Hydrogels**

Crosslinked poly(1-vinyl imidazole-co-acrylic acid) and crosslinked poly(1-vinylimidazole-co-2-acrylamido-2-methyl-1-propanesulfonic acid) were synthesized by radical polymerization by Rivas et al. Synthesis of crosslinked poly(1-vinyl imidazole-co-acrylic acid) was carried out by mixing 0.03 mol (2.7 mL) of 1-vinyl imidazole, 0.03 mol (2.5 mL) of acrylic acid, 2.0 mol % of MBAAm as crosslinker, and 1.0 mol % of ammonium persulfate as initiator. Similarly, crosslinked poly(1-vinylimidazole-co-2-acrylamido-2-methyl-1-propanesulfonic acid) was synthesized by mixing 0.016 mol (1.44 mL) of 1-vinyl imidazole, 0.016 mol (3.4 g) of 2-acrylamido-2-methyl-1-propanesulfonic acid, 0.00064 mol (2.0 mol %) of N,N-methylene-bisacrylamide, and 0.00032 mol (1.0 mol %) of ammonium persulfate. Both the reaction mixtures were kept under nitrogen at 70°C for 24 h. The resins were filtered and washed with abundant water and dried up to constant weight.

Batch metal uptake experiments were performed using standard metal salt Cu(NO$_3$)$_2$ . 6H$_2$O solution in a concentration range 1–5. The capacities for Cu(II) and UO$_2^{2+}$ under noncompetitive and competitive conditions were determined as a function of pH. To obtain the maximum adsorption capacity for the metal ions, 50 mL of an aqueous solution, 1 g/L, was shaken with 0.1 g of the resin for 1 h at 25 °C. The mixture in the flask was filtered and washed with water, and the filtered solution was transferred into a calibrated flask. The process was repeated three times, the volume was made up to 250 mL, and then the metal ion was determined by colorimetry by atomic absorption spectrometry [57].

**Poly(hydroxamic acid) Hydrogels**

Saraydin et al. reported the use of poly(hydroxamic acid) for uranyl ion uptake. In the first step of synthesis, an aqueous solution of acrylamide and MBAAm or EGDMA (95:5 in mole ratio in 0.4 mol water) with 0.01 mmole ammonium persulphate and 2.5 mmole TEMED were mixed and placed in PVC straws of 4 mm diameter at 4°C. Poly(AAm) hydrogel was formed after 20 min of reaction. After 24 h the hydrogel rods were cut into pieces 3-4 mm length. For preparation of acid form of poly(hydroxamic acid), a solution of hydroxylamine hydrochloride (3 M,
100 mL) was added to 20 g crosslinked poly(AAm) in 300 mL distilled water. The resulting mixture was stirred for 2 hours at ambient temperature. To prepare the sodium salt of poly(hydroxamic acid), a solution of NaOH (7.5 M 50 mL) was added to 20 g acid-form of poly(hydroxamic acid) in 300 mL distilled water and stirred for 24 h.

For the study of the binding kinetics of uranyl ions, spectrophotometric measurements were carried out using a Hitachi model UV-Vis spectrophotometer by using uranyl nitrate or uranyl acetate solutions and sodium salicylate as a complexing agent at a wavelength of 327 nm [58].

**Polyethylene/Acrylonitrile, Polyethylene/Acrylic acid Adsorbents**

The polyethylene (PE) adsorbents were prepared by a radiation-induced grafting of acrylonitrile (AN), acrylic acid (AAc), and the mixture of AN/AAc onto PE film, and by subsequent amidoximation of cyano groups of poly-AN graft chains. The PE film was irradiated by γ-ray from Co-60 source (Co-60 Gamma-ray Irradiator IR-79) under atmospheric pressure and ambient temperatures, and then immediately the irradiated PE film was grafted with a monomer. The unreacted monomer and homopolymers after grafting were removed with DMF using Soxhlet apparatus, and then methanol. AN-grafted PE film obtained by grafting copolymerization was dried in a vacuum oven at 60°C for 7 h.

The amount of UO$_2^{2+}$ absorbed onto the PE adsorbent was determined by ICP. First, the initial molar concentration of UO$_2^{2+}$ was set at 100 mg per liter (100 ppm). After, uranyl ion was adsorbed by PE adsorbent for 24 h, the PE adsorbent (0.20±0.24 g) was taken out of the solution, and then the concentration of the remained solution was [59].

**Poly(AAm-co-AAc) and poly(AAm-co-MAAc) Hydrogels**

We reported the synthesis and characterization of two copolymeric hydrogels based on AAc and MAAc with AAm for use in the removal and sorption of the uranyl ions from saline conditions. In a novel research plan, the hydrogels were synthesized by polymerizing AAm separately with equimolar amount of AAc and MAAc using APS as initiator and EGDMA as crosslinker to get crosslinked bifunctional hydrogels namely poly(AAm-co-AAc) hydrogel and poly(AAm-co-MAAc) respectively.

The hydrogels are bifunctional and have both amide and acid functional groups. Uranyl ion uptake was investigated on Cary 300 UV-Spectrophotometer. Known weight of the dried hydrogel was subjected to swell in the solution of desired concentration of uranyl nitrate (0.0025, 0.005, 0.01, 0.02, 0.03, 0.04 and 0.05 m mol/L) in different concentrations of sodium chloride solution (1%, 2% and 3%) and 0.1 M sodium carbonate solution. The hydrogels were immersed in 50 mL solution of uranyl nitrate for different time intervals (1h, 2h and 4h) at five different temperatures i.e. 25°C, 30°C, 35°C, 40°C and 45°C. The rejected filtrate of each solution was spectrosopically analyzed on Cary 300 UV-vis Spectrophotometer at an absorption maxima 215 nm [60].

**CONCLUSION**

From the foregone discussion, it is evident that in the recent past much attention has been paid in the direction of recovering uranium from sea water, coal and natural waters. The recovery of uranium from contaminated water of flooded mines is also a very important environmental problem to be solved. Presently, many research groups are engaged in the enrichment and separation of uranyl ions for both environment management as well as to be used as fuel in nuclear plants. In the recent past use of hydrogels or copolymers as adsorbents for the removal of uranium from sea water, coal, various effluents, and natural waters has tremendously increased. A variety of hydrogels and copolymers have been designed for this purpose and many methods for separation of uranyl ions have been developed. Most of such hydrogels/copolymers involve amidoxime, carboxyl, amide, nitrile, amine and sulphonic acid groups. Most of these hydrogels are prepared by free radical polymerization reactions involving persulphate initiator and suitable crosslinkers. Most commonly used method for determination of equilibrium concentrations of UO$_2^{2+}$ ions is UV-visible spectrophotometry. In some cases ICP and differential pulse polarographic techniques are also used for this purpose. Although many researchers have been working in the field of enrichment and separation of uranium/uranyl ions for last four to five decades, but yet a lot has to be done in this field.

**REFERENCES**


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