Application of Highly Swollen Novel Biosorbent Hydrogels in Uptake of Uranyl Ions from Aqueous Solutions

Erdener Karadağ* and Semih Kundakçı

Department of Chemistry, Fen-Edebiyat Faculty, Adnan Menderes University, Aydın TR-09010, Turkey
(Received July 10, 2015; Revised September 3, 2015; Accepted September 10, 2015)

Abstract: The aim of this study was to investigate the equilibrium swelling and uranyl ion sorption properties of chemically crosslinked copolymeric hydrogels as biopotential sorbent consisting of acrylamide (AAm), sodium acrylate (SA), gelatin (GEL) and poly(ethylene glycol) (PEG). Semi-interpenetrating polymer network (semi IPNs) hydrogel, composed of AAm with SA as co-monomer, with PEG and GEL and a multifunctional crosslinker such as poly(ethylene glycol) diacrylate (PEGDA) was prepared by free radical solution polymerization by using ammonium persulphate (APS)/N,N,N',N'-tetramethylethylenediamine (TEMED) as redox initiating pair. Swelling experiments were performed in water at 25 °C, gravimetrically. The hydrogels showed enormous swelling in water and displayed swelling characteristics that were highly dependent on the chemical composition of the hydrogels. For characterization, FT-IR, thermogravimetric analysis (TG and DTG) and surface morphology (SEM) studies have been realized. FTIR spectroscopy was used to identify the presence of different repeating units in the semi IPNs. Some swelling and diffusion characteristics were calculated for different semi IPNs and hydrogels prepared under various formulations. For sorption studies, uranyl ion into the hydrogels was studied by batch sorption technique at 25 °C. Sorption capacity, removal efficiency and partition coefficient of the hydrogels was investigated. Swelling and uranyl ion sorption properties of AAm/SA, AAm/GEL/SA, AAm/PEG/SA and AAm/GEL/PEG/SA hydrogel systems were investigated as a function of chemical composition of the hydrogels.

Keywords: Swelling, Hydrogel, Interpenetrating polymer networks, Acrylamide, Sodium acrylate, Uranyl ion

Introduction

The use of polymer hydrogels as biopotential sorbent or carriers for the removal of the model molecules from aqueous solutions or controlled release studies of them has been continued to attract considerable attention in recent years. Hydrogels are polymers in three-dimensional network arrangement, which are able to retain large amount of water. In order to keep the spatial structure, the polymer chains are usually physically or chemically crosslinked. Due to their swelling capacity, hydrogels can be easily rinsed to remove reagents residues. On the other hand, the big water content that makes hydrogels such a special class of materials [1-10]. Hydrogels are macromolecular polymer networks immersed in a solvent, synthesized to exhibit large volumetric swelling in response to a variety of environmental stimuli [11-18]. Materials with the ability to absorb water in high amounts are again under investigation, because of their potential applications in bioengineering, biomedicine, food industry, communication technology, building industry, chromatography, water purification, separation processes and agriculture [19-27]. Studies have been reported on the use of hydrogels or hydrophilic characteristic crosslinked polymers or copolymers as adsorbents for the removal of heavy metals, for the recovery of dyes, for removal of toxic or radioactive elements from various effluents and for metal pre-concentration for environmental sample analysis from aqueous solutions [3,7,8,11,14,18,19,22,23,25-27].

For removal of toxic heavy metals, in connection with wastewater treatment strategy, still remains a major topic of present research. The removal and recovery of heavy metal ions such as uranyl ion, or others has a potential a wide range of applications in conservation of the environment and use of resources. Radionuclide migration in natural aqueous systems is an ongoing concern in environmental research. Knowledge of the transport of radio nuclides through the environment is important for assessing the risk posed by long-term storage of nuclear waste and also for determining the migration of naturally radioactive materials in the geologic environment near population centers. Uranium is an element of considerable technological importance. Nuclear power is derived from uranium, which has no significant commercial use other than as a fuel for electricity generation [27-39].

In recent years polymeric gels (hydrogels) are the objects of intensive studies. The use of polymer hydrogels for the removal of uranyl ion from wastewater or aqueous solutions has been continued to attract considerable attention in recent years. Many methods have been proposed for the removal of dyes, heavy metals and other hazardous materials. Chemical precipitation, membrane extraction, coagulation, solvent extraction, ion change, and adsorption are some of the commonly used processes, but each has its own merits and demerits in its applications. Adsorption procedures are a way of the most widely used for pollutants such as dyes and organic compounds from industrial effluents. Adsorption is a well-known equilibrium separation process. Recently, new effective, efficient and economic methods for water decontamination applications and for separation analytical purposes

*Corresponding author: ekaradag@adu.edu.tr
have been investigated [3,9,11,13].

Polyacrylamide based hydrogels have received considerable attention because of their use in many applications. In our and others previous studies, copolymeric hydrogels of acrylamide with some acidic monomers were prepared by free radical solution polymerization and used in separation and adsorption of some dye molecules [3,14,19,22,26,34-38,40,41].

Gelatin (GEL) is a biopolymer and a commonly used natural polymer which is derived from collagen. GEL has got some properties such as biodegradability, non-carcinogenicity and hydrophilicity. So, corporation of this biopolymer into the polymeric or copolymeric systems could improve its properties because of some functional groups in the gelatin. GEL is an important material used for the manufacture of hard and soft capsules, microspheres, wound dressing and adsorbent pad for surgical use [40-47].

A linear polymer, (PEG) can be used for mechanical stability agent for semi-interpenetrating polymer networks (semi IPNs). PEG is of great interest in numerous biomedical applications for several purposes. PEG is water-soluble and is non-toxic for body immune system. PEG based hydrogels have good biocompatibility. PEG based hydrogel systems have been used at many biotechnological applications [48-50]. In order to improve its mechanical strength and increase porosity, polymers such as PEG can be added to hydrogel systems.

The present paper reports that swelling study in water and sorption study of uranyl ions by a novel type of new polymeric adsorbent containing AAm, SA, GEL and PEG. In this study, it was of interest to increase the water and uranyl ions sorption capacity of AAm hydrogels with highly hydrophilic functional groups containing chemical reagents such as SA with GEL and PEG via free radical solution polymerization method. It was reported that some groups have been synthesized SA based crosslinked polymers and/or copolymers [51-56]. AAm is a highly hydrophilic monomer, SA is an anionic monomer, GEL is a natural polymer, and PEG is a linear synthetic polymer. The main purpose of this study was to combine both monomers and the polymers in a new polymeric system. In this respect, a series of copolymeric hydrogels were synthesized by changing the content of SA, GEL and PEG. Then, some swelling, and some diffusional properties of AAm/SA, AAm/GEL/SA, AAm/PEG/SA and AAm/GEL/PEG/SA hydrogel systems were studied in water by dynamic swelling studies for swelling characterization. Water uptake and uranyl ions sorption properties of AAm/SA, AAm/GEL/SA, AAm/PEG/SA and AAm/GEL/PEG/SA hydrogel systems were investigated as a function of chemical composition of the hydrogels.

**Experimental**

**Materials**

AAm as monomer was supplied from Aldrich, Steinheim, Germany. SA as co-monomer, PEG, (Mn=4000), PEGDA, (Mn=700) as crosslinker were supplied from Aldrich, Steinheim, Germany. The initiator, APS was purchased from Merck, Darmstadt, Germany and the activator TEMED was purchased from Merck Schuchardt, Germany. Natural polymer, GEL (250 g Bloom) was supplied from Fluka, Steinhelm, Germany. Uranyl acetate, (UA) used in sorption studies, and sodium salicylate were purchased from Merck, Darmstadt, Germany. All chemicals were used as received.

**Preparation of AAm/SA, AAm/GEL/SA, AAm/PEG/SA and AAm/GEL/PEG/SA Hydrogel Systems**

To prepare AAm/SA hydrogel systems, 1.0 g AAm (14.07 mmol) was dissolved in 1.0 mL water. Then 0 mg, 10 mg (0.106 mmol), 20 mg (0.213 mmol), 30 mg (0.319 mmol), 40 mg (0.425 mmol), 50 mg (0.532 mmol), 60 mg (0.638 mmol), 70 mg (0.744 mmol), 80 mg (0.851 mmol) SA were added to each AAm solution, respectively. After that, 0.25 mL (0.004 mmol) of 1% concentration of PEGDA, 0.2 mL/0.0438 mmol aqueous solutions of APS (5.0 g APS/0.022 mol/100 mL water) and 0.25 mL/0.0167 mmol of 1% concentration of TEMED were added these aqueous solutions. The solutions were placed in PVC straws of 3 mm diameter. After gelation, fresh hydrogels obtained in long cylindrical shapes were cut into pieces of 3-4 mm in length. They were washed 4 days in distilled water to remove unreacted materials, blotted dry with filter paper, dried in air and vacuum, and stored for swelling studies [40,41,44].

To prepare highly swollen AAm/GEL/SA/PEG semi IPNs containing various contents of PEG, same method was used as mentioned above with addition of 0.125; 0.25; 0.375 and 0.50 g PEG to aqueous monomer solution per 1.0 g of AAm, 60 mg (0.638 mmol) SA, 0.5 mL of water and 0.5 mL of 10% of aqueous GEL solution mixtures.

To prepare of AAm/GEL hydrogels, the mixture of 0.5 mL of 10% of aqueous GEL solution and 0.5 mL of water was used. For AAm/SA/PEG/GEL hydrogel systems containing various amount of GEL, same method was used as mentioned above with addition of 0.25, 0.75 and 1.00 mL of 10% aqueous GEL solution to aqueous monomer solution per 1.0 g of AAm, 60 mg (0.638 mmol) SA and 0.25 g PEG with 0.75, 0.25 and 0.00 mL of water. The quantities of AAm, SA, GEL and PEG were presented in Table 1 [40,41,44].

**FT-IR Analysis**

For structural characterization, FT-IR analysis was made. Spectra were obtained by VARIAN FTS 800 FT-IR spectrophotometer using KBr discs.

**Thermogravimetric Analysis**

The dynamic weight loss tests were conducted on a SEIKO SII TG/DTA 6300 thermogravimetric analyzer. Effect of the contents of monomer or co-monomers onto synthesis of the gels thermogravimetric analysis was performed. In order to