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Synthesis and characterization of uranyl ion-imprinted microspheres based on amidoximated modified alginate

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ABSTRACT

Surface ion-imprinting technique was utilized for the preparation of surface ion-imprinted chelating microspheres based on amidoximated modified alginate (U-AOX) in presence of uranyl ions as a template and glutaraldehyde cross-linker. Different instrumental techniques such as elemental analysis, scanning electron microscope (SEM), FTIR, X-ray photoelectron spectroscopy (XPS) and X-ray diffraction spectra were employed for full investigation of the manufactured materials. The synthesized microspheres displayed a higher ability for selective extraction of UO_2^{2+} when compared to the non-imprinted microspheres (NI-AOX). In addition, the essential parameters such as pH, temperature, time and initial uranyl ion concentration were evaluated in order to optimize the conditions of the adsorption process. The results indicated that pH 5 was the best for the UO_2^{2+} removal, also, the adsorption was endothermic in nature, follows the second-order kinetics and the adsorption isotherm showed the best fit with Langmuir model with maximum adsorption capacity of 155 ± 1 and 64 ± 1 mg/g for both U-AOX and NI-AOX respectively. Desorption and regeneration had been carried out using 0.5 M HNO_3 solution and the results indicated that the microspheres maintained about 96% of its original efficiency after five consecutive adsorption-desorption cycles.

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1. Introduction

Uranium is considered one of the most important radio-active elements that have been extensively utilized in the applications of nuclear power. Due to its high chemical activity and toxicity, it could be dangerous on the human health particularly at high concentrations. Hexavalent uranyl ion (UO_2^{2+}) regarded as the most stable form in aqueous medium, through this form, uranium can easily coordinate to the plasma protein in blood and accumulate in the sensitive body organs such as liver, kidneys, lung and even bones, which will subsequently lead to a sever diseases like renal failure or cancer [1–3]. For these reasons, and in view of the environmental risks, several attempts were performed for efficient extraction of uranyl ions from the contaminated aqueous media [4–7].

Many environmental aquatic pollutants such as toxic heavy metals in addition to organic species were successfully removed using adsorption technique [8–12]. Adsorption is not regarded as

just an extraction technique; it can also be employed in the recovery and enrichment of the adsorbate, particularly when we deal with valuable species like precious metals [13,14]. The ease of performance as well as the availability of the adsorbents, made the adsorption technique one of the most preferred extraction technique, particularly from the economic point of view [1]. Different materials such as clay [15], modified natural polymers like chitosan [16,17] and cellulose [18], in addition to modified synthetic polymer like PET [19,20] were extensively utilized as an effective adsorbents reducing the heavy metal contents in aqueous media. Among these types of adsorbents polysaccharide biopolymers such as alginate have displayed an obvious efficiency as a bio-adsorbent for such aquatic pollutants [21–23]. Sodium alginate (SA) is the salt of alginic acid, which consists of guluronic and mannuronic acid residues was employed in the extraction of some pollutants from aqueous media as a result of its excellent hydrophilicity, bindingability, low-cost, biocompatibility and renewability [21,24]. However, the absence of selectivity considered a vital disadvantage concerning the specific extraction of certain species in presence of other interfering ones. That is why; more efforts are needed to develop novel techniques for enhancement of the adsorbent selectivity toward specific targeted species.

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Ion imprinting considered as one of the most promising strategies for manufacturing of smart polymeric materials containing active binding sites that are able to selectively interact with specific targeted ionic species due to the high match in size, charge and coordination geometry [25,26]. Several heavy metal ions such as chromium [26], zinc [27], uranyl [28] and lead [29] were successfully extracted using various types of ion-imprinted polymers (IIPs). However, the IIPs manufactured by conventional entrapment methods possess several drawbacks such as the large diffusion barrier, complicated manufacturing process and deformation of some recognition sites as a result of the mechanical crushing and grinding [19]. In order to effectively reduce these disadvantages, several studies were performed to develop surface ion-imprinted polymers, where the active recognition sites were created on the surface of a suitable support [4,18,19,30,31].

In this current study a modified uranyl surface ion-imprinted microspheres based on Al(III) cross-linked amidoximated alginate (U-AOX) were prepared and fully characterized using several instrumental techniques such as scanning electron microscope, FTIR, XPS and XRD spectra. Both ion-imprinted U-AOX and non-imprinted NI-AOX were employed in a series of batch experiments to evaluate the potential of the utilized surface ion-imprinting technique for selective extraction of uranyl ions from aqueous media.

2. Experimental

2.1. Materials

Sodium alginate (SA) ($M_w = 60,000\text{--}80,000$), acrylonitrile (AN), hydroxyl amine and Uranyl nitrate hexahydrate $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were all supplied from Sigma–Aldrich. AN was treated with 3% aqueous NaOH solution to remove the stabilizer and then washed with distilled water until alkali free and stored over anhydrous CaCl_2 and molecular sieves. Potassium permanganate (KMnO_4) and oxalic acid were purchased from Adwic and used as received.

2.2. Preparation of alginate cross-linked microspheres

Water/oil (W/O) emulsion method was employed for the ionic cross-linking of alginate; 5 g of the SA were vigorously stirred in 100 mL distilled water till complete dissolution. Then, SA solution was added dropwise to the dispersion medium that composed of a mixture of 300 mL cyclohexane, 150 mL n-hexanol and 1.5 mL Triton X-100 emulsifier. The mixture was then mechanically stirred at 1000 rpm for about 15 min. The ionic cross-linker AlCl_3 aqueous solution (50 mL 50%, w/v) was then injected into the reaction mixture and stirring was continued for 1 h. The obtained cross-linked alginate microspheres were then filtered, washed with distilled water, ethanol and finally dried at 40 °C in a vacuum oven.

2.3. Graft copolymerization of PAN onto alginate microspheres

The grafting reaction was carried out utilizing KMnO_4 /oxalic acid combined redox initiator. In a conical flask, the redox initiator system consists of 10 mL 2 mM KMnO_4 and 10 mL 4 mM oxalic acid was mixed, to which 1 g of the previously prepared cross-linked alginate microspheres was added and the flask was vigorously shaken at room temperature. After about five minutes, the temperature raised to 70 °C, 0.15 mol of the AN monomer was gradually injected into the reaction mixture and shaking was continued for 2 h. The resulted polymeric crude was then filtered, washed with ethanol and hot DMF to extract the PAN homopolymer. The grafted alginate microspheres (PAN-g-AG) were extracted and dried in

oven at 40 °C overnight. The grafting percentage (GP) was estimated according to the following equation.

$$GP = \left(\frac{A - B}{B} \right) \times 100 \quad (1)$$

where A and B are the weight of grafted and native alginate microspheres, respectively.

2.4. Preparation of (U-AOX) ion-imprinted microspheres

The surface ion imprinted U-AOX microspheres were prepared according to the following steps.

First of all the previously prepared PAN-g-AG was implemented in further modification by converting the $-\text{CN}$ into amidoxime ($\text{H}_2\text{N}-\text{C}=\text{N}-\text{OH}$) groups through treatment with NH_2OH . 1 g of the grafted PAN-g-AG copolymer was immersed in a mixture of 25 mL aqueous 20% (w/v) hydroxylamine hydrochloride solution and 25 mL aqueous 20% (w/v) NaOH solution. The reaction flask was then fitted with a reflux condenser and the reaction continued for 6 h at 80 °C with magnetic stirring. The obtained chelating microspheres were named PAO-g-AG.

The coordination with uranyl ions was carried out by equilibrating the previously modified PAO-g-AG with 100 mL UO_2^{2+} aqueous solution (100 mg/L) at pH 5, 150 rpm and for 3 h. The obtained UO_2^{2+} loaded microspheres were then separated and washed with distilled water to remove the non-adsorbed metal ions.

In the next step, the uranyl loaded microspheres were soaked in round bottomed flask containing 50 mL 25% glutaraldehyde solution and the mixture was refluxed at about 80 °C with continuous magnetic stirring. After 2 h, the microspheres were filtered, washed with distilled water and ethanol. The ion-imprinted U-AOX microspheres were then obtained by leaching the template uranyl ions out of the surface cross-linked network by continuous stirring with 100 mL 0.5 M HNO_3 till no uranyl ions detected in the filtrate solution. For comparison, non-imprinted microspheres (NI-AOX) were prepared using the aforementioned procedure but without loading with uranyl ions. Schematic presentation for the synthesis and imprinting processes were displayed in Schemes 1 and 2, respectively.

2.5. Characterization of samples

PerkinElmer 240 C Elemental Analytical Instrument (USA) was employed in the performance of the elemental analysis of the prepared polymeric materials

FTIR spectra were carried out in a PerkinElmer Fourier transform infrared instrument. The studied samples were mixed with KBr and compressed in form of discs.

The morphology of the manufactured microspheres were visualized using FEI Quanta-200 scanning electron microscope (SEM) (FEI Company, USA)

ASAP 2010 Micromeritics instrument was utilized in the surface area measurements via Brunauer–Emmett–Teller (BET) method and Micromeritics software.

X-ray diffraction (XRD) spectra were executed using X-ray powder diffractometer (Japanese Dmax-rA, wavelength = 1.54 Å, Cu $K\alpha$ radiation). The samples were scanned from $2\theta = 5\text{--}70^\circ$, in step of 0.02° using generator intensity of 40 kV and generator current of 50 mA.

X-ray photoelectron spectra (XPS) were performed in FAT mode using a Kratos XSAM-800 multifunctional spectrometric apparatus (VG Science Instrument Co. Ltd., Britain) with the X-ray gun of Mg target (1486.6 eV) at the power of 12 kV 3 15, the channel energy of 100 eV and the step length of 0.1 eV/s.

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