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MCM-41 silica particles grafted with polyacrylonitrile: Modification in to amidoxime and carboxyl groups for enhanced uranium removal from aqueous medium

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ABSTRACT

The uranium ion adsorption on the pristine MCM-41, amidoxime (AMD) and carboxyl (CA) groups modified particles was studied. The amounts of adsorbed U(VI) ions onto the pristine MCM-41, CA and AMD modified MCM-41 particles were found to be 58.9, 296.7 and 442.3 mg/g, respectively. The experimental equilibrium data was found to fit the Langmuir model well for all the tested adsorbents. The pristine, CA and AMD modified particles can be regenerated using 10 mM HNO_3 solution with more than 95% recovery. Hence, AMD and CA modified particles are stable, and easily regenerated. Particularly, AMD modified MCM-41 particles with high adsorption capacity seems to be a promising adsorbent for removal of U(VI) ions from aqueous solutions.

1. Introduction

Uranium is a heavy metal having both radiochemical and toxicological effects [1,2]. It is found in the environment in the hexavalent form, and it has biologically dynamic activity and chemical toxicity, leading to potential long-term harm to mammalian reproduction systems in the form of reduced fertility [3–5]. The removal of uranium ions from aqueous medium can be performed by physical and chemical methods such as adsorption, ultrafiltration, coagulation, precipitation, membrane filtration and electrochemical techniques [4–6]. The adsorption is considered to be an efficient and promising method for removal of U(VI) and other metal ions. Adsorption of U(VI) ion on different functional groups containing adsorbents from aqueous solutions had been extensively studied, and results indicated that the adsorption of U(VI) ion was mostly dominated by ion-exchange and/or surface complexation at acidic pH values. A number of absorbents such as, silica particles [7], functionalized synthetic resins [8], metal oxides [9], chitosan [10], and various biomass [2] have been investigated for the removal of U(VI) from aqueous solutions. Among them, silica particles have attracted much attention for development of novel adsorbents with high surface areas, uniform pore structures, excellent thermal and mechanical stability, and high sorption capacities for removal of radionuclides [7,11–13]. Additionally, silicate is stable both chemically and mechanically, thus highly resistant to microbial attack. Moreover, they can easily be modified with various functional groups [14–18]. Adsorption of U(VI) using modified silica is reported in literature [13,19,20]. For examples, Incili and Aycık studied the adsorption of U(VI) from aqueous solution using hydrazone derivative ligand immobilized silica gel, and the maximum U(VI) uptake capacity was found to be 8.5 mg g^{-1} [7]. Zhao et al., studied uranium adsorption from aqueous solution using amidoxime-functionalized magnetic mesoporous silica particles, and the maximum adsorption capacity was reported as 277.3 mg g^{-1} [11]. Gao et al., prepared dopamine-functionalized mesoporous silica particles, and the maximum adsorption capacity of the adsorbent for U(VI) ions was 196 mg/g at pH 6.0 [12]. Yuan et al., studied the adsorption of U(VI) from aqueous solution using phosphonate modified silica and the maximum sorption capacity of the adsorbent was 303 mg g^{-1} [13]. The adsorption properties of the silica particles can be further improved by grafting of their

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surface with comb type polymer, and subsequence modification of the grafting polymer into various functional groups which results in an increase surface area and binding sites for the target metal ions. Some recent studies have reported on the use of grafted comb type polymeric materials via surface-initiated atom transfer radical polymerization (SI-ATRP) technique for the removal of metal ions and organic pollutants from aqueous solution [21–28]. For example, Saito et al. prepared a novel adsorbent using ATRP combined with radiation-induced graft polymerization for uranium recovery from seawater [29]. As reported in these studies, grafting fibrous polymer chains can improve the surface area of the adsorbents, and thus, reduce the required dosage of the adsorbent in the adsorption medium for elimination of metal ions and other target molecules.

The purpose of the present study is to construct a novel comb type polymer chain grafted particles with enhanced adsorption capacity for uranium ions. The silica particles were prepared by sol gel methods, and grafted with PAN via the ATRP method, and modified into AMD and CA groups with reaction of hydroxyl amine and HCl hydrolysis. The amine and hydroxyl groups on the AMD ligand can act as chelation sites for U(VI) or other metal ions. On the other hand, CA group can act as an ion-exchange group for metal ions. ATR-FTIR spectroscopy, SEM, zeta-sizer analyses and analytical methods were used to characterize pristine and modified particles. To evaluate the removal mechanism and kinetics, the effects of the removal parameters such as: pH, temperature, equilibrium time and effect of initial uranium (VI) concentrations on the removal efficiency were investigated.

2. Materials and methods

2.1. Material

Cetyltrimethylammonium bromide (CTAB, purity ≥99%), sodium silicate, ammonium hydroxide solution (28.0%), sodium hydroxide, absolute ethanol (purity ≥99.5%) were supplied from Sigma–Aldrich (Germany). Acrylonitrile, bipyridine, triethylamine, dimethylformamide (DMF), CuBr, 2-bromo-2-methylpropionyl bromide, tetrahydrofuran (THF), acetonitrile (ACN), hydroxylamine hydrochloride ($NH_2 \cdot OH \cdot HCl$), and methanol were supplied by Sigma–Aldrich.

2.2. Preparation of MCM-41 particles

Cetyltrimethylammonium bromide (CTAB) (4.0 g) was transferred in a solution composed of water (186 mL) and 2-proponal (14 mL), and the mixture was stirred magnetically at room temperature for 2.0 h. Sodium silicate (2.2 mL) was mixed with purified water (66 mL), and stored at 4 °C for 2.0 h. Then, CTAB solution was added to the sodium silicate solution drop-wise about 1.0 h, and sonicated at 25 °C for 2.0 h. After this period, ethylacetate (20 mL) was added to this mixture, and further sonicated for 5 min. Final solution was stirred at 30 °C for 5.0 h, and incubated at 80 °C for 72 h. Then, the solution on the precipitate was removed by aspiration and washed with purified water. The resulting product was collected by centrifugation at 5000 rpm for 10 min, and dried in a vacuum oven at 35 °C for 18 h. The dried MCM-41 particles were transferred in porcelain crucible, and heated at a rate of 1.0 °C/min to 540 °C in an oven for calcinations of particles.

2.3. Br-end surface modification of MCM-41 particles

For the immobilization of ATRP initiator, the MCM-41 particles (about 3.0 g) in 3-aminopropyltriethoxy silane (9 mL) were sonicated for 30 min at 25 °C. Then, the reaction medium was refluxed at 70 °C for 18 h. After the reaction period, MCM-41 particles were washed with ethyl alcohol, and dried at 45 °C for 6.0 h. For Br-end modification of the particles (3.0 g), tetrahydrofuran (50.0 mL), and triethylamine (2.0 mL) were transferred into a flask, and stirred under nitrogen atmosphere at −5.0 °C. Then, 2-bromo-2-methylpropionyl bromide (2.0 mL) was added drop wise within 30 min, and incubated at 25 °C for 4.0 h. The Br-end functionalized silica particles were dried at 35 °C for 18.0 h, and used for the grafting polyacrylonitrile (PAN) brushes.

2.4. Grafting of PAN brushes by ATRP and amidoximation

For grafting reaction, Br-end modified MCM-41 particles (about 2.0 g) were transferred into a flask (100.0 mL), and monomer acrylonitrile (6.0 mL), CuBr (0.1 g), bipyridine (0.5 g), and dioxane (5.0 mL) were added. The reaction medium was purged with nitrogen, and then sealed. The grafting reaction was carried out at 65 °C for 6–24 h. After the reaction, the product was washed with acetone (100.0 mL), in order to remove copper ion, PAN grafted particles were transferred in EDTA solution (2.0%, w/v), and stirred continuously for 48 h. The MCM-41-g-PAN particles were washed sequentially with water and ethanol.

The grafted PAN on MCM-41 particles, were converted to amidoxime groups by the reaction with hydroxylamine on the basis of a previously reported method [30]. The AMD group carrying MCM-41 particles were washed with a sodium hydroxide solution (2%, w/w), and the final product was washed with purified water before U(VI) ion adsorption studies.

2.5. Acid hydrolysis of PAN brushes on the MCM-41 particles

The PAN grafted MCM-41 particles were subjected to dilute HCl hydrolysis for creation carboxyl groups. The MCM-41-g-PAN particles (5.0 g) were transferred in HCl solution (0.1 M). The reaction was carried out at 65 °C for 6.0 h under reflux conditions (Equation (1)). After reaction, carboxyl groups modified MCM-41-g-PAN particles were collected and then washed with purified water (250 mL). The CA groups modified particles were dried in an oven at 45 °C for 18 h under reduced pressure.

$$\underset{\textstyle C{\equiv}N}{\text{-}[CH_2\text{-}\overset{|}{C}H]\text{-}} + 2H_2O + HCl \rightarrow \underset{\textstyle COOH}{\text{-}[CH_2\text{-}\overset{|}{C}H]\text{-}} + NH_4Cl \quad (1)$$

2.6. Adsorption studies

The adsorption of U(VI) ion on the pristine and ADM and CA groups modified MCM-41 particles was investigated in a batch system. Uranium acetate "($UO_2(CH_3COO)_2$)" was used for the preparation of stock solution (2000 mg/L in Milli-Q water). Adsorption experiments were carried out at 25 °C while rotating on a shaker at 150 rpm for 2.0 h. The MCM-41 based adsorbent (10 mg) was suspended in adsorption medium (5.0 mL). The concentration of the U(VI) ion in the medium was determined spectrophotometrically [2]. Briefly, it was based on the formation of colored complexes of U(VI) ion with sodium salicylate in aqueous medium. The absorbance of the solution was measured at 468 nm using an UV/Visible spectrophotometer (PG Instrument Ltd., Model T80+; PRC). For each set of data reported, standard statistical methods were used to determine the mean values and standard deviations. The amount of U(VI) ion adsorbed per unit of adsorbents (mg U(VI) ions g^{-1}) was obtained by using the following equation: