



Improving adsorption of uranium ion onto silica nanoparticles by modification its surface using N₂-type Schiff base

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Abstract

Inorganic complexing agents in the structure of nanoparticles can be used for improve the separation and removal of uranium ions from nuclear waste. In this study, the effect of the presence of Schiff base ligand on the structure of silica nanosilica for improve uranium adsorption was investigated. The results show that modification causes pH of the quantitative adsorption of studied metal ion shifts to the lower pH values. The effect of various parameters such as pH, contact time and amount of adsorbent on the process was investigated. A quantitative removal of the studied metal ions (99.56%) was achieved at pH 4, by 0.05 g of the modified adsorbent disperse in 20 ml of the sample containing the metal ion (20 mgL⁻¹) after 20 min. of magnetically stirring.

Keywords: Schiff base, Nanoparticle, Uranium, adsorption

Introduction

Uranium is one of the most important heavy metals because of its chemical toxicity and radioactivity. Excessive amounts of uranium have entered into the environment through the activities of the nuclear industry. Uranium is one of the most dangerous polluting metals, not because of its radioactivity but because of its high toxicity, threatening the environment's health [1]. For this reason, the removal of uranium from wastewater is of great importance. Various methods used for this purpose are liquid-liquid extraction, electrodialysis, ion exchange, chromatography and solid-phase extraction.

Nowadays, nanometer materials have become important in metal ion separation studies owing to their special physical and chemical properties. So in this study, we report on the application of nanoparticles silica as sorbent for removing uranium ions from aqueous solutions. On the other hand, the adsorptive properties of adsorbents can be improved by modifying their surface with complexing agents [2].

A Schiff's base, named after Hugo Schiff, is a functional group with the general formula of R₁R₂C=N-R₃. These bases can be synthesized from an aromatic amine and a carbonyl compound (e.g., aldehydes, ketones) by nucleophilic addition, forming a hemiaminal, and then dehydration to generate an imine. An imine (Schiff's base) mainly binds metal ions via the two donor atoms N and O [3]. This report concerned the application of silica nanoparticles modified by a Schiff base ligand named pyridylmethylidenepropyltriethoxysilane, for removal and separation of uranium ions from aqueous phase.

Experimental

Preparation of the materials

A stock solution of uranium ion is prepared by dissolving appropriate amount of UO₂(NO₃)₂·6H₂O (Merck) in deionized water. Methanol, aminopropyltriethoxysilane and pyridyl 2-carbaldehyde (Merck) was used as received for the synthesis of Schiff base ligand. Silica nanoparticles purchased from the market (Iranian Nanomaterials Co., APS 20-30 nm).

Results and discussion

Absorbent preparation: The pyridylmethylidene-propyltriethoxysilane ligand by aminopropyltriethoxysilane and pyridyl 2-carbaldehyde in methanol by following a similar process to the previous methods was synthesized and characterized [4]. Refluxing this product with silica nanoparticles in toluene resulted modified nanoparticles shown in Figure 1. This product has been characterized by using FT-IR and CHN. The peaks 1652 and 2928 cm⁻¹ are related to organosilane and imine groups stretching vibration, respectively, which confirm the Schiff base ligand in the silica surface (Figure 2). Also, the amount of grafted imine showed that the pyridylmethylidene loading in modified nanoparticles was 0.26 mmol imine/g of nanosilica. This article was used as an adsorbent for uranium ions.

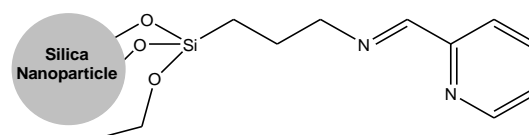


Figure 1. Structure of the modified nanoparticles.

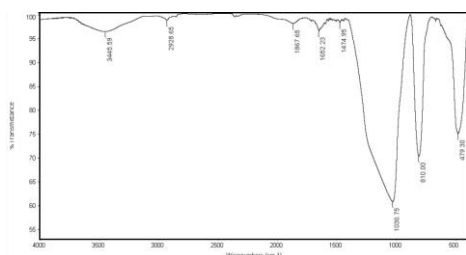


Figure 2. FT-IR spectrum of the modified nanoparticles

Adsorption procedure. 0.05 g of the modified adsorbent and 20 mL of metal ion solution (20 mg/L) were placed in a 50 mL glass vial, and shaken on a stirrer at $25 \pm 1^\circ\text{C}$ for 30 min. The concentration of the solution before and after equilibration was measured by ICP. The uptake percentage of the ions was calculated by equation 1.

$$U_p = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (1)$$

where “ C_0 ” and “ C_e ” are the initial and equilibrium concentration of ions (mg/L), respectively.

Effect of pH: Competitive adsorption of uranium ions on unmodified and modified nanoparticles was studied at different pH values in the range 2-6.5. The results show the pH dependency of adsorption process with both types of adsorbents (Figure 3). The modification of nanoparticles affects in the removal of uranium ions. In fact, due to the presence of donor atoms N, a shift of the uptake percentage towards lower pH values, and at pH 4, a quantitative removal of uranium ions was achieved.

Shaking time: The adsorption of uranium ions at pH 4 with the modified nanoparticles was studied at different shaking time in the range of 5-120 min. The results indicate that within 20 min. of shaking, uranium ions was totally removed from the aqueous solution. This shows more rapid adsorption kinetics of uranium ions.

Amount of adsorbent: the effect of amount of adsorbent on the process was performed by using 0.01-0.1 mg of the modified adsorbent (Figure 4). A quantitative uptake (>99.5%) was attained for uranium ions by using 0.05 g of the studied adsorbent.

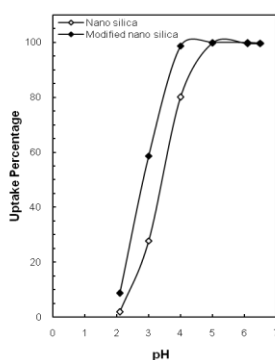


Figure 3. Effect of pH

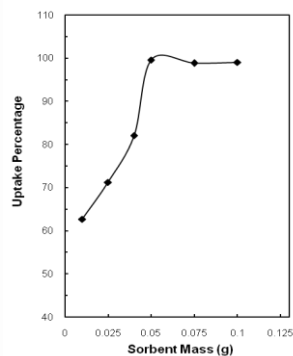


Figure 4. Effect of the amount of modified nanoparticle

Table 1. Absorption and desorption of uranium ions from the surface of modified nanosilica using different acids

% Uptake	% Desorption		
	HCl	H ₂ SO ₄	HNO ₃
99.56	98.38	82.30	80.05

Table 1. The effect of interfering ions in adsorption of uranium and lanthanide ions onto modified silica nanoparticles

Metal ions	Modified nanoparticle
U(VI)	97.5
La(III)	2.85
Ce(III)	0.4
Sm(III)	2.75
Eu(III)	3.85
Dy(III)	3.85
Ho(III)	4.2
Er(III)	11.55

Experimental conditions: initial concentration of each metal ions, 20 mg/L; aqueous sample pH, 4; amount of adsorbent, 0.05 g.

Conclusions

Modification of SiO₂ nanoparticles by Pyridylmethylidenepropyltriethoxysilane results efficient adsorbents for removal of uranium ions from aqueous solutions. Under optimal conditions (pH 4, adsorbent dosage 0.05 g, contact time 20 min.), uranium ions (20 mg/L) were quantitatively removed from the sample solution. Comparison of the adsorption efficiency of studied modified nano-particles with those unmodified ones shows a shift of uptake of the metal ions vs. pH curves towards lower pH values by applying the modified adsorbents. As well as modified silica nanoparticles with pyridylmethylidenepropyltriethoxysilane can be used as an efficient adsorbent for removal-separation of uranium from lanthanides in aqueous solutions.

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