

Nano-diamond particles functionalized with single/double-arm amide–thiourea ligands for adsorption of metal ions



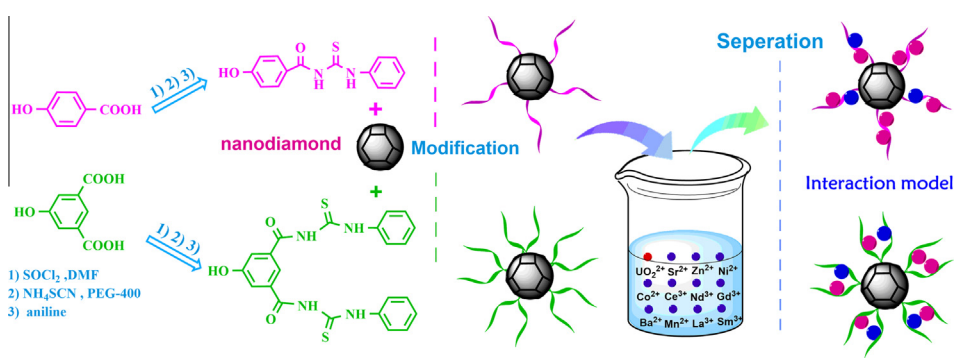
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HIGHLIGHTS

- Nanodiamond-based adsorbents for separation of uranium were synthesized firstly.
- The adsorbents were composed with single or double arms of amide thiourea chains.
- Comparative studies were carried out on adsorption behaviors of the adsorbents.
- Single-armed adsorbent exhibited higher selectivity for uranium.
- The mechanism basing on spatial configuration and chelate ability was proposed.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 6 January 2016
Accepted 4 February 2016
Available online 10 February 2016

Keywords:

Adsorption
Uranium
Nanodiamond
Spatial configuration
Amide–thiourea

ABSTRACT

Separation efficiency of solid-phase extractant is greatly subjected to the spatial configurations of functional ligands attached to the matrix, which has not been studied efficiently till now. In order to further understand the relationship between spatial configurations of the attached functional ligand and the adsorption ability of the extractant, two novel molecules (single-armed ligand, SA and double-armed ligand, DA) with identical coordination unit (amide–thiourea) but different spatial configurations (single-/double arms) were designed and synthesized. The corresponding extractants, ND-SA and ND-DA were obtained by modification of nanodiamond (ND) with SA and DA and both the extractants displayed good chemical and thermal stabilities. The batch adsorption experiments showed that ND-SA and ND-DA possess large adsorption capacities ($\sim 200 \text{ mg g}^{-1}$), very fast adsorption kinetics (reaching equilibrium within 2 min) and excellent selectivities (up to 82% and 72%, respectively) for uranium. The study of the possible mechanism indicated that ND-DA tends to utilize its tweezer-like double arms to “clamp” metal ions and the stronger chelate interaction could to some extent weaken the coordination selectivity of attached DA ligand. In contrast, single-armed adsorbent ND-SA unexpectedly exhibited better adsorption selectivity for uranium than ND-DA owing to its more flexible spatial configuration and moderate complexing ability.

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1. Introduction

As the core of nuclear fuel, uranium could provide us with clean nuclear power, but at the same time it could be a potential environmental pollutants and biotoxins [1]. What's more, uranium is also a kind of limited reserves and non-regenerated natural

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resource [2]. So, efficient separation and recovery of uranium from various uranium containing effluents are of great significance. In aqueous solution, uranium exists mainly as a hexavalent state, structured as the linear, triatomic uranyl cation (UO_2^{2+}) with the charge mainly distribution in the equatorial plane. It usually offers four or six coordination sites [3–5]. How to make use of the structure and coordination properties of the uranyl cation to efficient separation uranium is one of the most significant researches. It is not only one of the keys to both uranium-bearing wastewater treatment and uranium recycling but also can be meaningful examples for further understanding the coordination chemistry of actinides. Researchers have been committing in finding suitable solid matrixes [6–8], designing different kinds of new functional ligands [9,10], researching the coordination properties and coordination regularities of the uranyl ions under various conditions for the purpose of designing and synthesizing new solid-phase extraction (SPE) adsorbents with high separation selectivity toward uranium without blindness.

In recent years, many kinds of SPE adsorbents have been reported in uranium selective separation field. Specifically, SPE adsorbents which generally employed carbonaceous materials such as hydrothermal carbon [11,12], graphene oxide [13,14], mesoporous carbon [15] and carbon nanotubes [16,17] as matrixes are becoming more attractive. Because they possess higher thermal and chemical stability, good radiation resistance and facile surface modification compared with other matrixes such as matrixes based on organic polymers. Nanodiamond (ND) powders, produced by detonation synthesis have a pristine diameter 4–10 nm combining an inert diamond core with a large number of covalently bonded surface groups such as hydroxyl, carboxyl, anhydride, ester, or ketone groups [18,19], which also possess good physical and chemical stability, excellent radiation resistance properties [20,21], low cytotoxicity and also high surface area [22,23]. Because of its' outstanding properties, ND could be a good candidate for matrix of SPE adsorbents for uranium separation. What's more, carboxylated nanodiamond can be obtained through chemical oxidation [24]. This kind of oxidation can not only improve the hydrophilicity of nanodiamond but also facilitate our further modification. Therefore, nanodiamond could be the most versatile platform or the best matrix of SPE adsorbents for studying the influence of different structures and different heteromolecular conformations of the ligand on the complexation and separation of uranium.

Previously reported SPE adsorbents usually employed N/O donor-containing ligands as the functional components [11,25,26]. Uranium was separated from uranium-containing aqueous through the interaction between uranyl ions and SPE adsorbents. The separation efficiency usually depends on the contents of nitrogen or oxygen, the structures and configurations of the ligands and also the chemical environment of the adsorbents [2,11,12]. But it still remains a challenge in this area to obtain a SPE adsorbent with both high selectivity and large adsorption amount toward uranium. Therefore, researching on how new ligands and their compositions or configurations effect on the separation efficiency are of great significance. It is instructive to the design of new ligands with great uranium separation abilities. Kanatzidis recently found that strong UO_2^{2+} –S bonding interactions contribute to uranium removal from aqueous solutions containing competitive ions, such as Na^+ , Ca^{2+} , and also from seawater [27,28]. Merdivan and Zhao demonstrated that SPE adsorbents with benzoylthiourea derivatives as functional ligands can some extent selectively separate uranium from aqueous through the interaction between N–CS–NH–CO–Ph chelating group and uranyl ions [29,30]. These triggered works suggested that ligands contain softer donor atoms, such as sulfur, are also effective in selective separation of uranium. What's more, ligands' spatial configurations

and the number of available coordination sites are significantly influence the interactions between ligands and uranyl ions [31,32] and also influence the separation efficiency. However, we are badly in need of such fundamental research. For this reason, we designed two benzoylthiourea derivatives (SA and DA) which contain O, N and S donor atoms located in single or double-armed amide–thiourea structures and act as the functional ligands. We expected to preliminary research the coordination properties of uranyl ions by two nanodiamond-based SPE adsorbents, which are functioned with two benzoylthiourea derivatives (SA and DA) contain the same donor atoms, similar structure and different spatial configurations. The research can help us to design and synthesis ligands with high separation selectivity and large adsorption amount toward uranium and also supply available reference data to future research. It is the first time that this kind of comparative study in the uranium selective separation field have been made.

As show in the above, we firstly synthesized two benzoylthiourea ligands with single arm (SA) and double arms (DA). Then, two innovative nanodiamond-based SPE adsorbents (single-arm assembled nanodiamond, ND-SA and double-arm assembled nanodiamond, ND-DA) were made through one step classic esterification of the carboxylated nanodiamonds with the pre-synthesis two benzoylthiourea ligands. The physicochemical properties of the obtained adsorbents were characterized by FT-IR, XRD, TEM, TG, elemental analysis, etc. The adsorption behavior of uranium onto the as synthesized ND-SA and ND-DA adsorbents were investigated in detail using batch sorption experiments. Especially, a comparative study of the two new SPE adsorbents were conducted at different adsorption conditions such as: time, pH, initial uranium concentration, competitive ions and so on. Finally, a possible mechanism based on the spatial configurations and the chelate abilities of the adsorbents was proposed.

2. Experimental

2.1. Chemicals

The nanodiamond powder (with purity greater than 95%) produced by detonation was come from Heyuan Zhonglian Nanotechnology Co., Ltd. (China). Chemicals and reagents such as 5-hydroxyisophthalic acid, ammonium thiocyanate (NH_4SCN), macrogol 400 (PEG-400), thionyl chloride (SOCl_2), tetrahydrofuran (THF), aniline, and 4-dimethylaminoipyridine (DMAP) used in this research were purchased from Tianjin Kermel Chemical Reagent Co., Ltd. (China). 1-(3-Dimethylaminopropyl)-3-ethyl-carbodiimide hydrochloride (EDCI) was purchased from Asta Technology Co., Ltd. (China). All metal oxides and nitrates were purchased from Aladdin Chemistry Co., Ltd. (China). All reagents were of AR grade or of the highest purity available and were used without further purification.

2.2. Synthesis and characterization of SA and DA

The synthesis procedures of SA and DA are presented in Scheme 1 [33,34]. FT-IR, ^1H NMR and EI-MS spectra were employed to characterize the ligand molecules. More detailed information of the synthesis process and characterization data of the SA and DA can be found in Supplementary material.

2.3. Oxidation of ND

200 mg ND was oxidized in air at 425–430 °C for 5 h, further purification was done by boiling in 35 wt% HCl for 24 h to remove the metal impurities [24]. The obtained carboxylated nanodiamond (CND) was washed with deionized water repeatedly until

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