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Selective solid-phase extraction of uranium by salicylideneimine-functionalized hydrothermal carbon

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HIGHLIGHTS

- ► Hydrothermal carbon material as solid-phase extractant matrix.
- ► An excellent hexavalent cation ligand, salicylideneimine, is grafted on the matrix.
- ► Adsorbent shows high affinity and selectivity to U(VI) in simulated nuclear effluent.
- ► Process is fast, endothermic, spontaneous, and pseudo-second-order chemisorption.

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ABSTRACT

A new salicylideneimine-functionalized hydrothermal-carbon-based solid-phase extractant was developed for the purpose of separating uranium selectively for sustainability of uranium resources. The resulting adsorption material was obtained via hydrothermal carbonization, calcination at mild temperature (573.15 K), amination, and grafting with salicylaldehyde in sequence. Both Fourier transform infrared spectra and elemental analysis proved the successful grafting of salicylideneimine onto hydrothermal carbon matrix. Adsorption behaviors of the extractant on uranium(VI) were investigated by varying pH values of solution, adsorbent amounts, contact times, initial metal concentrations, temperatures, and ionic strengths. An optimum adsorption capacity of 1.10 mmol g^{-1} (261 mg g^{-1}) for uranium(VI) was obtained at pH 4.3. The present adsorption process obeyed pseudo-second-order model and Langmuir isotherm. Thermodynamic parameters (ΔH = +8.81 kJ mol^{-1}, ΔS = +110 J K^{-1} mol^{-1}, ΔG = −23.0 kJ mol^{-1}) indicated the adsorption process was endothermic and spontaneous. Results from batch adsorption test in simulated nuclear industrial effluent, containing Cs^{+}, Sr^{2+}, Ba^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, La^{3+}, Ce^{3+}, Nd^{3+}, Sm^{3+}, and Gd^{3+}, showed the adsorbent could separate uranium(VI) from those competitive ions with high selectivity. The adsorbent might be promising for use in certain key steps in any future sustainable nuclear fuel cycle.

1. Introduction

Nuclear energy is primarily derived from uranium [1]. The most common isotope of natural uranium is ^{238}U, having a negligible radiotoxicity due to its geologically long half-life (4.5×10^9 a). However, because of its superior binding affinity toward biomolecules [2], ingestion and inhalation of uranium could cause certain acute and/or chronic harmful effects, especially the kidney damage from acute internal exposure to uranium and its compounds [2,3]. Thus it actually is a highly biotoxic radionuclide while is being introduced into the fragile ecosystem through a combination of natural processes as well as anthropogenic activities [4]. On the other hand, limited quantities of uranium minerals in nature and the expected shortage of uranium in the near future [1] also restrict mining, production, and consumption of this metal. Therefore, separation and recovery of uranium are of great practical significance, not only in reutilization of uranium resources and sustainable development of nuclear energy, but also for protection of both human health and ecological environment.

Being an effective separation technique, solid-phase extraction (SPE) has risen to the forefront among the methodologies that have been extensively studied in the field of separation and analysis [5,6], and is providing alternative opportunities for the removal of hazardous species from wastewater, such as cadmium [7,8], lead [8,9], and chromium [10–12], as well as precious metals like gold [13,14] and platinum [15], including uranium [5,16,17]. SPE is arguably powerful in terms of its superiorities of minimal solvent consumption, flexibility, absence of emulsion [5,6,18], especially

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Nomenclature

b_L	Langmuir constant related to adsorption energy ($L\,mmol^{-1}$)
b_T	Temkin constant related to adsorption energy ($kJ\,mol^{-1}$)
c_0	initial concentration of metal ion in solution ($mmol\,L^{-1}$)
c_e	concentration of metal ion at equilibrium in solution ($mmol\,L^{-1}$)
c_t	concentration of metal ion at time 't' in solution ($mmol\,L^{-1}$)
E_{DR}	Dubinin–Radushkevich constant related to mean adsorption energy ($kJ\,mol^{-1}$)
K_F	Freundlich constant related to adsorption capacity ($mmol^{1-(1/n)}\,L^{1/n}\,g^{-1}$)
K_T	Temkin equilibrium binding constant ($L\,mmol^{-1}$)
m	adsorbent amount (mg)
n_F	Freundlich constant related to adsorption intensity (unitless)
q_{DR}	Dubinin–Radushkevich saturated adsorption capacity ($mmol\,g^{-1}$)
q_e	adsorption amount of metal ion at equilibrium ($mmol\,g^{-1}$)
$q_{e,cal}$	adsorption amount of metal ion at equilibrium calculated from kinetic model ($mmol\,g^{-1}$)
q_L	Langmuir saturated monolayer adsorption capacity ($mmol\,g^{-1}$)
q_t	adsorption amount of metal ion at time 't' ($mmol\,g^{-1}$)
R	gas constant ($J\,K^{-1}\,mol^{-1}$)
R^2	correlation coefficient (unitless)
T	temperature (K)
t	adsorption time (min)
V	volume of aqueous solution of metal ion (mL)

large volume-reducing ratio, high concentration factor, and ease of solidification, which has made the technique more attractive for separation of radionuclides over the last decade [18,19].

A solid-phase extractant consists of two parts: a matrix and functional components. Commonly used materials for the matrix can be divided into the following groups: (i) minerals: such as clay [20,21], diatomite [16], and zeolite [22]; (ii) simple inorganic oxides: for instance, alumina [23] or silica [9,13]; (iii) polymers/copolymers: e.g. resins and related materials [12,24,25]; (iv) carbonaceous materials: for example, activated carbon (AC) [5,26], mesoporous carbon [27,28], carbon nanotubes (CNTs) [29], graphite and its derivatives [8]; (v) biomass or biosorbent: like chitosan [30] and brown alga [31]; (vi) others: hybrid materials/composites [11,32,33], gels [34,35], metal-organic frameworks [36], etc.

Although these materials are now playing important roles in the fields of metal ion separation and wastewater treatment [11,37,38], there are still inevitable shortcomings, more or less, for practical use. Generally, most materials in groups (i), (ii) and (vi) are acid-nonresistant, group (iii) is radiolysable, and group (v) is not suitable for use in high-temperature-bearing application [39]. For these reasons, those materials are considered unsuitable for practical use in nuclear industrial effluent with extreme conditions (e.g. high temperature, high acidity, high salinity and strong radiation).

Here, a promising candidate maybe suitable for use in harsh environment could be group (iv), the carbons, basically for their greater thermal and radiation stabilities [1] than most organic or polymeric matrices, and especially, rigid and stable structure in strong acidic environments. Generally, unmodified carbonaceous materials more or less bear some oxygen-containing functional groups on their surfaces [40], yet they show poor selectivity toward nuclides of interest, and the amount of the functional groups could not meet the requirement of high capacity. Besides, activation or preparation of, for example, AC or CNTs, is energy-consuming and costly [41] as the process involves calcination at extremely high temperature or arc-discharge, chemical vapor deposition, or catalytic pyrolysis [42]; moreover, the functionalization of graphite would sometimes unavoidably involve dangerous chemicals like concentrated sulfuric acid with corrosiveness and oxidizing and explosive potassium permanganate [43].

For the reasons mentioned above, a newly developed carbon material, hydrothermal carbon (HTC), was chosen as the matrix for solid-phase extractant in this study. HTC possesses mostly spherical skeleton with relatively stable physico-chemical properties [40], and comparing with the other carbonaceous materials mentioned above, there are more oxygen-containing functional groups and/or active sties on the surface of HTC [40]. In addition, preparation of HTC can be performed at a relatively low temperature and mild condition without adding any catalyst, surfactant or other auxiliaries, and the process is green and environment-friendly [44].

On the other hand, salicylideneimine was chosen as a specific functional group to be grafted on the HTC matrix to prepare salicylideneimine-functionalized HTC-based adsorbent. As an excellent ligand, salicylideneimine could coordinate with hexavalent metal ions, such as chromium, molybdenum, and tungsten [45–47], effectively, and especially, there is usually no significant amount of other hexavalent ion besides uranyl ion in nuclear industrial effluent [48]. It was expected that the new designed adsorbent could separate uranium(VI) from multi-ion system with high selectivity.

So far, research literatures published on the topic of HTC are predominantly focused on the mechanism of transformations [40], preparation conditions [49,50], and adjustments for morphologies [51,52] and structures or textures [53] of HTC materials sourced from various carbohydrates [49,54] and biomasses [55–58]. There is hardly any basic research on selective functionalizations by grafting specified ligands on the surface of HTC and further modifications based on these functional groups. Here we used a "grafting from" approach for fixing salicylideneimine ligand on HTC matrix and employed the functionalized material in the area of radionuclides separation attemptively.

2. Experimental

2.1. Apparatus

Fourier transform infrared (FT-IR) spectra were obtained from PerkinElmer IR-843 spectrometer (USA). Contents of carbon, hydrogen, and nitrogen in samples were determined by elemental analyzer (Carlo-Erba 1106, Italy). The morphology of HTC material was examined by scanning electron microscope (SEM, FEI Company, Oregon, USA).

All concentrations of metal ions (excluding cesium ion) in solutions were measured by inductively coupled plasma atomic emission spectroscopy (Thermo Elemental, USA), while concentrations of cesium were analyzed by atomic adsorption spectroscopy (Beijing Haotianhui Science & Trade Co., Ltd., China).

2.2. Reagents

Glucose used for preparation of HTC was purchased from Tianjin Kermel Chemical Reagent Co., Ltd., and other organic reagents, including ethylenediamine, salicylaldehyde, ethyl acetate,