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The synergistic elimination of uranium (VI) species from aqueous solution using bi-functional nanocomposite of carbon sphere and layered double hydroxide

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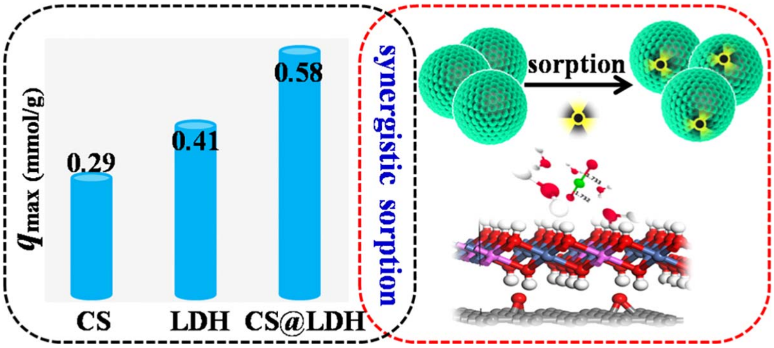
HIGHLIGHTS

- A novel carbon sphere@layered double hydroxide nanocomposite was fabricated.
- The bi-functional material was applied for efficient remove U(VI) from wastewater.
- The adsorption of U(VI) was mainly dominated by inner-sphere surface complexation.
- The sorption of U(VI) was a typical spontaneous and endothermic process.

GRAPHICAL ABSTRACT



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ABSTRACT

Hydrangea-like carbon sphere@layered double hydroxide (CS@LDH) nanocomposite was fabricated by one-step hydrothermal synthesis strategy using carbon sphere and Ni-Al LDH as monomer molecules. The CS@LDH nanocomposites were then applied as adsorbents to eliminate U(VI) from aqueous solutions and showed excellent elimination performance to U(VI) from aqueous solutions because of its strong synergistic effects between metal-oxygen functional groups (Ni-O and Al-O) and free-metal functional groups (C—O, C—O—C, and O—C═O). The removal of U(VI) on CS@LDH was mainly dominated by inner-sphere surface complexation, which was confirmed with batch sorption experiments, FTIR and XPS analysis. Furthermore, the maximum sorption capacity of U(VI) on CS@LDH (0.6 mmol/g) was 2.0 times higher than that of U(VI) on Ni-Al LDH (0.3 mmol/g) and approximately 1.5 times higher than that of U(VI) on CS (0.4 mmol/g) at pH = 5.0 and *T* = 298 K. The thermodynamic parameters suggested that the sorption of U(VI) was a typical spontaneous and endothermic process. The sorption isotherms were well simulated by Langmuir model, suggesting that the sorption was monolayer coverage. The CS@LDH can be used as superior adsorbent for efficient elimination of radionuclides in environmental pollution remediation. This study also demonstrated a new strategy to improve the physicochemical properties of other low efficiency adsorbents through polymerization reaction.

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1. Introduction

With the growth of population and the depleting of fossil energy, the increasing energy crises have been one of the major issues and research hotspots [1–3]. Nuclear power, a clean efficient fission or fusion energy, has become the leading candidate energy for solving this energy crisis [4,5]. Uranium resources have been regarded as the core of the development of nuclear power, and there is large amount of uranium in soils, minerals, and seawater. In the past few decades, uranium mining and processing, nuclear safety accidents, and improper nuclear waste management have led to the emission of considerable amounts of soluble U(VI) ions into natural environment, mainly through migration in surface or ground water systems [6–8]. Due to the long half-life and high toxicity, U(VI) ions can result in environmental toxicology and radiation damage, which can decrease the biological activity of cells and even leading to cancerization [9–11]. Therefore, it is significant and urgent to eliminate U(VI) species from wastewater to protect the environment and life safety.

Many advanced physical and chemical processes, such as chemical precipitation, solid-phase extraction, ion exchange, catalysis and membrane separation, have been adopted to recover and aggregate radionuclides from natural environment [12–17]. Among these methods, the sorption technique has been shown as the most economical and convenient way for removing radionuclides due to its simple, cost-effective, and mild reaction condition [18–20]. Various adsorbents, including clay mineral-based materials, carbon-based materials, metal-organic framework-based materials, zero-valent iron-based materials and biomass-based materials, have been widely applied to the elimination of U(VI) from wastewater [21–24]. These materials showed different physicochemical properties and merits/demerits in the removal of radionuclides. For instance, the carbon-based materials have abundant oxygen-containing functional groups (i.e., −COOH, −OH and −O−), while the cost was relative high and the synthesis process was complexity [25,26]. The clay mineral-based materials can be obtained in natural environment and exhibits high chemical stability, but the removal efficiency was relative low than others [27,28]. Metal-organic framework, zero-valent iron and biomass-based materials also showed excellent sorption efficiency and elimination capacity, while the performances were significantly influenced by environmental conditions [29–31]. Simultaneously, the preparation of multi-functional materials derived from at least two kinds of functional monomers was developed and their application was expanded in the environmental pollution management, hence the nanocomposites with synergistic effects should be strengthened and applied in multidisciplinary fields including environmental pollutant elimination [32,33].

Hydrothermal carbonization has been demonstrated as a very effective method to prepare different carbon nanostructures such as carbon sphere (CS) [34], mesoporous carbon [35] and carbonaceous nanofiber (CNF) [36]. Glucose has been the focus in the low temperature hydrothermal carbonization field [37]. Their potential in pollution treatment and environmental restoration has proved to be sustainable alternatives to traditional carbon-based materials for environmental pollution management. Compared with carbon nanotube and CNF, the greatest advantage of CS is that it can be prepared directly from one-step hydrothermal carbonization of glucose. In addition, due to the aromatization of glucose, the CS was abundant in −OH and C═O groups, which were produced from hydrated or partially dehydrated glucose molecules. Wang et al. [38] reported that the removal capacity of rare earth doped titanium dioxide coated carbon sphere composites (C@La-TiO_2) reached 383.3 mg/g for GO and 50.5 mg/g for Cr(VI) at pH 5.0. Zhou et al. [39] found that the carbon-alumina particles were powerful adsorbents for the removal of Orange-II dye from water.

Layered double hydroxides (LDHs) are a different class of 2D hydrotalcite-like materials with topological transformation, intercalation, and moderate chemical stability, have aroused increasing attention in environmental pollution cleanup [40–42]. Generally, LDHs were described by the formula of $[M^{II}_{1-x}M^{III}_{x}(OH)_2]^{x+}[(A^{n-})_{x/n}]^{x-}\cdot mH_2O$ (where M^{II} and M^{III} represent the di- and trivalent metal cations, respectively, A^{n-} represents the interlayer anion or gallery anion, x is considered as the molar ratio of $M^{III}/(M^{II} + M^{III})$). Such LDHs were widely employed in adsorbing various contaminants, such as heavy metal ions, radionuclides and organic pollutants [43–45]. Nevertheless, the pure LDHs as single adsorbent exhibited low removal efficiencies for various contaminants (such as Pb(II), aniline or U(VI)). Zou et al. [40–43] coagulated LDH-based materials and graphene oxides for the elimination of radionuclides with high removal capacities, indicating the introduction of CS enhanced the binding capacity and resolved the low-efficiency problem of pure LDHs as adsorbents. Thereby, a high removal rate and elimination capacity can be predicted for the CS@LDH nanocomposites.

Herein, we reported the efficient sorption of U(VI) on carbon sphere @ layered double hydroxide (CS@LDH) nanocomposites, including the detailed synthesis of the nanocomposites, the investigation on its interaction performance with U(VI) ions, and the interaction mechanism using different characterization techniques. The results showed a new strategy for the efficient elimination of U(VI) with CS@LDH, which employed the synergistic effects between metal-oxides and metal-free materials in wastewater management and enhanced the elimination of radionuclides from aqueous solutions.

2. Materials and methods

2.1. Chemicals and materials

Glucose, aluminum nitrate nonahydrate ($Al(NO_3)_3\cdot 9H_2O$), nickel nitrate hexahydrate ($Ni(NO_3)_2\cdot 6H_2O$), urea (> 99%), sodium hydroxide (NaOH), sodium nitrate ($NaNO_3$) and nitric acid (HNO_3, 68%) were purchased from Sinopharm Chemical Reagent Co., Ltd. All the chemicals were analytical grade and used without any further purification. Milli-Q water (18.25 MΩ cm^{-1}) was used across the whole experiments.

2.2. Preparation of CS@LDH

CS@LDH nanocomposites were synthesized by hydrothermal method, and the well-designed preparation process was clarified in Fig. 1. Firstly, CS was prepared by one-step hydrothermal carbonization of glucose based on our previously reported procedure [38]. Briefly, 7 g of glucose was dissolved to 70 mL of Milli-Q water, and followed by ultrasonication for 30 min to get a clear suspension. The solution was then transferred into a stainless-steel Teflon lined autoclave (100 mL in capacity) and heated at 180 °C for 8 h. After cooling to room temperature, the products were collected by centrifugation, washed with Milli-Q water and ethanol, followed by drying in a vacuum oven at 60 °C for 12 h. Secondly, CS@LDH was fabricated by a conventional hydrothermal technique. Briefly, 0.07 g CS, 1.5 g $Ni(NO_3)_2\cdot 6H_2O$, 0.6 g $Al(NO_3)_3\cdot 9H_2O$ and 1.0 g urea were dissolved into 30 mL of Milli-Q water. The final solution was sealed into a Teflon-lined stainless-steel autoclave (50 mL in total volume) and placed at 110 °C for 8 h. The obtained composites were cooled to room temperature and then washed with Milli-Q water for three times, and dried in vacuum oven at 60 °C overnight.

2.3. Characterization

The scanning electron microscopy (SEM, S-4800, Hitachi, Japan) and transmission electron microscopy (TEM, JEM-1011, Japan) were applied to obtain the microscale morphologies of as-prepared CS and CS@LDH. The phase composition and structural characteristics of samples were performed by the X-ray diffraction (XRD, D/max2500) at $2\theta = 5°–70°$ using Cu Kα source ($\lambda = 1.541$ Å). The surface functional groups were confirmed by Fourier transformed infrared spectroscopy