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Synthesis of novel flower-like layered double oxides/carbon dots nanocomposites for U(VI) and ^{241}Am(III) efficient removal: Batch and EXAFS studies

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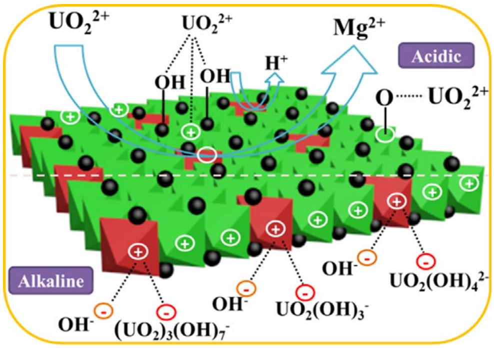
GRAPHICAL ABSTRACT



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ABSTRACT

Herein, a practical and simple calcination method was used to synthesize layered double oxides (denoted as LDO) and layered double oxides/carbon dots nanocomposites (denoted as LDO-C) for U(VI) efficient removal. The U(VI) adsorption on LDO and LDO-C were investigated under various experimental conditions, and the results indicated that U(VI) uptake on LDO and LDO-C were consumingly dependent on pH and ionic strength at pH > 6, and independent of ionic strength at pH < 6. The adsorption processes of U(VI) on LDO and LDO-C were spontaneous and endothermic, and well simulated by pseudo-second-order model. The maximum adsorption capacity of U(VI) on LDO-C was calculated to be 354.2 mg/g at pH = 5.0 and T = 298 K, which was significantly higher than that of U(VI) on LDO (237.6 mg/g). Particularly, BET, F T-IR, XPS and EXAFS analysis suggested that the higher adsorption capacity of LDO-C was mainly attributed to higher specific surface area and more abundant surface oxygen-containing functional groups (e.g. C-OH), and the main interaction mechanisms were surface complexation and electrostatic interactions. In addition, LDO-C also showed higher adsorption capacity of ^{241}Am(III) than LDO. All in all, the efficient removal performance and superior versatility of LDO-C

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indicated that it could be applied as promising candidate for efficient immobilization of radioactive pollutant in environmental pollution management.

1. Introduction

Uranium (U(VI)), one of the major components of the nuclear reaction, has attracted high-profile interest and widely used in nuclear energy due to its strategic and ecological significance with the rapid development of nuclear technology and industry [1–3]. Corresponding to this increasing application, one serious consideration of potential risks from nuclear fuel is the toxic pollutants directly released into the environment and thereby results in the hazardous effects to human health and ecological balance [4]. Therefore, the removal of uranium-containing waste is significant for real environmental pollutant cleanup [3,5–7]. For this purpose, many methods such as precipitation, membrane filtration, liquid-liquid extraction, adsorption and ion exchange, had been continuously reported for U(VI) removal [8,9]. Among these methods, adsorption was considered as one of the most popular technology owning to its easy operation and practical application [10,11].

Carbon materials, with abundant oxygen-containing functional groups, have been one of the most effective materials for environmental pollution treatment [12,13], and have attracted increasing attention recently [4,14]. Our group reported graphene-based materials as remarkable adsorbents for the removal of U(VI) (138.9 mg/g) [4], Eu(III) (28.7 mg/g) [10], and Sr(II) (54.6 mg/g) [11]. However, high cost greatly hindered their practical application in real works. Therefore, novel, efficient and low-cost carbon-based adsorbents are critically needed for U(VI) uptake from waste streams. Recently, carbon quantum dots (CQD) as a novel carbon nano-material have attracted considerable attention benefitting from their unique physicochemical properties such as small particle size, high specific surface area and abundant functional groups on its surface, which can be more inclined to bind with U (VI) in aquous solutions [15–17]. However, CQD also formed aggregates irreversibly which reduced the surface area and adsorption capacity significantly, and CQD had superior substrate-free and water-dispersed properties, which enabled the CQD to have great difficulties in separation and reuse from aqueous solutions, and thereby strongly limited its application in this area [18,19]. Meanwhile, effective approaches to reduce the aggregation of CQD in aqueous solutions and providing a proper substrate for the functionalization of CQD to improve the separability and reusability from aqueous solutions are still scarce.

Layered double hydroxides (LDHs), known as a class of 2D hydrotalcite-like materials, are built by positively-charged host layers and exchangeable interlayer anions, and can be expressed as $[M^{2+}_{1-x}M^{3+}{}_{x}(OH)_2]^{x+}(A^{m-})_{x/m}{\cdot}nH_2O$, where M^{2+} and M^{3+} are the divalent and trivalent metal ions, respectively [20–22]. A^{m-} is the interlayered anion to stabilize the structure of LDHs. Recently, various LDHs-based materials with hierarchical architectures have been widely investigated in gas adsorption and separation, energy storage and catalysis [22–24]. More importantly, LDHs have also attracted increasing interest in real environmental pollution cleanup due to their low-cost, non-toxic and moderate chemostability [25,26]. However, particle size, morphology and crystalline orientation of pristine LDHs restricted their removal efficiency. Thus, seeking for feasible method to enhance adsorption capability of pristine LDHs is increasingly necessary. Calcination technology as an efficient improvement method was widely applied to enhance surface defect of derivatives and beneficial for inner reaction [23]. Moreover, after the material calcination at the temperature higher than 400 °C, the interlayer water and anions of pristine LDHs were completely disappeared. The calcined LDH (donated as LDO) had more active sites, higher specific surface area, higher chemical and thermal stability than the pristine LDHs [27]. Recently, our group synthesized abundant LDO materials and used as adsorbents for heavy metal ions' removal, and evidenced that LDO presented higher removal capacities than pristine LDHs due to its higher surface area and more reaction sites [23,28]. However, to some extent, the removal capacity of LDO was still significantly limited by its low amount of surface functional groups. If the high chemical stability of LDO is combined with high amount active sites of carbon materials, the high removal ability should be anticipated. Wang et al. [18] and Liu et al. [19] reported and evidenced that magnetic ferrite-MoS_2-CDs and $NiFe_2O_4$/CDs nanocomposites exhibited excellent capacities and reusability for Pb(II) and tetracycline efficient removal, respectively, which were higher than those of the pure ferrite-MoS_2 and $NiFe_2O_4$. Furthermore, to our best knowledge, LDO-CQD nanocomposites have never been reported as versatile adsorbents for U(VI) uptake from aqueous solutions.

Herein, pristine LDH and chitosan modified LDH (donated as CS-LDH) were successfully synthesized by coprecipitation method. Then, LDO and LDO-C nanocomposites were synthesized using prepared LDH as a precursor and using CS as carbon source by a facile and environmental-friendly calcination method at 500 °C. The as-prepared LDO and LDO-C samples were used and compared as versatile adsorbents for U (VI) immobilization from aqueous solutions. The effects of various environmental conditions (e.g., pH, ionic strength, contact time and temperature) on U(VI) adsorption to LDO and LDO-C were investigated by batch experiments. ^{241}Am(III) adsorption was also studied to evaluate the practical application of LDO and LDO-C for the efficient elimination of actinides. The XPS and EXAFS techniques were applied to deeply investigate the interaction mechanism between U(VI) and LDO or LDO-C.

2. Experimental section

2.1. Materials

Magnesium chloride ($MgCl_2{\cdot}6H_2O$), aluminium chloride ($AlCl_3{\cdot}6H_2O$), chitosan (CS), sodium carbonate (Na_2CO_3), sodium hydroxide (NaOH), nitric acid (HNO_3), sodium nitrade ($NaNO_3$) and Milli-Q water (18.2 MΩ·cm^{-1}) were used. All chemicals were purchased from Sinopharm Chemical Reagent Co. (China) and used without any further purification.

2.2. Preparation of LDO and LDO-C

2.2.1. Preparation of LDO

In general, $MgCl_2{\cdot}6H_2O$ (2.71 g) and $AlCl_3{\cdot}6H_2O$ (0.81 g) were dissolved in 20 mL Milli-Q water, then stirred the mixed solution for 3 h to achieve the sufficient dissolution in a 100 mL beaker (A). NaOH (1.47 g) and Na_2CO_3 (0.18 g) were dissolved in 20 mL Milli-Q water in another beaker (B). Solution B was dropwise added into solution A at nearly 10 min under constant stirring condition. And then, NaOH and HCl were used to adjust the pH of mixed suspension at ~9.5. In order to obtain uniform mixture, the mixed suspension was continuously stirred for 2 h, and poured into a 50 mL Teflon-lined stainless-steel autoclave, and settled in a sealed oven at 110 °C for 10 h, then maintained at 80 °C for 8 h to crystallize well. After filtration, the precipitates were rinsed with ethyl alcohol and Milli-Q water alternately, and dried at 80 °C for 12 h to eliminate the ethanol, and then the LDH was successfully synthesized. Finally, the LDO was obtained by calcination the LDH at 500 °C for 6 h under N_2 conditions.