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Adsorption property of Br-PADAP-impregnated multiwall carbon nanotubes towards uranium and its performance in the selective separation and determination of uranium in different environmental samples

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ABSTRACT

A newer efficient U(VI) ion adsorbent was synthesized by impregnating Br-PADAP [2-(5-Bromo-2-pyridylazo)-5-(diethylamino)phenol] onto multiwall carbon nanotubes (MWCNTs). The effects of various operation conditions on uranium adsorption (i.e., pH contact time, temperature, and initial uranium concentration) were systematically evaluated using batch experiments. The results indicated that the uranium adsorption on modified MWNCTs (5.571×10^{-3} g/mg × min) reached faster equilibrium than that on pristine MWNCTs (4.832×10^{-3} g/mg × min), reflecting the involvement of appropriate functional groups of Br-PADAP on the chelating ion-exchange mechanism of U(VI) adsorption. Modified MWNCTs (83.4 mg/g) exhibited significantly higher maximum Langmuir adsorption capacity than pristine MWNCTs (15.1 mg/g). Approximately 99% of uranium adsorbed onto modified MWNCTs can be desorbed by 2.5 mL of 1 M HNO_3 solution. Therefore, Br-PADAP-modified MWNCTs can server as a promising adsorbent for efficient uranium adsorption applications in water treatment. Subsequently, the proposed solid-phase extraction (using a mini-column packed with Br-PADAP/MWCNT) was successfully utilized for analysing trace uranium levels by the ICP-AES method in different environmental samples with a pre-concentration factor of 300-fold. The coexistence of other ions demonstrated an insignificant interference on the separative pre-concentration of uranium. the detection limit was recognized as 0.14 μg/L, and the relative standard deviation was approximately 3.3% ($n = 7$).

1. Introduction

Radioactive metals, especially uranium, have been extensively used in many military sectors (i.e., nuclear weaponry), civilian sectors (i.e., nuclear power plant), and other industries. The hazardous environmental impacts of radioactive metals originated from natural sources and industries have been an emerging research area during the recent decades (Schierz and Zänker, 2009; Wang et al., 2014; Kumar et al., 2017). Exposures to a low level of radioactive metals can cause a variety of potentially harmful impacts (i.e., acute and chronic toxicity), which is arisen from radiation release and chemo-toxic effect. Therefore, the World Health Organization sets the limitation of maximum uranium concentration in drinking waters to 15 ppb (Lu et al., 2017). Moreover, there is an increasing demand for devising more effective approaches for removing radioactive metals from water media and their determination in different environmental samples at the ultra-trace levels (Hosseini and Hosseini-Bandegharaei, 2011; Omidi et al., 2017).

Nanomaterials with large specific surface area and other proper

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properties have been acknowledged as a promising adsorbent for removing various dissolved pollutants from environmental water. Additionally, nanomaterials are possibly used for the solid-phase extraction and determination of some interested analytes at trace levels. Similarly, multiwall carbon nanotubes (MWCNTs) is also considered a potential adsorbent for removing various kinds of contaminants from solutions and separative pre-concentration of some hazardous contaminants in different environmental samples (Vellaichamy and Palanivelu, 2011; Sengupta and Gupta, 2017). Recently, a review work on MWCNTs-based adsorbents for nuclear waste management was published by Sengupta and Gupta (2017). They concluded that (1) MWCNTs will be a potential candidate for nuclear waste management and in near future, (2) modified MWCNTs (i.e., functionalized MWCNTs, MWCNTs composites, and ligands-impregnated MWCNTs) exhibited their highly dispersive property in aqueous media and excellent adsorption capacity toward the *f*-block elements.

Previous studies showed that the adsorption capacity of MWCNTs to potentially toxic metals can be remarkably enhanced if their surface was modified or oxidized. Some effective chemicals used for the modification process of MWCNTs surface comprised organophosphorus extractants (i.e., di-(2-ethyl hexyl phosphoric acid and tri-n-octyl phosphine oxide)) (Vellaichamy and Palanivelu, 2011), 4-(2-thiazolylazo) resorcinol (Alothman et al., 2012), 8-hydroxyquinoline (Kosa et al., 2012), and iminodiacetic acid (Wang et al., 2011). Meanwhile, several common oxidizing agents applied to oxidize MWCNTs surface included HNO_3 (Yang et al., 2009) and the mixture of HNO_3 and H_2SO_4 (Schierz and Zänker, 2009). However, poor selectivity is the most important problem of these new ion-exchange adsorbents constructed from the simple functionalization of carbon nanotubes. Therefore, few modification approaches, including impregnation or chemical bonding of desired ligands onto nanotubes, have been recently developed to synthesize chelating ion-exchange carbon nanotubes with highly desirable affinity for selective adsorption of potentially toxic metal ions (Vellaichamy and Palanivelu, 2011; Alothman et al., 2012).

Notably, although the high selectivity of carbon nanotubes makes them more useful for removing some toxic adsorbates from aqueous solution, perhaps the most important benefit of such selective adsorbents is their suitability for the pre-concentration and determination of trace levels of special pollutants in complicated matrixes and samples (Alothman et al., 2012). Hence, up to now, many researchers have applied a solid-phase extraction (an attractive separation-pre-concentration technique for potentially toxic metal ions) to determination of potentially hazardous metal ions in various aquatic environmental samples using the chelating ion-exchange carbon nanotubes (Vellaichamy and Palanivelu, 2011; Alothman et al., 2012).

According to the literature, 2-(5-Bromo-2-pyridylazo)-5-(diethylamino)phenol (Br-PADAP) can be considered as a promising selective chelating agent for removing U(VI) ions from aqueous solution (Jones, 1985; Hu et al., 2017). Therefore, in this study, we developed an innovative adsorbent by the impregnation of Br-PADAP ions onto multiwalled carbon nanotubes (MWCNTs). Br-PADAP/MWCNTs were used for (1) the removal of uranium from aqueous solution, and (2) solid-phase extraction and determination of uranium in different environment samples. Namely, the U(VI) adsorption characteristics onto Br-PADAP-modified MWCNTs and pristine MWCNTs was conducted in batch experiments under different operation conditions (i.e., solution pH, contact time, initial uranium concentration, and temperature). Subsequently, Br-PADAP/MWCNTs were packed into a mini-column and applied for separative pre-concentration and determination of trace levels of uranium in various natural and synthetic environmental samples.

2. Experimental

2.1. Materials

All chemical reagents used in this study were of analytical reagent grade and supplied by Merck (Darmstadt, Germany). MWCNTs were purchased from US Research Nanomaterials Inc. (CNI, Houston, TX, USA). The specific surface area of commercial MWCNTs was approximately 195 m^2/g. A uranium stock solution (500 mg/L) was prepared by dissolving $UO_2(NO_3)_2 \cdot 6H_2O$ in deionized water and acidifying with a small amount of concentrated HNO_3, to prevent hydrolysis. Solution pH was adjusted by adding 1.0 M HNO_3 or 1.0 M NaOH solution.

2.2. Apparatus

A VEGA/TESCAN instrument was used for taking field emission scanning electron microscopic (FESEM) micrographs, at an accelerating voltage of 15 kV, after gold-palladium sputter coating of the samples by a sputter coater instrument (Model SC 7620). The uranium concentration in solution was determined by a Shimadzu ICPS-7000 sequential inductively coupled plasma atomic emission spectrometer (ICP-AES). The operating condition of ICP instrument was listed in Table S1. The pH values in the aqueous solutions were measured by employing a PHS-3BW Model pH-meter (Bel, Italy) with a combined glass–calomel electrode. The flow rate of sample and eluent solutions through the mini-column was controlled by a BT100–1L peristaltic pump and a DG-2 head pump (Longer pump, China). A membrane filter (Sartorius; pore size 0.45 µm) was used to separate the adsorbent and adsorbate in solution.

2.3. Preparation and characterization of Br-PADAP/MWCNTs

The modification method of MWCNTs with Br-PADAP has been published in the previous literature (Alothman et al., 2012, 2015). To prepare the impregnated MWCNTs adsorbent, 0.5 g of dry MWCNTs was transferred into a 250-mL Erlenmeyer flask containing 60 mL methanolic solution of Br-PADAP (0.5%). The mixture was agitated for 24 h to complete the impregnation process and then heated at 373 K in a drying oven until the completely removed solvent. The modified MWCNTs were then washed successively with HCl (3 M) solution and distilled water. Finally, the Br-PADAP/MWCNTs sorbent was dried overnight at 373 K and stored in airtight brown bottles.

2.4. Adsorption experiments

The effect of operation conditions (i.e., solution pH, initial adsorbate concentration, contact time, and temperature) on the adsorption process of U(VI) onto pristine MWCNTs and Br-PADAP/MWNTs was investigated in batch experiments. Briefly, a 100-mL portion of uranium solution with a known initial concentration at an adjusted pH was transferred to a 250-mL Erlenmeyer flask, followed by adding 10 mg of adsorbent and agitating the mixture magnetically. After a prescribed time, the suspension was filtered, and the uranium concentration in the liquid phase was determined. The amounts of U(VI) uptake at time t [q_t (mg/g)] and at equilibrium [q_e (mg/g)] were determined by Eqs. (1) and (2), respectively. The removal efficiency of uranium (*RE*; %) was calculated from Eq. (3).

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{1}$$

$$q_t = \frac{(C_0 - C_t)V}{m} \tag{2}$$

$$RE = \frac{(C_0 - C_e)}{C_e} \times 100 \tag{3}$$

where C_0 (mg/L), C_t (mg/L), and C_e (mg/L) are the uranium