Progress in Nuclear Energy 100 (2017) 183–191

Contents lists available at ScienceDirect

Progress in Nuclear Energy

journal homepage: www.elsevier.com/locate/pnucene

Preparation, characterization and evaluation of a hybrid material based on multiwall carbon nanotubes and titanium dioxide for the removal of thorium from aqueous solution

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A R T I C L E I N F O

Article history:
Received 9 May 2016
Received in revised form
3 June 2017
Accepted 14 June 2017

Keywords:
Hybrid
Thorium
Multiwall carbon nanotubes
Titanium dioxide
Adsorption

A B S T R A C T

In the present work, a novel adsorbent based on oxidized multiwall carbon nanotubes (ox-MWCNTs) and titanium dioxide (TiO_2) has been synthesized and characterized. The obtained result from thermogravimetry analysis shows that the amount of TiO_2 inserted on ox-MWCNTs was about 44%. The adsorption behavior of thorium as a functional of initial concentration of thorium, pH, sodium nitrate concentration, adsorbents mass and shaking time was studied. The results showed that thorium adsorption on all the studied materials were strongly dependent on solution pH value, mass adsorbent and independent on sodium ion concentration. The gotten maximum adsorption capacity (q_{max}) of thorium on ox-MWCNTs, hybrid and TiO_2 was observed to be 62.11, 58.15 and 19.30 mg g^{-1}, respectively. This study suggests that hybrid and ox-MWCNTs can be a promising candidate for the removal of thorium from aqueous solution.

1. Introduction

Thorium as one of the naturally occurring radioactive elements has a wide distribution in a large number of minerals in minor or trace amounts. Since the last century, thorium has been extensively used in a various applications such as commercial lantern mantles, refractory materials, electronic components, alloys utilized for jet engine components, as a catalyst in the chemical industry, electrodes for arc welding, nuclear medicine, and in nuclear reactor fuels (Khazaei et al., 2011; Zhang et al., 2005). Various applications of thorium produce different gaseous, liquid and solid radioactive wastes. The inherent radioactivity of the most abundant radioisotope of thorium (Th-232) and the formation of its radioactive daughter products (Rn, Po, Bi, Ra) are the most important limiting factors in most industrial uses of thorium (Kaygun and Akyil, 2007). In addition, thorium is a well-known element to be carcinogen and hazardous pollutant due to both its radioactivity and toxicity. When thorium enters into the living organisms through ingestion, it accumulates mainly in liver, spleen and marrow as thorium hydroxide precipitation and could damage cells and might also cause cancer (Khazaei et al., 2011; Metaxas et al., 2003). Therefore, from the point of view of environmental protection, special attention has been given to the removal and separation of thorium from wastewater in an economical and safe manner.

A literature survey reveals that many various methods such as evaporation, chemical precipitation, ion exchange, adsorption, electrodeposition, solvent extraction, membrane and reverse osmosis techniques have been widely used for the removal of thorium from public and radioactive wastewater (Anirudhan et al., 2013; Zuoa et al., 2008; Patkar et al., 2009; Yongqi et al., 2012). Among these techniques, adsorption is the most commonly and well known technique because of its simplicity, low cost with easy operation conditions and regeneration for possible reuse. Various types of materials have been utilized as an adsorbent for this purpose (Weijuan and Zuyi, 2002; Hongxia et al., 2006; Guerra et al., 2009; Bhainsa and D'Souza, 2009 Chen and Wang, 2007; He et al., 2007; Kaygun and Akyil, 2007; Talip et al., 2009; Baybaş and Ulusoy, 2011; Anirudhan and Rejeena, 2011; Pan et al., 2011; Schmidt et al., 2012; Yusan et al., 2012; Anirudhan et al., 2013; Zhang et al., 2014). However, the preparation of new material with the superior performance is always of interest and worthwhile.

Recently, MWCNTs due to their remarkable and outstanding characteristics such as their large specific surface area, small size with highly porous, hollow and layered structures, light mass

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http://dx.doi.org/10.1016/j.pnucene.2017.06.009
0149-1970/

density, easily modified surfaces and large length/diameter ratio as a new adsorbent have attracted the interest of researches (Yavari and Davarkhah, 2013). The obtained results from various studies have proven that modified MWCNTs have great potential for removing of hazardous and toxic organic, inorganic and radionuclides pollution from waste water (Yavari et al., 2012; Sun et al., 2012; Yu et al., 2014). Moreover, MWCNTs due to their high surface area can also act as supporter for the adsorption materials to prepare the new hybrid materials. The aim of preparation and design of hybrid materials is to take advantage of the best properties of two worlds of chemistry (organic and inorganic) with complementary properties in a single material. Recently, synthesis of hybrid material containing MWCNTs decorated with metal oxides species has showed unique adsorption properties (Penga et al., 2005; Peng et al., 2005; Di et al., 2006; Wang et al., 2007; Chen et al., 2009).

For many years, nano-sized titanium dioxide due to its high chemical, thermal and radiation stability, good mechanical properties for column operation, high adsorption capacity for some of radioisotopes and reasonable adsorption kinetics, has been extensively studied as one of the various classes of inorganic ion exchanger. The ability of this material for reasonable adsorption of some ions and radionuclides such as thorium, cesium, strontium, fluoride and uranyl has been proved in the literature (Shabana and El-Dessouky, 2002; Li et al., 2010; Zhijun et al., 2004, 2005; Hua et al., 2012; Karen et al., 2011). Newly, many studies have been performed on the investigation of hybrid material based on TiO_2 and CNTs in electrical, catalytic, optical and sensing application. However, no studies have been yet reported on preparation of this hybrid material for the removal of thorium or other ions in the literature. Therefore, in continuation of our research study on the preparation of new hybrid material for the removal application of hazardous and toxic metal ions from aqueous solution (Asadollahi et al., 2015), we synthesize a new adsorbent based on TiO_2 and MWCNTs for evaluation of its ability for removal of thorium from aqueous media.

2. Experimental

2.1. Materials

All chemicals and reagents were of analytical grade and obtained from E. Merck or Fluka. Demineralized water was used throughout the whole process. The pristine MWCNTs with length range of 5–15 μm, outer diameter range of 10–20 nm and purity of over 95% were purchased from Chengdu organic chemical Co. Ltd., China. The chemical vapor deposition (CVD) method along with small amount of Fe as a catalyst was used to synthesize MWCNTs.

2.2. Preparation of thorium stock solution

Thorium stock solution (1000 mgL^{-1}) was prepared freshly by dissolving specific amount of $Th(NO_3)_4.5H_2O$ in 7 mL of concentrated nitric acid. The resulting solution was diluted to 1 L using demineralized water and the required solution with definite concentrations (5–100 $mgL^{-1}mg\ L^{-1}$) was further prepared from stock solution, meanwhile the nitric acid concentration in all the solution was adjusted at 0.1 M using the negligible amount of concentrated nitric acid.

2.3. Apparatus

Crystalline or amorphous feature of sample were investigated by X-ray powder diffraction (XRD) using a STIDY-MP diffractometer (model STOe) and nickel-filtered Cu-K_α radiation at 298 K. The Fourier Transform InfraRed (FT-IR) spectra were recorded on a FT-IR spectrophotometer (Bruker spectrometer, Vector 22) in transmission mode with the wave number range of 400–4000 cm^{-1}. Thermogravimetric analysis (TG) was performed with a PL-STA1500, Rheometric science from 20 to 700 °C at a heating rate of 10 °C min^{-1} and a nitrogen flow of 200 mL min^{-1}. The Brunauer-Emett-Teller (BET) surface area and pore parameters of the samples were measured using a Covantocrom (model NOVA2000). Transmission electron microscopy (TEM) micrograph were obtained with a transmission electron microscope (CM30, Phillips) using the acceleration voltage of 200 kV.

2.4. Purification and functionalization of MWCNTs

Since the prepared pristine MWCNTs mainly contains impurities such as amorphous carbon, carbon block, fullerene, graphite sheet, nanoparticles and metal catalyst, the purification of those is very important. On the other hand, oxidation of the purified MWCNTs can offer higher specific surface area and a large number of functional groups containing oxygen to improve its hydrophilic properties and adsorption or attachment site on the external and internal surfaces of MWCNTs. Therefore, purification and functionalization of MWCNTs were performed according to literature method described elsewhere (Yavari et al., 2011). In this procedure, 1 g of pristine MWCNTs was immersed in 50 mL nitric acid solution (3 M) for 24 h to dissolve the catalyst support and then dispersed in a 100 mL concentrated nitric acid and refluxed for 2 h at 140 °C. The mixture were filtered through a polytetrafluoroethylene (PTFE) filter membrane (0.45 μm pore size) and washed repeatedly using hot demineralized water until the solution reached a pH value of 6.5. Finally, the samples were dried in an oven at 80 °C for 24 h.

2.5. Synthesis of amorphous titania

Nanosized TiO_2 can be prepared by sol-gel method using $TiCl_4$ as a precursor. In the first stage, a certain amount of $TiCl_4$ was dissolved in 50 mL of cooled demineralized water into 250 mL conical flask while the container was placed in an ice water bath. The concentration of titanium was adjusted to 0.3 M and after that pH of this aqueous solution reached 7 by using 2.5 M NH_3 solution. The prepared precipitate is filtered and repeatedly washed with demineralized water in order to remove the remaining ammonium and chloride ions. Finally, sample was dried over night at 30 °C.

2.6. Synthesis of MWCNTs/TiO_2 hybrid

To prepare hybrid material, it was performed according to literature method described elsewhere (Sun et al., 2004). To this end, an appropriate amount of $TiCl_4$ was added to HCl solution until the 3 M titanium solution in 0.5 M HCl was achieved. Then, 5 mL of 3 M titanium was added to 295 mL of demineralized water and in the next step, 1.5 mL of 50 ppm polyethylene imine (PEI) solution was added while the solution was stirred. After that, the container was covered by aluminum foil and put in an oven for 3 h at 70 °C. Subsequently, 0.1 g ox-MWCNTs were added to this mixture and put in an ultrasonic for 10 min. Ultimately, the mixture was refluxed at 70 °C for 2 h and the synthesized hybrid was separated by filtration, washed frequently with demineralized water and dried in ambient temperature for 24 h.

2.7. Batch adsorption experiment

To investigate the adsorption behavior of thorium as a functional of initial concentration of thorium, adsorbents mass, solution ionic strength, pH, and equilibrium time onto prepared materials,