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Hierarchically porous bismuth oxide/layered double hydroxide composites: Preparation, characterization and iodine adsorption

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ABSTRACT

The discharge of iodine-containing wastewater into environment will lead to the water pollution due to the toxicity and radioactivity of iodine and iodine isotopes. A versatile adsorbent which can effectively adsorb the iodine is in high demanded for this issue. In this work, the hierarchically porous bismuth oxide/layered double hydroxide (Bi_2O_3/LDHs) composites were prepared based on biological template techniques, and the as-prepared composites show enhanced iodine adsorption capacity compared with LDHs fibers. The Mg–Al LDHs fibers with hierarchical architectures are synthesized by directly growth of nanoscaled LDHs platelets on Al_2O_3 fiber surfaces. The Bi_2O_3/LDHs composites with sponge-like structures are prepared by desorption of Bi_2O_3 on the surfaces of LDHs fibers. The iodine adsorption behavior on Bi_2O_3/LDHs composites was examined in sodium iodine aqueous solutions. The appropriate iodine adsorption was obtained at a neutral pH with maximum adsorption capacity of 101.9 mg/g. The Langmuir model successfully describes the iodine adsorption isotherms, while the pseudo-second-order kinetic model is better at describing the iodine adsorption kinetics onto the Bi_2O_3/LDHs composites. Since the Bi_2O_3/LDHs composites show near complete removal of iodine ions, the as-prepared Bi_2O_3/LDHs composites are expected to have practical applications as iodine adsorbent in wastewater treatment.

1. Introduction

With the increasing stress on environmental pollution and energy shortage, much attention has been focused on the development of clean energy and pollution control technologies. Nuclear energy, as a reliable and clean energy source, can solve problems of energy shortage if the challenge of radioactive wastes pollution can be tackled (Ma et al., 2014). However, appropriate management of radioactive waste has gained considerable interest in nuclear chemistry since the extensive application of nuclear energy (Montaña et al., 2013). The nuclear power plant accidents, such as Chernobyl and Fukushima disasters, have reminded people that radionuclides are highly acutely toxic. Large amounts of radionuclides especially ^{129}I and ^{131}I are released in Chernobyl and Fukushima nuclear disaster (Liu et al., 2016), which are the potential radionuclide contaminants and toxic anion pollutants. Radioiodines, as the inevitable by-products of nuclear fission, have generated immense interest and concern, because of their high toxicity to human and animals' thyroid gland through bioaccumulation (Mao et al., 2016). Therefore, effectively treatment of the radioiodine pollution is quite necessary, and the selectively iodine separation with high separation efficiency and environmentally friendly processes is still an important challenge.

In addition, iodine ions can be found in environment derived from the contamination of chemical industry, pharmaceutical industry, food industry and high-tech industries such as production of pesticides and pharmaceuticals (Han et al., 2016). The discharge of such iodine-containing wastewater into the surface water will lead to the contamination of drinking water and groundwater. Unlike organic contaminants, iodine ions are non-degradable and tend to accumulate in thyroid gland of human and animals through the food chain (Outokesh et al., 2012). Thus, the removal of

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inorganic iodide ions from industrial wastewater is critically important for protecting human and animals' health. Currently, solvent extraction (Fujiwara, 2016), chemical precipitation (Xu et al., 2016), membrane separation (Gryta, 2013) and adsorption (Dultz et al., 2005) are the four basic approaches to remove iodine ions from aqueous solution. However, solvent extraction and chemical precipitation have some undesirable sides such as high operation costs, low iodine removal efficiency and the generation of secondary pollutants, while membrane processes are relatively expensive to install, and prone to scaling, fouling, or membrane degradation. Among them, the surface adsorption is the most extensively used one because of its cost-effectiveness, easy handling and high treatment efficiency (Ling et al., 2016). There has been an increasing amount of research on the synthesis of functional adsorbents for removal of iodine ions from water, including zeolitic imidazolate frameworks (Yuan et al., 2016), SBA-15 mesoporous silica (Shakeri et al., 2013), and Ag_2O grafted titanate nanolamina (Bo et al., 2013). However, high cost, low adsorption capacity, slow adsorption rate and poor regeneration of these adsorbents are still challenges to large scale applications (Rong et al., 2016). Therefore, an effective and inexpensive iodine adsorbent material with high iodine removal efficiency is extremely urgent.

Layered double hydroxides (LDHs), which are composed of positively charged metal hydroxide layers and exchangeable interlayer anions (Ragavan et al., 2006), are promising compounds for developing materials with adsorption (Wang et al., 2016a,b), optical (Liu et al., 2006), catalytic (Lei et al., 2011), and electrochemical properties (Li et al., 2011). The LDHs have a permanent positive charge layer due to the partial substitution of the divalent metal ions by trivalent metal ions (Wang et al., 2010). Recently, a variety of LDH based materials with different morphologies, microstructures and chemical compositions (M^{2+}/M^{3+} molar ratio) have been reported as good candidates for halogen ions adsorption. Nevertheless, the practical applications of LDHs based materials in halogen ions adsorption have been constrained due to their low surface activity and limited adsorption sites (Zhang et al., 2013). To enhance the surface adsorption properties of LDHs, our group has done some work focusing on the fabrication of hierarchically porous LDHs based composites for applications in biomolecules separation and fluoride ions adsorption (Wang et al., 2014).

Besides, inorganic solid adsorbents, such as silver-based adsorbents (Bo et al., 2013), bismuth-based adsorbents (Liu et al., 2016) and metalloporphyrin-based adsorbents (Sigen et al., 2014), are used to capture iodine ions from wastewater. However, these metal-loaded adsorbents have low adsorption capacities, owing to their low surface areas and less ordered pore structures. In particular, the main disadvantages of metal-loaded iodine adsorbents are related to their high cost and inherent instability in aqueous environments. As environmental material, bismuth-based materials are making a positive effort in water pollution control, which was widely used for removal or degradation of pollutants from aqueous solutions due to its advantages such as simple synthesis, high stability, low toxicity and low cost. Many efforts have been made to design and prepare the bismuth-based materials for application in water treatment.

Though iodine adsorption on bismuth-based materials and LDHs-based materials is evident by some research workers, there are no reports on the removal of iodine ions from aqueous solutions using hierarchically porous Bi_2O_3/LDHs composites. Enhanced iodine removal efficiency could possibly be achieved by the combination of the anion intercalation of LDHs and strong attraction between iodine ions and Bi_2O_3. In the present work, we synthesized the hierarchically porous Bi_2O_3/LDHs composites by combining biological template method, *in* situ growth and deposition techniques. Using the Al_2O_3 fibers as aluminum source, the porous LDHs fibers are prepared by an *in* situ growth method, involving the growth of nanoscaled LDHs platelets on the surfaces of Al_2O_3 fibers. The hierarchically porous Bi_2O_3/LDHs composites are prepared by the impregnation and calcination method. The attached Bi_2O_3 nanocrystals have high iodine ions capture properties because they are on the external surface of the hierarchically porous LDHs and can be readily accessed by iodine ions.

2. Materials and methods

2.1. Chemicals and materials

The absorbent cotton, as biotemplates for fabrication of porous LDHs fibers, was purchased from Sinopharm Chemical Reagent Co., Ltd. All other reagents and chemicals were of analytical grade without purification. Hexamethylenetetramine (HMT, $C_6H_{12}N_4$), Aluminum nitrate nonahydrates ($Al(NO_3)_3\cdot 9H_2O$), Bismuth nitrate pentahydrate ($Bi(NO_3)_3\cdot 5H_2O$), Anhydrous ethanol (C_2H_5OH), Magnesium nitrate hexahydrate ($Mg(NO_3)_2\bullet 7H_2O$) were obtained from Sinopharm Chemical Reagent Co., Ltd. Potassium iodide (KI) were supplied by Aladdin Reagents Co., Ltd. Polyethylene glycol (PEG; MW = 20 000) was purchased from Shanghai Reagents. Double-distilled water was employed in all experiments.

2.2. Fabrication of porous Mg–Al LDHs fibers

The Al_2O_3 fibers, as aluminum source for fabrication of porous LDHs, were prepared by biotemplating method using the cleaned cotton fibers as templates. The processes of fabrication of porous LDHs fibers were similar to that described in our previous work (Zhang et al., 2016). In a typical preparation, 0.98 g HMT and 1.538 g of $Mg(NO_3)_2\cdot 6H_2O$ were dissolved in 60 mL of distilled water in an 80 mL autoclave. Then, 0.153 g of as-prepared Al_2O_3 fibers was placed in the above mixed solution. The autoclave was tightly sealed and kept at 110 °C for 12 h. After that, the reacted products were taken out of the autoclave, washed with distilled water several times, and dried under vacuum at 80 °C for 24 h. Finally, the as-synthesized samples were calcined at 500 °C for 4 h to obtain hierarchically porous Mg–Al fiber composites.

2.3. Preparation of hierarchically structured Bi_2O_3/LDHs composites

The fabrication of hierarchically structured Bi_2O_3/LDHs composites involved the impregnation and calcination process using the $Bi(NO_3)_3$ and LDHs fibers as starting materials. The procedure for the preparation of Bi_2O_3/LDHs composites as follows: 0.970 g of $Bi(NO_3)_3\cdot 5H_2O$ was dissolved in 200 mL of polyethylene glycol under vigorous stirring for 2 h. Then, 0.2 g of Mg–Al fiber composites was immersed into the $Bi(NO_3)_3$ solution for 3 h, followed by ultrasonic treatment for 1 h. The infiltrated fiber composites were centrifuged, washed with water and ethanol, vacuum-dried at 80 °C for 24 h. Finally, as-obtained products were calcined at given temperatures for 4 h to obtain hierarchically structured Bi_2O_3/LDHs composites.

2.4. Sample characterization

Scanning electron microscopy (SEM, S-3400N) was used for detecting the microstructures and morphologies of Mg–Al LDHs fibers and Bi_2O_3/LDHs composites. The general structures of as-prepared products were verified by an X-ray diffractometer (Shimadzu XRD-6100) with Cu Kα radiation, a scanning rate of 4°/min was used to record the patterns in the 2 theta angle ranging from 10° to 80°. The nanoporosity and surface areas of as-obtained samples were estimated by using nitrogen adsorption