Materials Research Bulletin 68 (2015) 54–59

Contents lists available at ScienceDirect

Materials Research Bulletin

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

Copper ions removal from water using functionalized carbon nanotubes–mullite composite as adsorbent

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ARTICLE INFO

Article history:
Received 13 December 2014
Accepted 5 March 2015
Available online 9 March 2015

Keywords:
A. Composite
A. Ceramics
A. Nanostructures
B. Vapor deposition
D. Surface properties

ABSTRACT

Carbon nanotubes–mullite composite was synthesized by direct growth of carbon nanotubes on mullite particles via chemical vapor deposition method using cyclohexanol and ferrocene as carbon precursor and catalyst, respectively. The carbon nanotubes–mullite composite was oxidized with concentrated nitric acid and functionalized with chitosan and then used as a novel adsorbent for copper ions removal from water. The results demonstrated that modification with concentrated nitric acid and chitosan improves copper ions adsorption capacity of the prepared composite, significantly. Langmuir and Freundlich isotherms and two kinetic models were applied to fit the experimental data. The carbon nanotubes growth on mullite particles to form the carbon nanotubes–mullite composite with further modification is an inherently safe approach for many promising environmental applications to avoid some concerns regarding environment, health and safety. It was found that the modified carbon nanotubes–mullite composite can be considered as an excellent adsorbent for copper ions removal from water.

1. Introduction

Heavy metal ions as the main components of industrial wastewaters have caused great environmental problems today. As a result of poisonous effects of heavy metal ions in water on human beings and their accumulation in organisms, their presence in water is a general health concern. Thus, research relating to heavy metal ions removal from water is essential for environment health [1–4].

Copper as one of the most important toxic heavy metals has many applications in industries. Copper contamination in water occurs mainly from metal cleaning and plating bath, paper and pulp, fertilizer, refineries, and wood preservatives. Copper can cause serious problems to human beings such as stomach intestinal distress, kidney damage, anemia and even coma and eventual death. Therefore, it is important to develop technologies that can be industrially used for copper ions removal from water. Several conventional methods e.g., ion-exchange, evaporation and concentration, chemical precipitation, reverse osmosis, adsorption, and electrodialysis have been applied for heavy metal ions removal from effluents. Considering from economy and efficiency points of view, adsorption is regarded as one of the most promising and widely used methods [3–5]. The most common adsorbent materials are activated carbon [6], alumina silica [7], metal hydroxides [8] and biosorption materials [9]. However, low adsorption capacities or removal efficiencies of heavy metal ions are the main problem of these adsorbents. Therefore, research for finding new and more effective materials to be used as adsorbents is very important subject [10–14].

Carbon nanotubes (CNTs), a new member in carbon family, are interesting adsorbent in wastewater treatment due to their characteristics for example small size, high capacity, uniform pore distribution, etc. As a result of chemical interactions between heavy metal ions and surface functional groups of CNTs, they have important potential for heavy metal ions removal [3,15–26]. As reported in literature [27], CNTs have demonstrated superior affinity toward copper ions, compared to other divalent heavy metal ions.

Chitosan (CS), a natural aminopolysaccharides polymer, with excellent properties such as high hydrophilicity, good film and fiber-forming ability, normal chemical resistance, wide availability and biocompatibility and its abundant amino and hydroxyl functional groups (as reactive sites), has great capacity for heavy metal ions adsorption [28–32].

Although nanotechnology has offered many beneficial applications in environmental fields, nanoparticles such as CNTs

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http://dx.doi.org/10.1016/j.materresbull.2015.03.017
0025-5408/

present large and somewhat unknown risks yet to be identified in health, safety and environmental (HES) management [33,34]. Therefore, economical wastewater treatment without CNTs leakage into water is preferable.

In the present work, the CNTs–mullite composite was synthesized by direct growth of CNTs on micron-sized mullite particles via chemical vapor deposition (CVD) method using cyclohexanol and ferrocene as carbon precursor and catalyst, respectively. The as-synthesized CNTs–mullite composite was oxidized with concentrated nitric acid and functionalized with chitosan as a good functionalizing agent and then used for copper ions removal from wastewater. Also, the Langmuir and the Freundlich isotherm models and the pseudo-first-order and the pseudo-second-order kinetic models were applied to fit the experimental data.

No prior investigation on synthesis and characterization of the functionalized CNTs–mullite composite as adsorbent for copper ions removal from water has been reported in the literature yet. Using the functionalized CNTs–mullite composite as adsorbent, economical wastewater treatment without CNTs leakage into water is feasible.

2. Materials and methods

2.1. Synthesis of the CNTs–mullite composite

The CNTs–mullite composite was synthesized via CVD method. A schematic diagram of the experimental CVD set-up is shown in Fig. 1. The CVD system consisted of a horizontal stainless steel tube housed in a one-stage cylindrical furnace. Cyclohexanol (purity ≥ 98%, Fluka) and ferrocene (purity ≥ 98%, B.D.H) were used as carbon source and catalyst, respectively. Nitrogen was used as carrier gas. A flask containing a mixture of ferrocene and cyclohexanol with certain mass ratios was connected to the reactor nearby the nitrogen inlet. Evaporating the reagent mixture was performed using an oil bath. The mullite particles (with diameter of about 1 μm) were initially cleaned in an ultrasonic acetone bath for 30 min. The cleaned mullite particles were placed in the middle of the reactor.

At first, the reactor was purged with nitrogen in order to eliminate oxygen from the reaction chamber and then the furnace was heated to the preset temperature. The reactor was preheated to a preset temperature (750 °C); subsequently the flask containing the reagent mixture was placed in the oil bath (at 250 °C) for immediate vaporization process. The obtained vapor was carried by nitrogen flow rate toward the higher temperature region of the reactor where the mullite particles were situated. Pressure inside the reactor was kept constant during the reaction. When the reaction time was over (after 1 h) the furnace was switched off and the reactor was cooled gradually to room temperature.

Scanning electron microscope (SEM, Philips: XL30) was used for analysis of the as-synthesized CNTs–mullite composite morphology.

2.2. Oxidation of the CNTs–mullite composite

The as-synthesized CNTs–mullite composites were immersed in concentrated nitric acid (65%, Merck) for 20 h and then washed using deionized water several times until pH of the washing water showed no change, then dried at 110 °C for 24 h.

2.3. Modification of the CNTs–mullite composite

Chitosan (CS) (Mw_{ave} = 190,000–310,000, Aldrich) polymeric solution (2 wt%) was prepared by dissolving distinct amount of chitosan powder in 1% (v/v) acetic acid solution with stirring at room temperature for 24 h. The CNTs–mullite composites were dipped in the polymeric solution for 15 min and then removed and placed on a glass plate. The samples were dried at ambient temperature for 1 day and then annealed at 90 °C for 1 h.

The acid treated CNTs–mullite composites were also dipped in the polymeric solution for 15 min and then removed and placed on

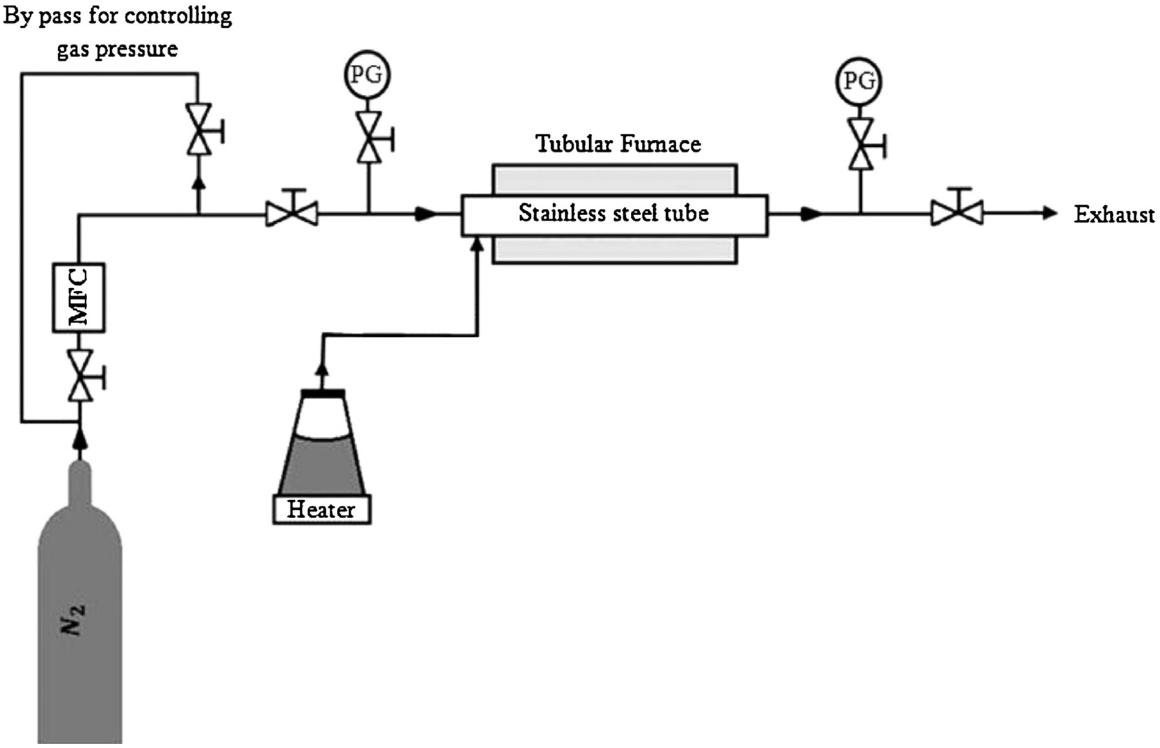

Fig. 1. Schematic diagram of the experimental CVD set-up.