Chemical Engineering Journal 284 (2016) 599–608

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Synthesis of functionalized carbon nanotubes by floating catalytic chemical vapor deposition method and their sorption behavior toward arsenic

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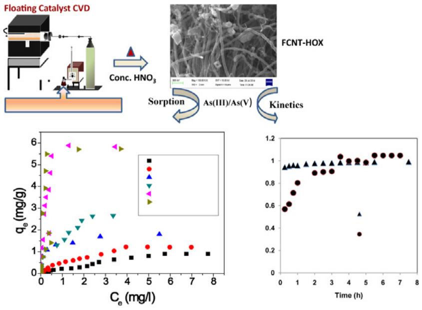
HIGHLIGHTS

- Floating catalyst CNTs (FCNT) prepared without substrate using Ferrocene at lower temperature.
- Ferrocene serves the dual purpose as catalyst for CNT and sorption of arsenic.
- Functionalized by physical and chemical methods.
- Studies on the removal of As(III) and As(V) for the first time.
- Mechanism proposed by XPS studies.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 29 June 2015
Received in revised form 20 August 2015
Accepted 21 August 2015
Available online 8 September 2015

Keywords:
Arsenic
Contamination
Floating catalyst
CNT
Adsorption

ABSTRACT

In this work carbon nanotubes (CNT) were prepared by floating catalytic chemical vapor deposition method using Ferrocene and Benzene as hydrocarbon source. Use of ferrocene serves the dual purpose as the floating catalyst for the CNT formation and as well as to facilitate arsenic sorption. CNTs were further activated by two ways (1) chemical treatment of CNTs using nitric acid which oxidized CNTs (FCNT-OX), (2) heat treatment at 1000 °C in N_2 atmosphere and further oxidized with nitric acid to obtain FCNT-HOX. The energy dispersive X-ray spectroscopy of FCNT, FCNT-OX and FCNT-HOX revealed the presence of iron in the CNTs. The specific surface area of FCNT, FCNT-OX and FCNT-HOX were found to be the prepared 74, 129 and 169 m^2/g respectively. The adsorption properties of As(III)/As(V) as a function of pH, contact time and initial metal concentration were evaluated. The adsorption kinetics fitted the Pseudo Second Order Kinetics with correlation coefficients >0.99. The equilibrium data were modeled with Langmuir and Freundlich isotherms and various isotherm parameters were evaluated. The maximum adsorption capacity of FCNT-HOX towards As(III) and As(V) were found to be 5.99 and 6.37 mg/g respectively. It was found that the As(III)/As(V) adsorption capacity for the prepared adsorbents were in the order of FCNT-HOX > FCNT-OX > F CNT. Using XPS studies suitable mechanism for sorption of As(III) and As(V) has been postulated.

1. Introduction

Arsenic contamination in ground water is widespread and its carcinogenic effects on human health are well documented [1–3]. World Health Organization (WHO) and Bureau of Indian standards

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http://dx.doi.org/10.1016/j.cej.2015.08.145
1385-8947/

(BIS) provide the maximum contamination limit to be 10 ppb in the drinking water [4,5]. It is well known that in aquatic environments arsenic exists in both trivalent (H_3AsO_3) and pentavalent states ($H_2AsO_4^-$ and $HAsO_4^{2-}$) [6]. Trivalent arsenic species are mobile and 25–60 times more toxic than pentavalent arsenic species [7]. A wide range of sorbents have been studied to remove arsenic, including activated carbon, natural minerals, biomasses and surface modified materials [8–10]. From the literature it is evident that iron based adsorbents exhibit higher arsenic uptake and various materials such as granular ferric hydroxide [11], iron ores [12], hydroxy iron oxides [13], zerovalent iron [14] have been reported. Though the adsorbents cited above are inexpensive, the main disadvantage of these sorbents is its inability to remove both inorganic forms of arsenic down to ppb levels from ground water matrix at neutral pH. To augment this challenge, arsenic decontamination using nanomaterials is expected to play an increasingly important role.

Nanomaterials include graphene, carbon nanotubes (CNTs), carbon nanofibers, fullerene, etc. are widely used in the environmental remediation applications [15,16]. The attractive features of CNTs such as the ability to establish p–p electrostatic interactions, large surface area, high porosity makes it an efficient adsorbent to tackle various pollutants like lead and cadmium [17] and Cr(VI) [18]. The sorption capacity of CNTs towards arsenic is increased by surface oxidation [19], introduction of functional groups [20] or doping of metal oxides such as zirconia [21], cerium/iron bimetal oxide [22], ZVI doped CNTs [23] and manganese oxide [24].

Synthesis of carbon nanotubes by chemical vapor deposition (CVD) has shown to be economical and more controllable when compared to other high temperature synthetic methods such as laser vaporization or arc discharge. Transition metal and metal compounds are mainly used as catalyst for growing CNTs [25]. Several iron (Fe) based precursors such as ferric nitrate, ferric chloride, and ferric sulfate, are widely used in environmental remediation applications. However, these precursors required substrate and multistep process including calcination and reduction [25]. Another main disadvantage in most CVD approaches is the use of hazardous and toxic gases such as acetylene and Iron pentacarbonyl, as the source of carbon and very often H_2 gas is used for improving tube graphitization [26–28]. To combat these issues there needs to be a metal precursor which can be directly used in the CVD process and also sustain its zerovalent state. Ferrocene is economically viable, non-toxic and could act as an iron precursor [29]. Use of ferrocene serves the dual purpose as the floating catalyst for the CNT formation and as well as to facilitate arsenic sorption. The main advantages of this method are the absence of hydrogen during pyrolysis, low temperature for CNT production, use of less toxic floating catalyst and synthesis of CNTs without any substrate.

To further improve the selectivity and reactivity of CNTs towards arsenic the prepared CNTs were further activated by two ways (1) chemical treatment of CNTs using nitric acid which oxidized CNTs (FCNTs-OX), (2) heat treatment at 1000 °C in N_2 atmosphere and further oxidized with nitric acid to obtain FCNT-HOX. Thus the sorbents obtained namely, FCNTs, FCNT-OX and FCNT-HOX were characterized by various techniques including SEM, TEM, BET, FTIR, Raman, XRD and XPS and evaluated as adsorbents for the removal of As(V) and As(III) from aqueous solutions. The possible adsorption mechanisms were also discussed.

2. Experimental details

2.1. Materials

Sodium arsenate hydrate, $Na_2HAsO_4{\cdot}7H_2O$ and sodium arsenite $NaAsO_2$ (Merck) were used to prepare stock solution of As(III) and As(V) standards. All standard solutions were prepared fresh daily and suitable dilutions were carried out. All reagents were of AR grade. A stock solution of As(III) and As(V) was made using milli-Q water. Standard acid and base solutions (10% H_2SO_4 and 10% NaOH) were used for pH adjustments.

2.2. Preparation of FCNTs by CVD method

The iron (Fe) metal doped multi walled carbon nanotubes (FCNT) was prepared using catalytic chemical vapor deposition (CCVD) techniques. The CCVD process is based on the catalytic decomposition of liquid hydrocarbons by pyrolysing of the solution (Fig. 1). A solution containing 10% ferrocene in benzene was used as the carbon source. The flow rate of nitrogen gas and ferrocene/benzene solution was controlled by mass flow controller (Bronkhorst high-tech. Netherland) and peristaltic pump, respectively. The nitrogen gas had dual roles, *viz.*, to produce inert atmosphere within the reactor and acted as a carrier during CVD process (to exert the pressure on the ferrocene/benzene solution that regulated the flow of liquid directed to the nozzle). The temperature of the electric furnace was gradually heated up-to 800 °C in the presence of nitrogen atmosphere. The flow rate of nitrogen gas and ferrocene/benzene solution was set to 100 sccm and 1 ml/min respectively. Next, the ferrocene/benzene solution was pumped into the reactor for 30 min at 800 °C reactor temperature. The reactor was gradually cooled to room temperature using nitrogen gas. The FCNT deposition occurred in the hot zone of the reactor. The prepared FCNT were removed from the reactor surface for further use.

2.3. Functionalization of FCNTs

As prepared FCNT (2 g) was dispersed in 30 ml of nitric acid (69 wt%) in 100 ml conical flask. Next, the resulting dispersed solution was heated at 80 °C until the acid evaporated completely. After cooling to room temperature, and washing with deionised water until pH of filtrate becomes neutral. Finally, FCNT-OX was dried in the oven at 80 °C overnight and used for further experiments. To prepare FCNT-HOX, 2 g of FCNT was placed in a perforated boat in the middle region (heating zone) of a reactor, and nitrogen was introduced into reactor with 150 sccm flow rate throughout the entire experiment. The reactor was heated at the rate of 5 °C/min up to 1000 °C and this temperature was maintained for 1 h. Finally, the heated material was cooled to room temperature under the vacuum. Finally the heated FCNT was oxidized by HNO_3 as described above to obtain FCNT-HOX.

2.4. Characterization

Images of as prepared and functionalized FCNT was obtained with a field emission scanning electron microscope (Carl Zeiss NTS GmbH, Oberkochen (Germany) Model: SUPRA 40VP) operated at an accelerating voltage of 10 kV. TEM analysis was carried on a Technai G2 T-20 (FEI, Eindhoven, Netherlands) transmission electron microscope operated at 200 kV. Raman spectra were obtained using Confocal Raman Microscope (Witec, Germany) using a striking wavelength of 514 nm. The X-ray diffraction (XRD) patterns of the CNTs were recorded at ambient temperature using Hecus X-ray Systems GmbH, Graz (Austria) Model: S3 MICRO. The samples were irradiated with monochromatized Cu Kα (1.5406 Å) X-ray source and analyzed between 20° and 80° (2θ). The operating current and voltage used were 40 mA and 45 kV, respectively. Nitrogen adsorption–desorption isotherms were obtained using an Autosorb-iQ of Quantachrome at 77 K, with degassing at 373 K prior to the measurements. The Brumauer–Emmett–Teller (BET) method was utilized to calculate the specific surface areas. Pore size distribution curves were determined by the