



Carbon nanofibers containing metal-doped porous carbon beads for environmental remediation applications



Prateek Khare^a, Neetu Talreja^b, Dinesh Deva^c, Ashutosh Sharma^{a,c}, Nishith Verma^{a,b,*}

^aDepartment of Chemical Engineering, Indian Institute of Technology, Kanpur 208 016, India

^bCenter for Environmental Science and Engineering, Indian Institute of Technology, Kanpur 208 016, India

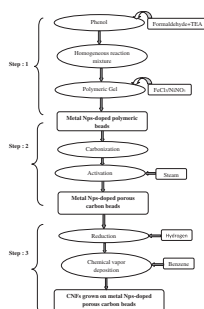
^cCenter for Nanosciences, Indian Institute of Technology, Kanpur 208 016, India

HIGHLIGHTS

- Metal Nps incorporated within polymeric beads in situ during a polymerization step.
- Porous carbon beads containing metal Nps produced on carbonization and activation.
- Carbon nanofibers grown within micro-mesopores by catalytic CVD.
- Significant adsorption capacity for the produced materials.

GRAPHICAL ABSTRACT

Flow diagram of preparing Fe- or Ni-Nps-doped carbon beads decorated with CNFs.



ARTICLE INFO

Article history:

Received 20 February 2013

Received in revised form 28 April 2013

Accepted 30 April 2013

Available online 16 May 2013

Keywords:

Carbon nanofiber (CNF)

Polymeric beads

Chemical vapor deposition (CVD)

Adsorption

Environmental remediation

ABSTRACT

Carbon nanofibers (CNFs) were grown in porous carbon beads (~0.5 mm) by chemical vapor deposition (CVD). The beads were prepared by the carbonization and activation of Ni- or Fe-doped phenolic beads produced by suspension polymerization, with the metals incorporated in situ during a polymerization step. The carbon beads decorated with Ni- or Fe-CNf were tested as adsorbents for the removal of different pollutants in the aqueous phase. The prepared material showed superior performance relative to the parent metal-doped porous carbon beads without CNFs. The loadings of vitamin B12 (vit B12) on Ni-CNf beads and that of arsenic (As) on Fe-CNf beads were determined to be 180 mg/g and 18 mg/g, corresponding to an aqueous phase vitamin B12 concentration of 250 ppm and an As concentration of 50 ppm, respectively. These loadings were significantly larger than those obtained for the parent materials. The *nanofibrous* carbon beads developed here with enhanced adsorption capacity is novel, effective and simple to synthesize.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Recently, carbon nanofibers (CNFs) have attracted great interest because of their unique physicochemical characteristics, such as their amorphous structure, relatively large surface area, stability in acidic/basic environments, being amenable to surface function-

alization, and high chemical reactivity because of the exposed edges and unsaturated bonds on their graphene layers [1]. CNFs have been used extensively as adsorbents, catalyst supports, and composite materials for battery electrodes and hydrogen storage [2–5].

CNFs are grown on various types of substrates, applied for different end-applications. The common substrates are inorganic materials, such as aluminum oxide, silicon oxide, zeolite and naturally available lava [6–9]. CNFs are grown on these materials by chemical vapor deposition (CVD). In recent times, activated car-

* Corresponding author at: Department of Chemical Engineering, Indian Institute of Technology, Kanpur 208 016, India. Tel.: +91 9839195854.

E-mail address: vermanishith@gmail.com (N. Verma).

bon (AC) and activated carbon microfibers (ACFs) have been used as the substrate to grow CNFs. These substrates are impregnated ex-situ with metals which act as the catalyst for CVD to grow CNFs [10–17]. The advantage of using ACFs as the substrate is that the prepared web of carbon micro-nanofibers can be directly used in an end-application without necessity of removing the substrate. CNFs have also been produced by the carbonization of electro- or melt-spun polymeric fibers made of polyacrylonitrile (PAN), polyethylene glycol (PEG), and polymethyl methacrylate (PMMA) [18,19].

Recently, spherical phenolic beads (~0.8 mm) were produced using suspension polymerization, incorporating nanoparticles (Nps) of different metals (Ni/Fe/Al) in situ during a polymerization stage. The metal Nps-doped beads were carbonized and activated using steam. The produced porous carbon beads with metal (Ni/Fe) Nps uniformly dispersed within its micro-mesopores exhibited significant adsorption for a number of solutes in the aqueous phase, including arsenic (As), fluoride (F), and Vitamin B12 (vit B12) respectively [20–22].

This study describes the preparation of multiscale carbon structures in the form of *nanofibrous* carbon beads produced by growing CNFs within the pores of carbon beads by CVD. The novelty of the study is that metal (Ni or Fe) Nps incorporated in situ into the beads during a polymerization stage catalyzed the growth of the CNFs. Such carbon beads decorated with Ni- or Fe-CNFs were demonstrated as adsorbents for different environmental remediation applications, viz. the removal of vitamin B12 (vit B12) and arsenic (As), and were found to have higher adsorption capacities than the parent metal-doped porous carbon beads without CNFs. The incorporated metal Nps thus have dual roles: (1) as the CVD catalyst, and (2) as the active sites for the adsorption of pollutants.

2. Materials and methods

All chemicals used in this study were of analytical grade. Phenol, hexamethylenetetramine (HMTA), formaldehyde (37–41%), triethylamine (TEA), polyvinyl alcohol (PVA) (MW = 95000), nickel nitrate, ferric chloride, benzene, sodium arsenate heptahydrate, and cyanocobalamin as vit B12 were purchased from Merck (Germany). All solutions were prepared in Milli-Q water.

2.1. Synthesis of Ni/Fe-doped polymeric beads

The phenolic resin beads were prepared by suspension polymerization. The preparation method is described in details elsewhere [20–23]. Briefly, phenol (50 g), formaldehyde (60 ml), and TEA (1.5 ml) were used as the monomer, solvent, and catalyst, respectively. The solution mixture was placed in a round bottom flask attached to a reflux-condenser and stirred at 35 °C for 8 h to achieve a homogenous mixture. The stirrer speed was maintained at 350 rpm. Next, 200 ml of water and 3.5 g of hexamine, used as the cross-linking agent, were added to the reaction mixture. The solution was heated (3 °C per min) until the mixture reached 100 °C. After 15 min, PVA (3 g) was added as a suspension-stabilizing agent. Gel began to form approximately 30 min after adding PVA. At the incipience of the gel formation, NiNO₃ or FeCl₃ (15% w/w of phenol) was added. The beads were produced after ~3 h. The produced beads were washed repeatedly with acetone, water, and methanol and dried at room temperature (~30 °C).

2.2. Growth of CNFs on metal-doped carbon beads

The produced metallic-salt-doped beads were carbonized at 900 °C for 1 h under nitrogen (N₂) flow (150 cc per min). Activation

was then carried out using steam as the activation agent. The N₂ flow rate was reduced to 100 cc per min during activation. The mixture of steam and N₂ was effective in producing stabilized carbon beads. After the activation of the metallic salt-doped beads, reduction was carried out using hydrogen (150 cc per min) to convert the metal (Ni/Fe) oxides into their respective metallic states. The reduction temperatures for the Ni- and Fe-doped activated carbon beads were set at 500 °C and 450 °C, respectively. After the reduction step, CVD was performed on the Ni- or Fe-doped carbon beads at 900 °C and 800 °C, respectively, using benzene as a carbon source and N₂ as a carrier gas (150 cc per min). The benzene concentration in N₂ was maintained at 15,000 ppm. Fig. 1 describes the synthesis steps for producing Ni- or Fe-Np-doped carbon beads decorated with CNFs.

Fig. 2 describes the experimental setup used for the carbonization, activation, reduction and CVD. As shown, the setup consisted of an inonel tubular reactor placed horizontally in an electric furnace equipped with a temperature controller and programmer. The beads were placed on a perforated stainless steel (SS) boat inserted into the reactor. An SS tubular bubbler was used to bubble N₂ into the liquid benzene. The temperature of the bubbler was set using a Freon (R-15) refrigerator unit to prepare the benzene-saturated N₂. The benzene-saturated N₂ was passed through the tubular reactor for CVD and the growth of CNFs on the activated carbon beads. As mentioned earlier, the incorporated metal (Ni/Fe) Nps acted as the catalyst for the CVD. In this paper, Ni_PhB, Ni_PhB_A, and Ni_Ph-

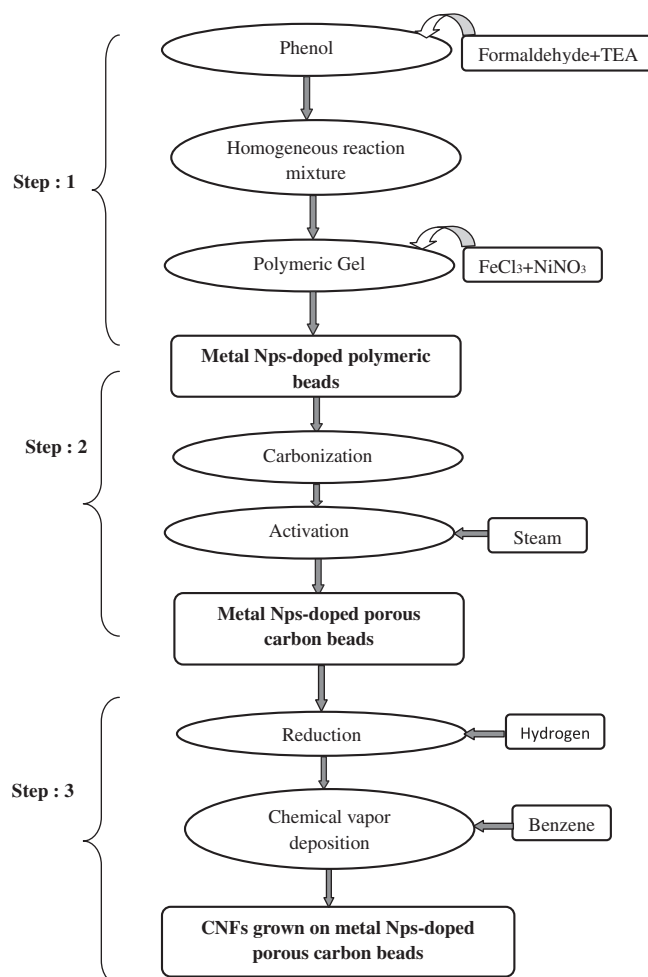


Fig. 1. Flow diagram of preparing Fe- or Ni-Nps-doped carbon beads decorated with CNFs.

Download English Version:

<https://daneshyari.com/en/article/6586907>

Download Persian Version:

<https://daneshyari.com/article/6586907>

[Daneshyari.com](https://daneshyari.com)