Surface functionalized composite nanofibers for efficient removal of arsenic from aqueous solutions

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HIGHLIGHTS

- Inexpensive and simple fabrication route for flexible composite nanofibers systems.
- High adsorption removal efficiency was obtained compared to other reported studies.
- Stability of the fabricated composite nanofibers allowing their reuse.
- The flexibility of the nanofibers allows use in a continuous operation mode.

GRAPHICAL ABSTRACT
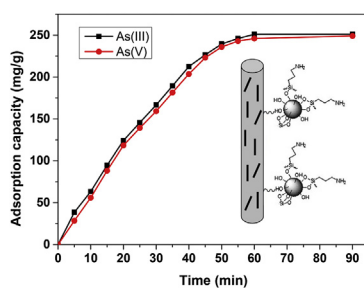
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ABSTRACT:

A novel composites nanofiber was synthesized based on PAN-CNT/TiO$_2$-NH$_2$ nanofibers using electrospinning technique followed by chemical modification of TiO$_2$ NPs. PAN-CNT/TiO$_2$-NH$_2$ nanofiber were characterized by XRD, FTIR, SEM, and TEM. The effects of various experimental parameters such as initial concentration, contact time, and solution pH on As removal were investigated. The maximum adsorption capacity at pH 2 for As(III) and As(V) is 251 mg/g and 249 mg/g, respectively, which is much higher than most of the reported adsorbents. The adsorption equilibrium reached within 20 and 60 min as the initial solution concentration increased from 10 to 100 mg/L, and the data fitted well using the linear and nonlinear pseudo first and second order model. Isotherm data fitted well to the linear and nonlinear Langmuir, Freundlich, and Redlich-Peterson isotherm adsorption model. Desorption results showed that the adsorption capacity can remain up to 70% after 5 times usage. This work provides a simple and an efficient method for removing arsenic from aqueous solution.

1. Introduction

Arsenic (As) has been recognized as one of the most toxic pollutants in an aqueous solution because of their toxicity, bioaccumulating tendency, and threat to human life and environment (Hubner et al., 2010; Sharma et al., 2014; Williams et al., 2009; Feng et al., 2013). According to the World Health Organization (WHO) the permissible maximum limit of As in drinking water is $10 \,\mu g \, L^{-1}$ (Yamamura, 2001). In an aqueous solution, arsenic exist in inorganic and organic forms as oxyanions of trivalent As(III) and pentavalent arsenic As(V). As(III) is ten times more toxic and

difficult to remove from aqueous solution than As(V) (Camacho et al., 2011; Boojari et al., 2016).

Due to their environmentally friendly nature, simplicity, and economy, adsorption process has been recognized as one of the most efficient techniques used for removal arsenic species from aqueous solution. Recently, many researchers have demonstrated that TiO$_2$ nanoparticles is effective for removal As(III) and As(V) from aqueous solutions for they easily self-aggregate in aqueous solution, which results in a fast reduction of active surface area (Niu et al., 2009; Xu and Meng, 2009; Jegadeesan et al., 2010; Pirilä et al., 2011; Guan et al., 2012; Vu et al., 2013a). Moreover, it is difficult to separate TiO$_2$ nanoparticles from aqueous solution after adsorption. Therefore, its need to develop an efficient technique for the removal of arsenic from contaminated water. In this regard, composite nanofibers are expected to solve these problems because they combine the advantages of nanomaterials (high specific surface area) and thin film (easy separation from water) (Mohamed et al., 2016a, 2016b). Polyacrylonitrile (PAN) has been recently used as support matrices for nanomaterials due to its excellent characteristics and commercial availability, as well as its non-toxic nature (Avila et al., 2014; Sugunan et al., 2010; Vu et al., 2013b).

In this work a novel technique has been developed to fabricate PAN-CNT/TiO$_2$-NH$_2$ nanofiber via electrospinning process using the PAN nanofibers as support matrix followed by further crosslinking of surface amino-modified TiO$_2$ NPs to PAN/CNT nanofibrous matrices in order to increase the adsorption of arsenic due to the large number of binding active sites incorporated on the surface of TiO$_2$ NPs. The effects of contact time, initial concentration, solution pH, adsorption kinetics, and isotherms were investigated. Finally, the mechanism for the removal of As using PAN-CNTs/TiO$_2$ has been explored.

2. Experimental

2.1. Materials

Carbon nanotubes (CNTs) with diameter between 10 and 40 nm and length 20 μm, was synthesis and the procedure is described elsewhere (Mohamed et al., 2014; Bahaa et al., 2016). Sodium arsenite (NaAsO$_2$), and sodium arsenate (Na$_3$AsO$_4$·12H$_2$O), Polyacrylonitrile, PAN (MW = 150,000); hydroxylamine hydrochloride (NH$_2$OH·HCl), sodium carbonate (Na$_2$CO$_3$), N, N-dimethylformamide (DMF), sodium hydroxide (NaOH), hydrochloric acid (HCl), titanium dioxide particulate powder (Degussa P-25), and 3-aminopropyltriethoxysilane (APTES), were purchased from Sigma Aldrich. All reagents and solvents were of analytical reagent grade and used without further purification.

2.2. Preparation of PAN-CNT/TiO$_2$-NH$_2$ composites nanofibers

CNTs were oxidized by refluxing at 120 °C in mixed acid (H$_2$SO$_4$:HNO$_3$ = 3:1) for 30 min and then the mixture was diluted with water and filtered. The obtained samples were washed with water and dried in the oven at 60 °C for 12 h (Khalil et al., 2016; Bahaa et al., 2017). Solution of PAN in DMF (10 wt%) was prepared and stirred for 4 h. Functionalized CNTs 3 wt% were dispersed in DMF; the dispersion was stirred for 15 min, and then sonicated for 30 min. A PAN solution was then added to the CNTs. The resulting mixture was stirred for 15 min and then sonicated for 2 h. The applied voltage was 25 kV and the distance from the tip to the collector was 15 cm. The feeding rate of the mixture solution was 0.5 mL/h.

After that the electrospun PAN-CNT nanofibers were dried in vacuum overnight to remove the excess amount of solvent. The fabrication of PAN-CNT nanofibers functionalized with amino groups was described elsewhere (Mohamed et al., 2016a). The nanofibers were placed into 100 mL solution containing a mixture of 8 g hydroxylamine hydrochloride, and 6 g of sodium carbonate. The solution and the prepared PAN-CNT nanofibers were heated to 40 °C for 6 h. The nanofibers were then washed three times with distilled water in order to remove the remaining salts and were dried in air. The surface functionalization of TiO$_2$ nanoparticles with the amino group was carried out according to a well established procedure (Xiang et al., 2012). Typically, 0.5 g of TiO$_2$ was first immersed in 10 mL of deionized water, of which pH value was adjusted to 11 by sodium hydroxide, to facilitate the adsorption of the hydroxyl group. The hydroxyl group rich TiO$_2$ NPs were washed twice with 20 mL of methanol to remove the excessive sodium hydroxide, and then dried in a vacuum oven at room temperature for use. Subsequent TiO$_2$ NPs was dispersed in 100 mL of toluene via Ultrasonication for 30 min. After that, 3 mL of silane coupling agents was added to the TiO$_2$ suspension. The suspension was further refluxed at 110 °C for 24 h leading to NH$_2$ functional group on the titania surface. The reaction product was centrifuged and washed three times with water followed by methanol to remove the unreacted silane coupling agents, and then dried in a vacuum oven prior to use. The crosslinking of the amino functionalized composite nanofibers (PAN-CNT-NH$_2$) to TiO$_2$-NH$_2$ via the amine side was carried out as follow: PAN-CNT-NH$_2$ composite nanofibers weighted and immersed in the crosslinking medium containing 2.5 wt% Glutaraldehyde (GA), and kept shaking for 24 h at room temperature. After the activation reaction of the composite nanofibers was completed, the GA crosslinking medium was removed and then 2 mL of an aqueous dispersion of functionalized TiO$_2$ nanoparticles was added to the composite nanofibers for 24 h. The crosslinked composite nanofibers were washed with ethanol followed by distilled water to remove the excess of non-crosslinked nanoparticles and then the composite nanofibers were dried in air at room temperature.

2.3. Adsorption of As

The Adsorption of As in an aqueous solution was carried out in a 100 mL quartz reactor containing 25 mg composite nanofibers and 50 mL 10 ppm of As (III) and As (V). The composite nanofibers were dispersed in As solution under shaking condition at room temperature, then 3 mL of the suspension was taken from the reactor at a scheduled interval. The concentration of arsenic was measured using a Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) (Thermo Fisher iCAP 6500). The pH values of the solution were adjusted by adding 0.1 M NaOH or 0.1 M HNO$_3$ and was varied within the range of 2–9. The equilibrium adsorption capacity (q$_e$) was determined using equation (1), while % removal of As (III) and As (V) was calculated using equation (2).

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{1}$$

$$(\%)\text{Removal} = \left(\frac{C_0 - C_e}{C_0}\right) \times 100 \tag{2}$$

where, C$_0$ is the initial arsenic concentration (mg/L) and C$_e$ is the arsenic concentration in the aqueous solution at equilibrium (mg/L), V is the total aqueous volume (L), and m is the mass of the composite nanofibers (g).

2.4. Characterization

The morphology of PAN and PAN-CNT/TiO$_2$-NH$_2$ composites nanofiber functionalized membranes was characterized using field