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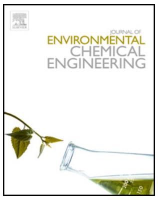

Polyaniline functionalized graphene sheets for treatment of toxic hexavalent chromium

Dilip K.L. Harijan, Vimlesh Chandra*

Department of Chemistry, Dr. Harisingh Gour University, Sagar, MP 470003, India

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ABSTRACT

The functionalization of graphene sheets with polyaniline (PANI) was carried out in the aqueous medium via polymerizing aniline in the presence of graphene oxide and reducing it with sodium borohydride. FTIR and powder X-ray diffraction pattern shows formation of PANI and PANI functionalized graphene sheets (PANI-G). The Cr(VI) removal capacity increases with graphene oxide loading and shows maximum for 10% loading (PANI-G10). The noncovalent interactions between PANI and graphene enhances surface area from 20 m^2/g (PANI) to 110 m^2/g (PANI-G10). The equilibrium adsorptions data were well-described by the Langmuir isotherm model and maximum adsorption capacity 192 mg/g for PANI-G10 and 136 mg/g for PANI was found at pH 6.5 and temperature 30 °C. The time dependent adsorption data shows pseudo-second-order kinetics and achieved equilibrium within 20 min onto PANI-G10. The adsorption capacity for hexavalent removal increases with decrease in pH and increase in the initial concentration of Cr(VI) solution. The effect of ionic strength shows drastic decrease in the Cr (VI) removal as ionic strength increases from 0 to 0.1 M.

1. Introduction

Water is the most precious natural resource on earth and supports life for people, animals, and plants. In spite of this, 1.2 billion people lack access to safe drinking water, and millions of people die annually from diseases transmitted through contaminated water [1]. Among various types of water pollutants, the trace amount of chromium contamination in water is highly toxic and carcinogenic to the humans and animals [2]. Chromium exist in the nature mainly in the three forms, Chromium(0), chromium(III), and chromium(VI). In comparison to high soluble Cr(VI); Cr(III) is less mobile and toxic in the environment and an important nutrient for human and animal [3]. In the neutral and low concentrated solution of $K_2Cr_2O_7$, Cr(VI) coexist as $HCrO_4^-$ and CrO_4^{2-} [4]. Chromium contamination in the drinking water is due to the effluents from mining, leather tanning, dye, cement, electroplating, metal alloys, steel, and metal corrosion inhibition [5]. US Environmental Protection Agency (EPA) has set a maximum contaminant level (MCL) of 0.1 mg/L for total chromium in drinking water [6]. On drinking water more than the permisible limit of Cr (VI) can cause dermatitis, cancer, damage to kidney and liver. The removal of Cr(VI) from wastewater is essential before disposal of industrial effluent conataining Cr(VI) into the driking water reservoirs such as river and lake [7]. The chemical reduction followed by precipitation, electrokinetic remediation, membrane separation, bioremediation photocatalysis and adsorption are used for removal of Cr(VI) from drinking water. Among these techniques, adsorption of Cr(VI) on the different adsorbents is the potential method as these are cheap, thermally and chemically stable, easy to handle and need no electricity so can be used in the remote areas [8]. Intrinsically conducting polymer, Polyaniline (PANI) is one of the most extensively investigated conducting polymers because of its good stability, low cost, environment friendly and can be synthesized at large scale at low cost [9]. It is well-known that polyaniline exists in three different oxidation states, polyemeraldine (EB), leucoemeraldine (LB) and pernigraniline (PB) and only polyemeraldine (EB) is electrically conductive. On doping with various anions via chemical routes PANI showed significant changes in the electronic transport properties [10].

PANI has shown very high removal capacity for hexavalent chromium due to reductive adsorption of hexavalent chromium [11–13]. It supplies the electron for reduction of Cr(VI)–Cr(III) and also provide active sites for adsorption of Cr(III). Olad et al. have studied the efficiency and kinetics of Cr(VI) removal by various forms of PANI, including film and powder at different oxidation states and found that powder form is more effective than film [14].

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* Corresponding author.
E-mail address: vchandg@gmail.com (V. Chandra).

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Zhang et al. synthesized sulfuric acid doped polyaniline and observed maximum uptake of Cr(VI) 95.79 mg g^{-1} [15]. Ansari reported adsorption of Cr(VI) from aqueous solutions using sawdust coated by Polyaniline, polyaniline composites with nylon 66 and polyurethane [16]. Karthic et al. reported removal of hexavalent chromium ions using PANI/silica gel composite with maximum Cr(VI) ion adsorption capacity 63.41 mg/g at 303 K. [17]. Polyacrylonitrile/PANI core/shell nanofiber mat was synthesized for removal of hexavalent chromium from aqueous solution [18]. The emergence of graphene as a single-atom-thick carbon nanosheet with high mechanical strength, surface area, thermal/ electrical conductivity, and transparent nature attracted great interest as a promising nanomaterial for a variety of applications in optoelectronics, solar/fuel cell, drug delivery, desalination, toxic materials removal, super-capacitor, batteries, energy generation/ storage, catalyst and many others [19–21]. Graphene has very high conductivity/charge density (π-electron cloud) and two free mesoporous surface with theoretically predicted surface area as being >2500 m^2 g^{-1} and experimentally measured to be 400–700 m^2 g^{-1} motivated to devlope functionalized materials for application in the toxic pollutants detectors and treatment to provide disease free water to society [22]. The graphene functionalised nanomaterials have been used for removal of heavy metal ions such as arsenic,mercury, lead, and copper [23,24]. Hexavalent chromium removal has been carried out using graphene/Fe nanoparticles nanocomposite [25], TiO_2/graphene [26], graphene-Fe_3O_4 nanocomposite [27]. Recently amine groups functionalized graphene sheets were synthesized and used for hexavalent chromium reomval [28,29]. Here we report synthesis of polyaniline functionalized graphene sheets (PANI-GRA) in aqueous medium via polymerizing aniline monomer using ammonium persulphate in the persence of graphene oxide. The reduction of graphene oxide to graphene was carried out using sodium borohydride as reducing agent.

2. Experimental

2.1. Chemicals

Graphite (Alfa), Sodium Nitrate (Merck), Potassium Permanganate (Aldrich), Hydrogen Peroxide (30 wt %, Alfa), Sulphuric Acid (Merck), Aniline (Merck), Hydrogen chloride acid (Merck), Ammonium persulphate (Alfa Aesar), Potassium dichromate (Aldrich), ethanol (CDH), sodium hydroxide (Merck) and potassium bromide (Aldrich).

2.2. Synthesis of Graphene Oxide (GO)

Graphene oxide was synthesized via chemical oxidation of graphite as reported earlier [30]. 5 g graphite was added in 125 mL of H_2SO_4 (95%) in a 1000 mL flask at ice temperature. 5 g $NaNO_3$ was added slowly and the mixture was stirred for 30 min at this temperature. 15 g $KMnO_4$ was added to the mixture very slowly and ice bath was removed and the mixture was stirred at 35 °C until it became brownish paste. It was diluted with slow addition of 800 ml water and finally 10 ml of H_2O_2 (30 wt. %). The solution mixture was washed with 10% HCl many times to remove metal impurities of graphite and finally washed with the deionized (DI) water several times. The resulting product was dried at room temperature under vacuum and the graphene oxide (GO) was obtained as a powder.

2.3. Synthesis of polyaniline functionalized graphene (PANI-Graphene)

50–200 mg graphene oxide (5–20% wt) and 1 g aniline were dispersed in 150 ml of 1 M HCl using ultrasonic bath. The polymerization of aniline was carried out by adding pre-cooled ammonium persulphate (APS) solution of 2.5 g in 20 ml 1 M HCl with continuous mechanical stirring for 3 h and resulting solution kept for overnight at room temperature. The product was washed with 0.1 M aqueous HCl solution and dispersed in water. 200 mg of sodium borohydride dissolved in 20 ml water was added to dispersion of PANI-GO to reduce graphene oxide to graphene. The reduction process was carried out for 8 h and resulting product was washed with copious amount of water and finally with ethanol. The product was dried at 100 °C for 10 h. The color of the resultant solution glows greenish and addition of base it converted to blue color.

2.4. Characterization of Samples

The powder X-ray diffraction patterns (XRD) were recorded on a Bruker with CuKα irradiation (λ = 1.5406 Å). Fourier transformed infrared (FT-IR) spectra were recorded using a Bruker Tensor 37. The morphology of the samples was characterized using a field emission scanning electron microscope (FEI-Nova-Nano SEM 450). The microscopic features of the samples were characterized by Transmission and high resolution electron microscopy (TEM and HRTEM) using FEI Tecnai G2F30 S-Twin with an accelerating voltage of 200 kV.

2.5. Adsorption of Cr(VI)

Standard stock solution 100 ppm of Cr(VI) was prepared in double distilled water by dissolving 282 mg of potassium dichromate ($K_2Cr_2O_7$, M.W. 294.19) in 1.0 l. All the solutions of Cr(VI) removal experiments were prepared by appropriate dilutions from the stock solution. The pH of the solution was adjusted using NaOH and HCl solution. The required amount of adsorbent was added to Cr(VI) solution and stirred for a given time interval and filtered out adsorbent. The concentration of Cr(VI) before (C_o) and after (C_e) adsorption were found out at wavelength 372 nm using Systronics UV–vis spectrophotometer. The adsorption capacities of the adsorbents were calculated using $q\ (mg/g) = (C_o - C_e) \times V/w$, where w (g) adsorbent dose, V (ml) volume of solution. The effects of pH, contact time, initial concentration and interfering ions of Cr(VI) adsorption onto adsorbents were investigated. The kinetics and adsorption isotherms were studied at pH = 6.5, which is the pH of the drinking water.

3. Results and Discussion:

3.1. Characterization

The scanning electron microscopy (SEM) imaging was carried without gold coating of sample which indicates formation of highly conducting PANI and PANI-G10. In the absence of graphene sheets, PANI particles show formation of coral-like dendritic nanofibers (Fig SI-1) where as in presence of graphene sheets the morphology is similar to graphene sheets (Fig. 1a–b). The graphene being electron acceptor and aniline electron donor makes aniline to absorb on the surface of graphene sheets. During polymerization graphene sheets provides a large number of active sites for nucleation of PANI for homogeneous coating on the surface of graphene sheets as evident from TEM image (Fig. 1b) [31]. This enhances surface area of PANI (20 m^2/g)–PANI-G10 (110 m^2/g) as measured from Belsorp MR6. The powder X-ray diffraction pattern of the samples was taken in order to estimate the degree of crystallinity and formation of phase. The powder X-ray diffraction of graphite shows a sharp peak at 26.5° and graphene oxide shows a peak at 11.7° (Fig. SI-2). The shift of the peak towards low Bragg's angle indicates intercalation of different functional groups on the