



# Chitosan-functionalized graphene oxide: A novel adsorbent an efficient adsorption of arsenic from aqueous solution



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## ABSTRACT

Nowadays, there is a wide variety of arsenic decontamination processes being adsorption processes the most efficient. In this concern, chitosan functionalized graphene oxide (GO), have been proposed as an efficient adsorbent to improve arsenic adsorption from aqueous solutions. The chitosan functionalized GO adsorbent acts as a good host of welcoming the incoming guest, arsenic oxyanion and several interesting interactions such as cation- $\pi$  interaction, ( $\text{RNH}_3^+$ -aromatic  $\pi$  moiety), electrostatic interaction ( $\text{H}_2\text{AsO}_4^-$ ,  $\text{HAsO}_4^{2-}$ - $\text{NH}_3^+$ ), inter and intermolecular hydrogen bonding as well as anion- $\pi$  interaction ( $\text{R-COO}^-$ -aromatic  $\pi$  moiety), ( $\text{R-O}^-$ -aromatic  $\pi$  moiety), could be conceptualized in this process, the abundant oxygen-containing functional groups on the adsorbent surfaces play an important role on As(V)/As(III) adsorption. The prepared chitosan-GO adsorbent was characterized by X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, thermogravimetric analysis (TGA) analysis, powder-X-ray diffraction (powder-XRD), transmission electron microscopes (TEM), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopes (SEM) and energy dispersive X-ray analysis (EDX) studies. The capability of ICP-MS for As(III)/As(V) adsorption was extensively studied under different optimal parameters in aqueous solutions, the applicability of this method is demonstrated economical and practical applications for efficient adsorption of arsenic from aqueous solutions.

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## 1. Introduction

Arsenic is known for its toxicity and carcinogenicity to human beings. Contamination with arsenic is increasingly becoming a significant issue in drinking water throughout the world. Long-term exposure to arsenic can cause cancers of the bladder, lungs, skin, kidney, liver, and prostate [1]. Contamination by arsenic includes both natural and anthropogenic sources, anthropogenic arsenic pollutants originate from mining and smelting of non-ferrous metals, burning of fossil fuels, use of arsenic-containing pesticides in agriculture and arsenic-containing chemicals used in the preservation of timber.

Arsenic can exist in both inorganic and organic forms. In general, inorganic arsenic compounds are more toxic than organic arsenic compounds, and arsenite [As(III)] is considerably more mobile and toxic than arsenate [As(V)]. Arsenate (i.e.,  $\text{HAsO}_4^{2-}$ ) is

the primary anion in the aerobic surface water and arsenite (i.e.,  $\text{H}_3\text{AsO}_3$  or  $\text{H}_2\text{AsO}_3^-$ ) is the primary species present in groundwater [2,3]. The US Environmental Protection Agency (USEPA) in 2001 adopted a new standard for arsenic in drinking water with a limit of 10 ppb, replacing the old standard of 50 ppb [3]. In the environment, heavy metals are persistent, non-biodegradable and they can accumulate in living tissues, causing various diseases and disorders. Thus, there is a need to develop eco-friendly and sustainable treatment technologies using renewable resources.

In recent years, various methods of heavy metal removal from wastewater have been extensively studied; these technologies include chemical precipitation, ion-exchange, adsorption, membrane filtration, coagulation-flocculation, flotation and electrochemical methods. One of the principal remediation techniques used against arsenic contamination is the adsorption technique, which is considered to be highly effective against arsenic removal of aquatic environments. The main advantages of this technique include its simple operation, economic reliability, and the least waste generation properties. Various adsorbents have been developed from different cost-effective sources and successfully applied so far [4].

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However, for practical utility, there is still a requirement for new adsorbent materials showing highly selective arsenic removal efficiency [5]. Among biosorbents, chitosan (CS), the linear cationic amino polysaccharide composed of  $\alpha$ -D-glucosamine, is a partially acetylated glucosamine and is extracted by a deacetylation procedure from chitin, one of the most abundant biopolymers in nature, second only to cellulose [3,6]. In recent years, the application of chitosan has attracted the interest in numerous scientists due to its outstanding properties. It is nontoxic, has high biocompatibility, is hydrophilic in nature, and it has been extensively used in various fields for environmental remediation [3,6,7]. Chitosan has been reported to be a suitable biopolymer for the removal of heavy metals from industrial wastewater, due to its high content of amino and hydroxyl functional groups, low toxicity, good biocompatibility, and biodegradability [6,7].

However, to improve its absorption capacity and enhance the removal efficiency, the design and functionalization of novel adsorbent still need to be explored [7]. Chitosan has one amino group and two hydroxyl groups on each glucosamine monomer that act as adsorption sites, especially the amino groups which are strongly interactive with metal ions. Moreover, the applications of chitosan are limited because of its solubility in acid solutions. Hence, it is necessary to crosslink chitosan in order to make it stable in acid solutions. The functionalization of chitosan is made between different kinds of a polar functional group such as graphene oxide [6,8] and multiwalled carbon nanotube [9]. Graphene oxide, which is one of the graphene derivatives, has a high adsorption capacity for environmental contaminant cleanup in practical applications and has gained considerable attention as a significant adsorbent [1,2,4,5,10]. There are abundant oxygen atoms on the graphitic backbone of GO in the forms of epoxy, hydroxyl, and carboxyl groups, which protrude from its surface; these groups can bind to heavy metal ions very well. Recently GO has been suggested as “a superior adsorbent” on account of its excellent sorption of heavy metals; oxidized graphene has shown exceptional adsorption capacity and high adsorption efficiency for metal removal [11–14]. Therefore, numerous graphene-based composite materials have been synthesized for the removal of various environmental contaminants. Graphene oxide can bind chitosan through coordination, electrostatic interaction, and covalent interaction which produces chitosan/GO composites [6,8,14,15], these chitosan/graphene oxide composites (chitosan-GO) can be prepared from the low-cost material graphite and have been intensively investigated as adsorbents for various heavy metals [6,13–15] and different dyes [16].

Here, we report on some chitosan functionalized GOs that have not, as yet, been examined for their arsenic adsorption capability. The chitosan-GO composites were synthesized and applied to the removal of As(V)/As(III) from aqueous solutions by batch and column experiments. The chitosan-GO is potentially an effective adsorbent; several interesting mechanisms such as cation- $\pi$  interactions, electrostatic interactions as well as anion- $\pi$  interactions could be conceptualized in the process of arsenic sorption. The interaction primarily involves the electrostatic affinity between the amino group ( $\text{NH}_2$ ), primary and secondary hydroxyl groups ( $\text{CH}_2\text{OH}$ ,  $\text{CHOH}$ ) of the chitosan and surface of carboxyl ( $\text{COOH}$ ) and hydroxyl groups ( $\text{OH}$ ) on the GO.

The novel chitosan-GO adsorbent composites show excellent adsorption characteristics for arsenic as substantiated through the comprehensive physicochemical characterization techniques, batch adsorption study and column dynamic up gradation to a large sample volume. The objectives of this study were: (1) to investigate the effect of pH on As(V)/As(III) adsorption; (2) to study the adsorption of As(V)/As(III) onto chitosan-GO as affected by the nature and concentration of cations and anions and (3) to discuss the interaction mechanism of As(V)/As(III) with chitosan-GO under

different experimental conditions. This study highlighted the broad applicability of this versatile material in environmental waste water treatment.

## 2. Materials and methods

### 2.1. Materials

The starting material graphite used in the preparation of GO was procured from Sigma-Aldrich. A stock solution to  $1000 \text{ mg L}^{-1}$  arsenic solutions were used in ICP-MS standard, a working solution for  $30 \text{ mg L}^{-1}$  arsenic for the batch adsorption studies was prepared by appropriate dilution with Milli-Q water, chitosan were purchased from Sigma-Aldrich chemicals. The other required reagents were procured from Merck chemicals respectively.

### 2.2. Instruments and characterizations

Raman spectra were recorded on a WITec Confocal Raman Microscope Alpha 300R using a 532 nm He-Ne laser with 5 mW. The TEM analysis was carried out using a PHILIPS CM-200 TWIN instrument an operating voltage of 200 kV, a drop of hexane solutions to the sample solutions was deposited on a carbon-coated copper grid. A PerkinElmer Fourier Transform Infrared Spectroscopy (FT-IR) spectrum100 spectrometer was used to characterize the material functional groups identifications in the range  $400\text{--}4000 \text{ cm}^{-1}$  by mixing 0.01 g of the material with 0.1 g KBr (spectroscopy grade). Kratos Axis Ultra X-ray Photoelectron Spectroscopy (XPS) instruments were used to record samples, X-Ray sources: 500 mm Rowland Circle Monochromator Al-Mg/Al achromatic Source 450W max power. The spectra were recorded using a monochromatic Al K $\alpha$  X-ray source (15 mA, 14KV). All obtained spectra were calibrated to a C 1s peak at 284.6 eV, and fitted with a mixed Gaussian-Lorentzian function by XPSPEAK (a freeware). The pressure in the analyzer chamber was  $1 \times 10^{-8}$  Torr. The conditions applied for the survey scans includes an energy ranges 0–1200 eV by the survey spectra was collected at a pass energy of 160 eV and a step size of 0.7 eV. High-resolution spectra were collected using 40 eV pass energies, the spot size of  $300 \times 700 \mu\text{m}$  slots and 0.05 eV step size. Thermogravimetric analysis (TGA) was done using a PerkinElmer (TGA-4000) thermal analyzer wherein the samples were heated in the range 30–700 °C at the rate of  $10^\circ\text{C min}^{-1}$  under a nitrogen atmosphere. X-ray diffraction (Powder-XRD) was carried out on a D8 Discover X-ray diffractometer with Cu K $\alpha$  radiation ( $k=0.1541 \text{ nm}$ , Bruker, Germany) was utilized to record the characteristic changes in the diffraction pattern of the adsorbent material. A JEOL JSM-6330TF analyzer was used to observe the morphological changes scanning electron microscope (SEM) were recorded and the energy dispersive X-ray analysis spectrum (EDX) was recorded adsorbent and after the adsorption of arsenic. The concentration of the arsenic in the aqueous solutions was measured using inductively coupled plasma mass spectrometry (ICP-MS) PerkinElmer, Sciex-Elan DRC Plus, Software which we used Elan-6100 DRC PLUS respectively. The pH adjustments of the aqueous solutions were done using METTLER TOLEDO pH meter S20.

### 2.3. Synthesis of graphene oxide from graphite

An improved method was used for the synthesis of GO, which was reported on earlier studies [17,18]. About 1.5 g of graphite powder was taken and gradually added to a 9:1 mixture of concentrated  $\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4$  (180:20 mL). Subsequently,  $\text{KMnO}_4$  (9 g) was gradually added to the mixture of stirring which maintaining the reaction temperature below 40 °C and reaction

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