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Multi-walled carbon nanotubes as an adsorbent material for the solid phase extraction of bismuth from aqueous media: Kinetic and thermodynamic studies and analytical applications

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ABSTRACT

The present work discusses the use of multi-walled carbon nanotubes (MWCNTs) as a solid phase for removal of bismuth from aqueous media. Different factors influencing on removal efficiency were investigated carefully to get a maximum performance. The results of this study showed that most of the Bi(III) ions were removed from the solution within 30 min, at pH 0.1, and using 100 mg of adsorbent. The kinetic nature of adsorption process was analyzed using different mathematical models and that provided valuable insights into the reaction pathways and the mechanism of adsorption. The study findings revealed that the adsorption of Bi(III) ions on MWCNTs follows the pseudo-second-order kinetic model, whereas, the adsorption mechanism occurs in two consecutive steps. Various thermodynamic parameters, including the Gibbs free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS), were calculated, and the numerical values of ΔH, ΔS and ΔG were equal to -10.02 ± 0.6 kJ mol^{-1}, -24.6 ± 0.8 J mol^{-1} K^{-1} and -17.35 ± 0.1 kJ mol^{-1} (at 293 K), respectively. The efficiency of MWCNTs for removal of Bi(III) ions from real samples was tested by extraction of bismuth from Red Sea water, wastewaters, and tap water, and the percentage of Bi(III) ions removed from these samples was in the range of 95.6–98.91% confirming suitability of MWCNTs as an adsorbent for extraction of bismuth.

1. Introduction

Although, bismuth concentration in the Earth's crust presents only 8 μg kg^{-1}, the chance of exposure of organisms to this element has increased recently due to its wide uses in medicine and industry [1,2]. Bismuth is used in many medical applications such as pharmaceutical industries, especially for the treatment of gastrointestinal tract disturbances (gastritis and peptic ulcer) and in preparation of creams and hair dyes. On the other hand, bismuth is employed as a catalyst in many manufactures e.g. the synthesis of methanol and in metallurgical process for production of low melting alloys [3–5]. Due to their effects on the nervous system in particular, in motor neurons, bismuth compounds are included in the list of potential toxins [6]. Hence, the development of low cost, and applicable methods for removal of bismuth from environmental samples is of interest.

Although, various analytical methods e.g. electro thermal atomic absorption spectrometry [7], hydride generation atomic absorption spectrometry [8], microvolume β-correction spectrophotometry [9], hydride generation atomic absorption spectrometry [10], atomic fluorescence spectrometry [11] and cathodic and anodic adsorptive stripping voltammetry [12–14] have been reported for the determination of bismuth in variety of samples, the direct determination of bismuth in some samples such as alloy, water, rock, and biological samples is sometimes impossible because of low sensitivity of method and/or the interferences of sample matrix. Therefore, a preconcentration step is often required to improve the analytical performance of method. Among preconcentration methods, solid phase extraction, SPE, has received considerable attention in recent years. However, the selection of appropriate solid phase plays an important role for getting full extraction of analyte.

Adsorption technology is one of the most effective techniques for extraction and preconcentration of analytes from aqueous solutions [15–19]. Adsorption has many advantages e.g. fastness, simplicity, and a lack of harmful byproducts, and moreover, both the adsorbent and the adsorbant can be regenerated by suitable desorption process [20]. Carbon nanotubes (CNTs) are an interesting new member in the carbon family after their discovery in 1991 [21] because of their individual morphologies and various potential applications. CNTs are shown to possess great potential for preconcentration of many types of analytes. On the other hand, CNTs are successfully and efficiently employed for the removal of several types of pollutants, including organic compounds [22–25] and inorganic species [26–29] from various aqueous environments. Although there are many research studies focused on the adsorption and removal of Bi(III) from aqueous solutions by different adsorbents [1,30–33], there is no sufficient study applied carbon

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nanotubes as a promising and potential adsorbent. So that, this study will be focused on the adsorption of Bi(III) from aqueous solutions by multi-walled carbon nanotubes (MWCNTs). The morphology of MWCNTs will be studied by a scanning electron microscope (SEM), and the kinetic and thermodynamic characteristics of Bi(III) adsorption on MWCNTs will be discussed in details. Finally, MWCNTs studied will be used for the recovery of Bi(III) from some real samples.

2. Experimental

2.1. Reagents and materials

All chemicals and solvents used were of analytical reagent-grade quality and were used without further purification. A stock solution of bismuth ions (1000 μg mL^{-1}) was prepared from bismuth (III) nitrate (Aldrich Chemical Co Ltd., Milwaukee, WC, USA). More diluted standard (0.1–100 μg mL^{-1}) solutions were prepared by diluting the stock solution with diluted nitric acid. A stock solution of potassium iodide KI (10% *w*/*v*) was prepared by dissolving the required weight in deionized water (100 mL) and ascorbic acid (0.5% *w*/*v*) was prepared to minimize the aerial oxidation of KI. A series of Britton–Robinson (BR) buffer of pH (2–11) and H_2SO_4 (1 mol L^{-1}) were used as an extraction medium in the sorption process of Bi(III) by the MWCNTs.

2.2. Apparatus

All spectrophotometric measurements were recorded with a Perkin-Elmer UV–visible (190–1100 nm) spectrophotometer (model Lambda 25, USA) with 10 mm (path width) quartz cell. An Orion pH meter (model EA 940) was employed for the test solutions and pH measurements and a digital micropipette (Volac) for the preparation of standard Bismuth. A digital sensitive balance ADP 110L with three decimal numbers. Deionized water was obtained from Milli-Q Plus system (Millipore, Bedford, MA, USA) and was used for preparation of solutions.

2.3. Characterization techniques

The microstructure of MWCNTs was characterized by the FEI — Field Emission Scanning Electron Microscope (FISEM) Quanta FEG 450, Netherlands, and a transmission electron microscope (TEM; type JEOL JEM-1230, operating at 120 kV, attached to a CCD camera), while the specific surface areas of the MWCNTs were determined from nitrogen adsorption/desorption isotherm measurements at 77 K, using a model NOVA 3200e automated gas sorption system (Quantachrome, USA).

2.4. Batch extraction step

An accurate weight (0.01 ± 0.002 g) of the MWCNTs was shaken with an aqueous solution (10 mL) containing Bi^{3+} ions (30 mg L^{-1}) in the presence of KI (1% *w*/*v*), H_2SO_4 (1 mol L^{-1}) and ascorbic acid (0.1% *w*/*v*) for 1 h on a mechanical shaker. The aqueous phase was separated out and the amount of Bi(III) remained in this phase was then determined spectrophotometrically using standard calibration curve plotted between absorbance of $[BiI_4]^-$ at 320 nm against Bi(III) concentration in a series of standard solutions. While, the amount of Bi(III) retained on the MWCNTs was calculated from the difference between the Bi(III) concentration in the aqueous phase before (C_b) and after extraction (C_f). The adsorption percentage (% E), the amount of Bi(III) retained at equilibrium (q_e) per unit mass of solid adsorbent (mol g^{-1}) and the distribution coefficient (K_d) of analyte onto the MWCNTs were calculated as reported in [1]. The values of % E are the average of five independent measurements and the precision in most cases was less than ±2%. Following this procedure, the kinetic behavior and thermodynamic characteristics of Bi(III) retention by the MWCNTs were fully studied.

2.5. Analytical application

Sea water, wastewater and tap water samples were used to evaluate the efficiency of MWCNTs for the extraction and recovery of Bi(III) ions from aqueous solutions. The Red Sea water collected from the Red Sea in front of Jeddah City KSA, the wastewater sample taken from the wastewater treatment plant at King Abdulaziz University, Jeddah City KSA, and tap water sampled from the laboratories of Chemistry Department, King Abdulaziz University, Jeddah City, KSA were filtered through 0.45 μm cellulose membrane filter prior to the analysis and stored in LDPE sample bottles (250 mL) at 5 °C in the dark. 500 mL of each sample was treated as mentioned in batch step and then shaken with MWCNTs for 1 h at 283 K. The percentage of Bi(III) removed from samples was determined spectrophotometrically and calculated as reported in batch extraction step.

3. Results and discussions

It is well known that iodide ion reacts with Bi(III) ion in the aqueous phase containing sulfuric acid and an excess of KI to form orange-yellow colored tetraiodobismuthate(III) complex with molecular formula of $[BiI_4]^-$ [34]. The negatively charged complex of $[BiI_4]^-$ may be capable of formation of ion pair with the positively charged sites present on the adsorbent surface. Therefore, we tested kinetic and thermodynamic behaviors of MWCNTs towards Bi(III) ions after their conversion to $[BiI_4]^-$ by KI.

3.1. Characterization of MWCNTs

Fig. 1 shows scan electron microscope (SEM) and the transmission electron microscope (TEM) images of the used pristine MWCNTs. It is clear from the figure that MWCNTs were arranged as curved and tangled tubes of various sizes and directions, which are overlapped over each other forming due to inter-molecular force. Also, the TEM analysis verified the hollow structure of the MWCNTs. The specific surface area of the MWCNTs calculated from nitrogen adsorption/desorption isotherms at 77 K using Brunauer Emmett and Teller model (BET) was 84.3 m^2 g^{-1}.

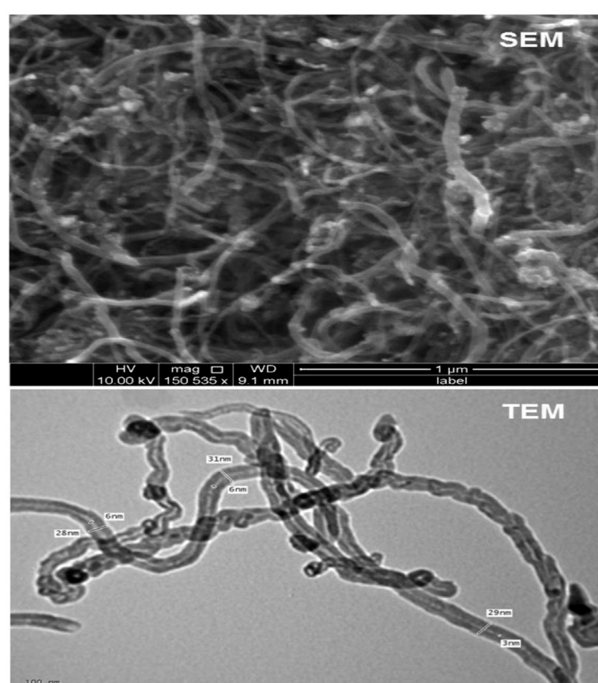

Fig. 1. SEM and TEM images of the pristine MWCNTs.