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Decontamination of selenate from aqueous solution by oxidized multi-walled carbon nanotubes

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A B S T R A C T

Selenium (Se) is emerging as a contaminant that must be dealt with in many areas of the world. In this study, we evaluated the effectiveness of oxidized multiwalled carbon nanotubes (MWCNT) as an adsorbent to remove selenate [Se (VI)] from aqueous solutions. A systematic study of the adsorption process was performed by varying pH, ionic strength, and temperature. The experimental results showed that MWCNT is an excellent selenate adsorbent with an adsorption capacity of up to 1.865 mg g^{-1} at an initial selenate concentration of 2.0 mg/L and temperature of 303 K. The adsorption kinetics was modeled by first- and second-order rate, Elovich and Weber and Morris intra-particle diffusion models. The results indicate that second order kinetics model was well suitable to model the kinetic adsorption of selenate. The adsorption isotherms were modeled by Langmuir, Freundlich and D–R isotherm models. Equilibrium data were well described by the typical Langmuir adsorption isotherm. Thermodynamics studies were carried out and the calculated values of enthalpy change (ΔH) and entropy change (ΔS) are 19.474 kJ/mol and 69.9058 J/mol K respectively. Further, these studies revealed that the adsorption reaction was spontaneous and endothermic process and the calculated activation energy is 19.474 kJ/mol.

1. Introduction

Selenium (Se), an emerging global contaminant, is extensively but irregularly distributed in rocks, soil, and coal, as well as other fossil fuels. In recent days selenium contamination in surface water and groundwater has attracted worldwide attention. Although selenium is an essential micronutrient for humans and other living organisms, when present in high concentrations, it has been shown to create toxicity problems for both humans and animals. High concentrations of selenium cause skin disease, gastrointestinal disturbance, damage to the central nervous system, and birth defects manifested in waterfowls [1]. Due to its high toxicity, most countries have adopted the World Health Organization (WHO) guideline [2] of 10 μg L^{-1}. Selenium exists in the environment in four oxidation states (+VI, +IV, 0, and −II), in which selenite (SeO_3^{2-}) and selenate (SeO_4^{2-}) are the common forms in oxidized systems [3]. Selenium occurs naturally in the environment in trace amounts. But the main sources of selenium in the environment are weathering of natural rock, anthropogenic activities, due to various industrial (pigmented glass, explosives, rubber, lubricants, ceramic, rectifiers, shampoos, photocells, batteries) operations and agricultural irrigation can also lead to release selenium [4]. Due to the high toxicity of selenium, removal of selenium from water bodies needs special attention.

Different types of treatment techniques have been tried and used to remove selenium from contaminated water. These techniques include alum and ferric sulfate coagulation, lime softening, adsorption by alumina or activated carbons, ion exchange, nanofiltration and reverse osmosis [5–10]. Physical methods like ion exchange, reverse osmosis and electro dialysis have proven to be either too expensive or inefficient to remove manganese from water. At present, chemical treatments are not used due to disadvantages like high costs of maintenance, problems of sludge handling and its disposal, and neutralization of effluent. Electrochemical and photochemical methods are also tried for water treatment [11–15]. Among these treatment methods, adsorption process using waste materials, biological material, carbon based materials and naturally available materials are more advantageous due to low cost and high treatment efficiency [16–35].

Carbon nanotubes (CNTs s) are large surface area, high mechanical strength and remarkable electrical conductivities indicate their tremendous potential for different applications. CNTs are classified into two categories viz., singlewall carbon nanotubes (SWCNT) and multiwall carbon nanotubes (MWCNT). The application of MWCNT as adsorbent to remove organic and inorganic pollutants have been studied intensively [36–39], and the results indicate that MWCNT are suitable candidate for water treatment. However, no report was available for the adsorption of selenium to MWCNT.

The objectives of the present studies are — to investigate the adsorption kinetics of selenate on the MWCNT, to study the effects of pH, ionic strength, and foreign ions on selenate sorption on the MWCNT, the

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adsorption isotherms by using Langmuir, Freundlich and D–R models and to calculate the thermodynamic parameters for the adsorption of selenate at different temperatures.

2. Experimental section

2.1. Materials

MWCNT were purchased from Aldrich, with 5–10 nm outer diameter, surface area of 40–600 m^2/g and purity above 95%.

2.2. Preparation of purified MWCNT and characterization

Ten grams of raw MWCNT were soaked in 50 mL of 8 mol/L of HNO_3 for 12 h at room temperature. Then the solution was filtered through a 0.45 μm membrane filter and the MWCNT were washed with Milli-Q water until the neutral pH. Then the MWCNT were refluxed with 8 mol/L nitric acid solution at about 125 °C for 2 h, filtered and then washed with Milli-Q water until neutral pH. Such prepared MWCNT was dried overnight in an oven at 80 °C, and then calcined at 45 °C for 4 h to completely remove amorphous carbon and nitrate ions.

The morphology and structure of MWCNT was characterized by SEM (Hitachi model s-3000 h, Japan). The FTIR spectrum of MWCNT was recorded with a FTIR spectrometer (Nexus 670, USA). Raman spectroscopy was performed with a Renishaw InVia Laser Raman Microscope. The X-ray diffraction (XRD) pattern of MWCNT was analyzed using an X'per PRO X-ray diffractometer (PANalytical, USA).

2.3. Batch mode adsorption experiment

Batch adsorption experiments were performed using 100 mL glass bottles with addition of 50 mg of MWCNT and 50 ml of sodium selenate (Na_2SeO_4, Sigma Aldrich) solution of concentration from 0.50 to 2.0 mg/L. The glass bottles were sealed with Teflon and then were placed on a shaker. The adsorption experiments were carried out at 250 rpm for 40 min (25 °C). The temperature of the selenate solution has been controlled to the desired value with a variation of ± 2 K by adjusting the rate of flow of thermostatically controlled water through an external glass-cooling spiral. The pH was adjusted by adding a suitable amount of 0.1 M HNO_3 or NaOH. All chemicals were purchased in analytical purity and used in the experiments directly without any further purification. All solutions were prepared by using Milli-Q water.

2.4. Analytical method

The ions, viz. selenate, sulfate, nitrate, fluoride and phosphate were measured using a Ion Chromatograph (Metrohm AG, Herisau, Switzerland) equipped with a Dual 3 column (250 mm × 4 mm), a RP guard column, and a conductivity detector. NaOH (5 mM) served as the eluent and sulfuric acid (2.0 mM) as the regenerant in the chromatogram analysis.

3. Result and discussion

3.1. Characterizations of MWCNT

The Raman spectrum of MWCNT in Fig. 1 is composed of three characteristic peaks. The peak near 1350 cm^{-1} is the D-band corresponding to the disordered sp^2 hybridized carbon atoms of MWCNT while the peak near 1580 cm^{-1} is the G-band corresponding to the structural integrity of sp^2 hybridized carbon atoms of MWCNT. The second order D-band (D^*-band) was also observer between 2680 and 2700 cm^{-1}. Together, these bands can be used to determine the extent of carbon-containing defects [40,41]. As can be seen, MWCNT (ID/IG = 0.85) have a higher ID/IG ratio (the intensity ratio of D-band to G-band) than the MWCNT (ID/IG = 0.79), which indicates that the MWCNT contain more amorphous carbon and multishell sp^2 hybridized carbon nanoparticles that can encapsulate residual metal catalysts.

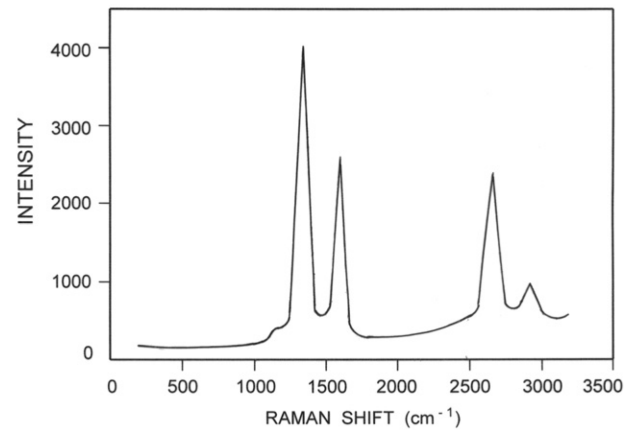

Fig. 1. Raman spectra of MWCNT.

The FTIR measurements were performed in order to verify the formation of oxygen-containing functional groups after oxidation. Fig. 2 shows the FTIR spectra of MWCNT. It is reported [42] that hydroxyl (-OH), carboxyl (-COOH) and carbonyal (>C = O) groups present on the surface of the MWCNT after oxidation either with nitric or sulfuric acid. In the present study the peak at 1450.41 cm^{-1} is associated with O-H bending deformation in carbocyclic acids and phenolic groups. The signature of >C═O functional groups is evident at 1645.87 cm^{-1} and −OH functional groups appear at 3424.45 cm^{-1}. These oxygen-containing functional groups present abundantly on the external and internal surfaces of MWCNT, which can provide numerous chemical sorption sites and thereby increase the sorption capacity of oxidized MWCNT [43,44].

The morphology of MWCNT was examined by using SEM. From the SEM it is found that the MWCNT have very smooth surfaces and are about 100–200 nm in diameter and several micrometers in length (Fig. 3). Energy-dispersive analysis of X-rays was used to analyze the elemental constituents of selenium-adsorbed MWCNT (Fig. 4). It shows that the presence of Pb, C and O appears in the spectrum. EDAX analysis provides direct evidence that selenium is adsorbed on MWCNT.

Fig. 5 shows the high resolution XPS spectra of the sample around 532.5 eV. With reference to the XPS studies of MWCNT, the experimental data shows that functional groups present on the surface of MWCNT: carboxyl oxygen [−O−-C═O(H), 533.6 eV] and carbonyl oxygen = C═O, 530.7 eV.

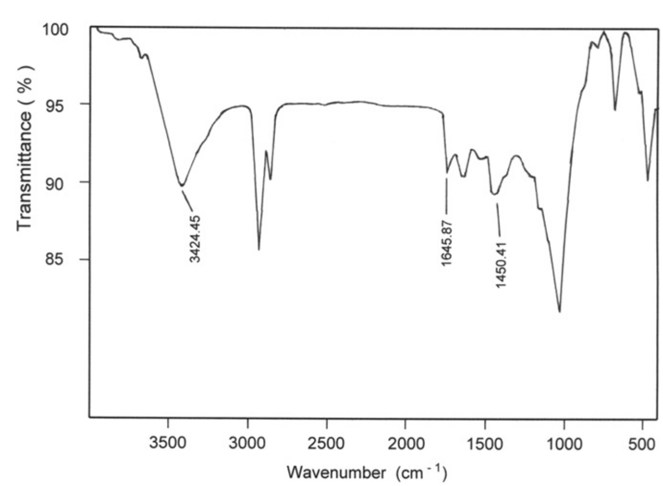

Fig. 2. Fourier transformed infrared spectra of MWCNT.