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Carbon Nanotubes Technology for Removal of Arsenic from Water

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Aims of the Study: This study was aimed to investigate the adsorption mechanism of the arsenic removal from water by using carbon nanotubes in continuous adsorption column.

Materials & Methods: Independent variables including carbon nanotubes dosage, contact time and breakthrough point were carried out to determine the influence of these parameters on the adsorption capacity of the arsenic from water. The experimental data were analyzed using Langmuir and Freundlich isotherm models.

Results: Adsorption capacities of single- and multi-walled carbon nanotubes were about 148 and 95 mg/g, respectively. The experimental data were analyzed using Langmuir and Freundlich isotherm models, and equilibrium data indicated the best fit obtained with Langmuir isotherm model.

Conclusions: Carbon nanotubes can be considered as a promising adsorbent for the removal of arsenic from large volume of aqueous solutions.

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Background

Arsenic (As) is a naturally occurring element present in food, water, and air. Known for centuries to be an effective poison, some animal studies suggest that arsenic may be an essential nutrient at low concentrations.

Non-malignant skin alterations, such as keratosis and hypo- and hyper pigmentation, have been linked to arsenic ingestion, and skin cancers have developed in some patients. Additional studies indicate that arsenic ingestion may result in internal malignancies, including cancers of the kidney, bladder, liver, lung, and other organs (1).

Arsenic occurs in two primary forms: organic and inorganic. Organic species of arsenic are predominantly found in foodstuffs. Inorganic arsenic occurs in two valence states, arsenite (As III) and arsenate (As V). Natural ground waters contain predominant As (III) since reducing conditions prevail. In natural surface waters As (V) is the dominant species (2).

Arsenic in natural waters is a worldwide problem. Arsenic pollution has been reported recently in the USA, China, Chile, Bangladesh, Taiwan, Mexico, Argentina, Poland, Canada, Hungary, New Zealand, Japan and India (3-6). The World Health Organization (WHO) provisional guideline of 10 ppb (0.01 mg/L) has been adopted as the drinking water standard. However, many countries have retained the earlier WHO guideline of 50 ppb (0.05 mg/L) as their standard or as an interim target including Bangladesh and China. In 2001, US-EPA published a new 10 ppb (0.01 mg/L) standard for arsenic in drinking water, requiring public water supplies to reduce arsenic from 50 ppb (0.05 mg/L) (7), which will be effective from January 2006.

The major arsenic removal technologies for drinking water include oxidation/precipitation, coagulation/electro-coagulation/co-precipitation, Ion-exchange technologies, membrane technologies and adsorption processes (8, 9).

Oxidation/precipitation processes mainly removes only arsenic (V) and accelerate the oxidation process. Otherwise in these processes efficient control of the pH and oxidation steps are needed (10, 11).

Coagulation/electro-coagulation/co-precipitation processes produce toxic sludge; low removal of arsenic and pre-oxidation may be required. These processes have medium removal of As (III) and sedimentation and filtration maybe needed.

Disadvantages of Ion-exchange technologies include: High cost medium; high-tech operation and maintenance; regeneration creates a sludge disposal problem and As (III) is difficult to remove (12-14).

Membrane technologies such as Nanofiltration, Reverse Osmosis and Electrodialysis have very high-capital and running cost, pre-conditioning processes may be required; water rejection is high and toxic wastewater produced (15, 16). Adsorption is one of the most effective methods for arsenic removal. Selective adsorption utilizing biological materials, mineral oxides, activated carbons, or polymer resins, has generated increasing excitement (17, 18).

In recent years, nanotechnology has introduced different types of nanomaterials to water industry that can have promising outcomes. Nanosorbents such as carbon nanotubes (CNTs), polymeric materials (*e.g.* dendrimers), zeolites have exceptional adsorption properties and are applied for removal of heavy metals, organics, and biological impurities (19).

CNTs are graphene sheets seamlessly rolled into cylindrical tubes. They are either single- or multi-walled carbon nanotubes (MWCNT), with the latter being relatively inexpensive (20, 21). Their unique characteristics such as high aspect ratio, superior mechanical, electrical and thermal properties make them well suited for many applications. CNTs also exhibit exceptional sorption properties towards various organic compounds and inorganic ions (21).

Aims of the study: The objective of this paper was to study the adsorption capacity of single- and multi-walled carbon nanotubes in the removal of arsenate from water to meet drinking water standards.

Materials & Methods

Preparation and purification of CNTs: CNTs were prepared by special chemical vapor deposition technique in Nanotechnology Research Center, Research Institute of Petroleum Industry, Tehran, Iran.

For synthesis of CNTs the catalytic reactions were accomplished in the presence of Co-Mo/MgO as the catalyst. The chemical vapor deposition method was carried out in a horizontal furnace consisting of a quartz tube.

The catalyst was set in a quartz boat that was placed into a quartz tube. The catalyst was purged in the hydrogen stream in order to reduce the catalyst. The reaction was carried out using methane as the carbon source and hydrogen as the carrier gas. The furnace was then cooled to room temperature under a nitrogen atmosphere and the final black product formed.

In order to purification and removing the metal nanocatalysts from carbon nanotubes, the final products were dissolved in 37% hydrochloride acid solution for about 16 h at ambient temperature and then washed several times with distilled water until the pH of the solution reached approximately neutral. Treated multi-walled carbon nanotubes were dried in vacuum at 40 °C overnight. For the elimination of amorphous carbons, all of the purified CNTs were placed in the furnace at 400 ºC for 30 min.

Ten ppm stock solutions of arsenic (V) were prepared by dissolving weighed amounts of Na_2HAsO_4 in measured volumes of ultra high quality water. The stock solutions were preserved with HNO_3. One ppm working solutions were then prepared from the stock for analysis. Residual Arsenic was measured using Agilent 7500 ICP-MS.

Characterizations of the CNTs: The CNTs was characterized using a scanning electron microscope (SEM) fitted with an Energy Dispersive X-Ray Spectrometer (EDS), X-ray diffraction, and BET (Brunauer, Emmett and Teller) theory used for determination of surface area. SEM Data was collected on a LEO 1530 VP Scanning Electron Microscopy equipped with an energy-dispersive X-ray analyzer, which used in collecting EDS data. X-ray diffraction was performed on a Philips X'Pert PW3040-MPD (Netherlands) diffractometer using Cu Ka radiation (k=1.5406 Å) at 25 ºC.

Continuous adsorption experiments: Adsorption experiments were carried out in a continuous system using arsenic as the compound to be adsorbed by CNTs. Figure 1 illustrates the schematic of apparatus for the study.

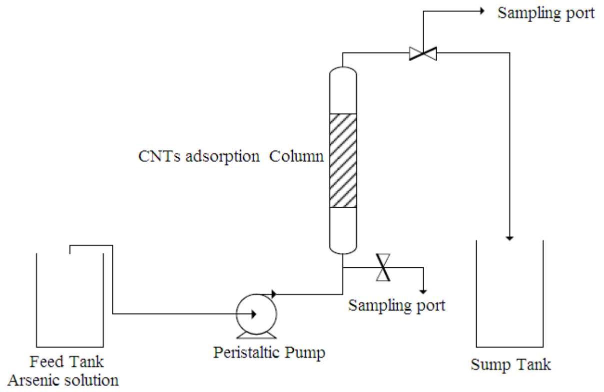

Figure 1) Schematic diagram of continuous adsorption experimental pilot

A 20 mm of CNTs was placed inside a fixed-bed column. The column dimensions were 12 mm internal diameter and 100 mm height. Prior to each experiment, distilled water was passed through the column to rid the column impurities and air bubbles.

The arsenic solution of known concentration was pumped upwards through the column at 15 mL/min. Effluent samples were collected from the top of the column at different intervals and the concentration of arsenic was analyzed by Agilent 7500 ICP-MS. All tests were carried out at room temperature, 25 ºC.

Data analysis: The experimental data were analyzed using Langmuir and Freundlich isotherm models.

Results

The X-ray diffraction spectra of CNTs have been shown in Figure 2. As shown in Figure 2, the peaks at 25 and 43 degree are related to graphene structure of carbon nanotubes.

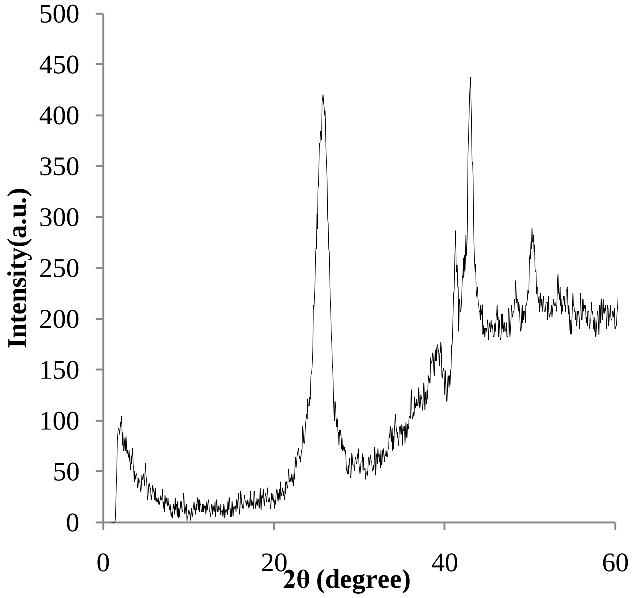

Figure 2) X-ray diffraction spectra of CNTs

The breakthrough curve of arsenic adsorption on to carbon nanotubes and effect of CNTs dosage have been shown in Figure 3.

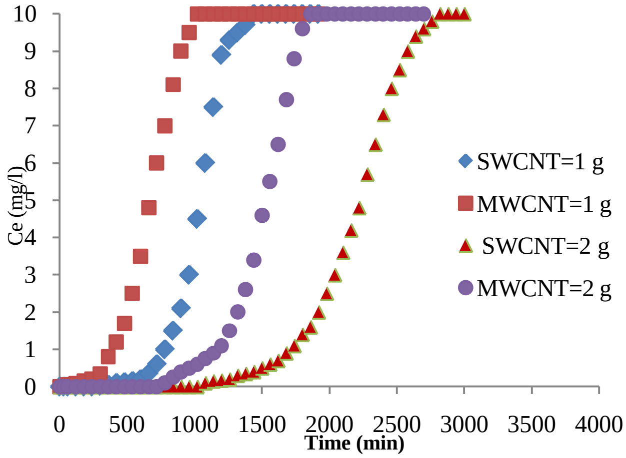

Figure 3) Breakthrough curve and effect of carbon nanotubes masses on arsenic removal

The results of this study showed that the adsorption capacity of single and multi-walled carbon nanotubes were 148 and 95 mg/g, respectively. Figure 4 illustrates the Freundlich and Langmuir isotherms model that are fitted to the experimental data obtained at 25 °C. The determined isotherm parameters are shown in Table 1.

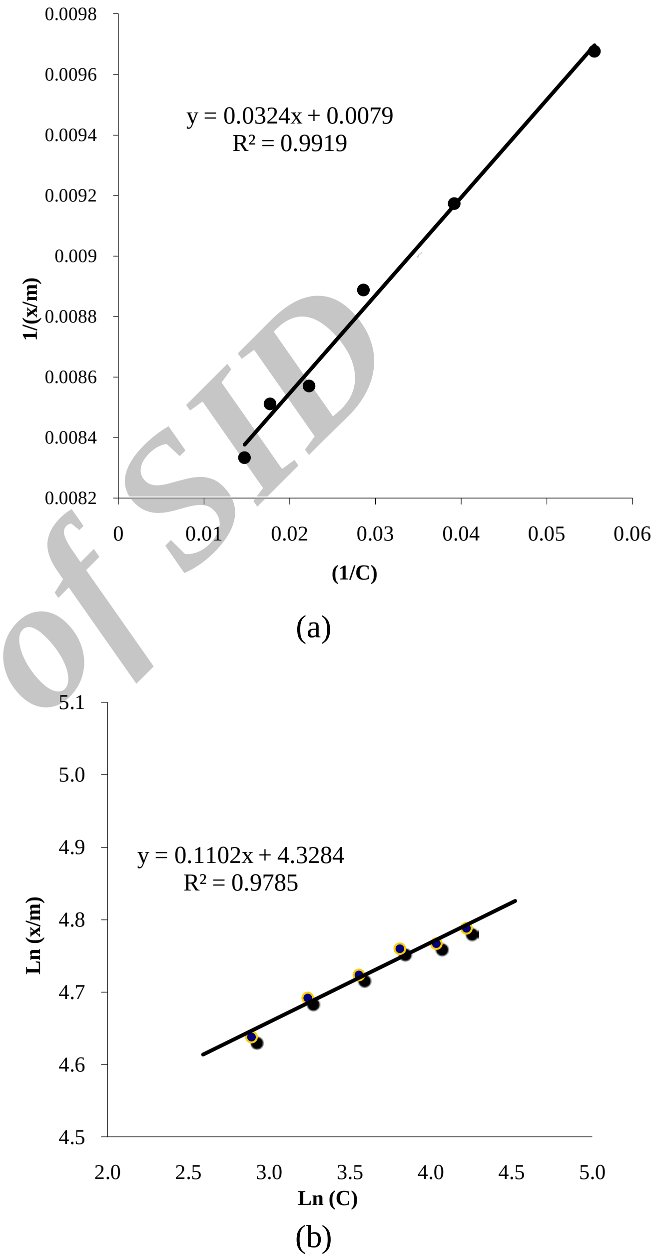

Figure 4) Adsorption isotherms of arsenic on to carbon nanotubes, (a) Freundlich, (b) Langmuir

Table 1) Determined isotherm model constants for the adsorption of arsenic on carbon nanotubes

Langmuir Isotherm			Freundlich Isotherm		
q_m (mg/g)	B (L/mg)	R^2	K_f (mg/g) $(mg/L)^n$	n	R^2
126.58	0.24	0.99	75.8	9.07	0.97

Discussion

Breakthrough curve characterization: The shape of the breakthrough curve and the time of breakthrough point are the predominant factors describing the column dynamic behavior.

An arbitrarily defined breakthrough time (t_b) is the time at which the concentration of the adsorbate material in the outlet stream from the adsorption column reaches 5% of the feed concentration. Similarly, the saturation time (t_s) is related to the time when the bed becomes saturated. In other words, no more adsorption occurs in the bed. The breakthrough curve is obtained by drawing the variation of the outlet dye concentration as a function of time.

Effect of CNTs dosage: The effect of mass of CNTs on the performance of the arsenic removal has been studied by testing at 1 and 2 g of CNTs with keeping the concentration of arsenic at 10 mg/L and the flow rate at 15 ml/min constant.

Figure 3 shows the adsorption curve of arsenic on single- and multi-walled carbon nanotubes in two adsorbent masses (1 and 2 g). As shown in Figure 3, by increasing the mass of CNTs, the volume of solution treated before breakthrough point was considerably increased.

Comparison between plotted curves indicates that decreasing adsorbent loading from 2 to 1 g caused a reduction in breakthrough time, saturation time and total adsorbed arsenic. This is explained by considering the number of active sites in the bed for arsenic adsorption.

By increasing the adsorbent loading, more active sites are available for arsenic to be adsorbed on the adsorbent, and therefore total quantity of the arsenic adsorbed on the bed is increased. These finding are in accordance with Naghizadeh et al. (18) and Gupta et al. (22).

Isotherm studies: For adsorption isotherm study, the data were analyzed employing Langmuir and Freundlich isotherm equations. The linearized forms of these equations can be expressed as follows respectively:

$$\frac{C_e}{Q_e} = \frac{1}{Q_{max}\,K_L} + \frac{C_e}{Q_{max}} \qquad [1]$$

$$Ln\,Q_e = \left(\frac{1}{n}\right) Ln\,C_e + Ln\,K_F \qquad [2]$$

Where Q_e (mg/g) is the equilibrium NOMs concentration in the solid phase; Q_{max} (mg/g) is the maximum amount of sorption; K_L (L/mg) is the Langmuir sorption equilibrium constant; K_F ($mg^{1-1/n}L^{1/n}/g$) is the Freundlich constant representing the sorption capacity and n is the constant depicting the sorption intensity (23).

According to Figure 4 and Table 1 and considering the values of the linear regression coefficients, the Langmuir model is more suitably fitted to the adsorption data in the studied concentration range with an R^2 value of 0.99 compared to the Freundlich model with 0.97. These finding are in agreement with the results that reported by Kundu et al. (24) and Wasiuddin et al. (25).

Conclusions: The continuous adsorption of arsenic has been studied in a fixed-bed column using carbon nanotubes as an adsorbent. The investigation on the effect of CNTs masses showed that the adsorption was more effective at higher masses of CNTs. The equilibrium data indicate the best fit obtained with Langmuir isotherm model. So, Carbon nanotubes can be considered as a promising adsorbent for the removal of arsenic from large volume of aqueous solutions.

Footnotes

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Conflict of interest:

The authors declare no conflict of interest.

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