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Adsorption of Arsenic on Multiwall Carbon Nanotube–Zirconia Nanohybrid for Potential Drinking Water Purification

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Abstract

The adsorptive removal of arsenic from water using a multiwall carbon nanotube-zirconia nanohybrid (MWCNT-ZrO₂) is presented. The MWCNT-ZrO₂ with 4.85% zirconia was effective in meeting the drinking water standard levels of 10 µg L⁻¹. The absorption capacity of the composite were 2000 µg g⁻¹ and 5000 µg g⁻¹ for As (III) and As (V) respectively, which were significantly higher than those reported previously for iron oxide coated MWCNTs. The adsorption of As (V) on MWCNT-ZrO₂ was faster than that of As (III), and a pseudo-second order rate equation effectively described the uptake kinetics. The adsorption isotherms for As (III) and As (V) fitted both the Langmuir and Freundlich models. A major advantage of the MWCNT-ZrO₂ was that the adsorption capacity was not a function of pH.

Keywords

Arsenic; carbon nanotubes; zirconia; water; adsorption; kinetics

1. Introduction

The problem of arsenic contamination of water has affected many parts of the world including North America and Asia[1–3]. Besides being classified as a Group 1 carcinogen [4], it is also responsible for other health effects such as spontaneous abortion[5]. The US-EPA maximum contaminant level for arsenic was reduced from 50 to 10ppb in 2001.

In a typical aquatic environment Arsenic is predominantly found in two different oxidation states. Arsenite As (III), which is neutral, uncharged and a soluble molecule is considered more toxic than arsenate As (V), and is more difficult to remove from aqueous media[6]. Existing techniques for Arsenic removal include oxidation/precipitation, coagulation/coprecipitation, nanofiltration, reverse osmosis, electrodialysis, adsorption, ion exchange, foam flotation, solvent extraction and bioremediation[7]. These well established approaches have been adapted for As removal and have their respective advantages and certain inherent limitations that include the generation of toxic waste, low arsenic removal efficiency and high cost[7].

Adsorption is one of the most effective methods for As removal and myriad materials including lanthanum/iron compounds, mineral oxides, and biological materials[8] have been

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studied. The use of polymeric resins, activated carbon, activated alumina, iron coated sand, hydrous ferric oxide, and natural ores have generated much interest, and novel metal modified adsorbents have demonstrated superior performance [9]. Zirconium oxides/hydroxides have been extensively investigated as adsorbents for the removal of cationic and anionic pollutants from water. They have been shown to be effective in the removal of dyes, Fluoride, uranium (IV), phosphate, mercury, and selenium[10]. While iron oxides represent some of the most common sorbent for As removal[7], the potential for using zirconium based compounds is also being investigated for As removal. Preliminary investigations using zirconium loaded materials such as activated charcoal, porous resin, chelating resin with lysine-Na, orange waste have shown promising results for As removal[10]. In general, for use as an environmental adsorbent, zirconium needs to be impregnated or loaded on a support because it has poor physical properties and moreover this also lowers the overall cost of this expensive material. Therefore, the development of effective support materials is of utmost importance.

Carbon nanotubes (CNTs) are graphene sheets seamlessly rolled into cylindrical tubes. They are either single-walled (SWCNT) or multiwall carbon nanotubes (MWCNT), with the latter being relatively inexpensive[11, 12]. 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[13]. The potential for sidewall functionalization and surface modification make them attractive as support phases for water treatment[14–16]. Effective arsenic removal with iron oxide coated MWCNT has been reported by us [9, 17]. Here the iron oxides were protonated forming OH_2^+ groups on the adsorbent surface at low pH values, and the arsenic species were removed by covalent ligand exchange.

Zirconia coated multiwall carbon nanotube was synthesized in our group and shown to remove fluoride from water and its capacity was significantly higher than other conventional sorbents [16]. It is anticipated that Zirconium oxide supported on MWCNT may remove arsenic species through a synergistic combination of chemisorption and physisorption. The objective of this paper was to study the adsorption capacity of MWCNT–Zirconia nanohybrid in the removal of arsenite and arsenate from water to meet drinking water standards.

2. Experimental

2.1 Materials and Methods

Multiwall carbon nanotubes (OD 20–40nm, Purity 95%) were purchased from Cheap Tubes Inc., and all other chemicals were purchased from Sigma Aldrich with purity higher than 95%. Ten ppm stock solutions of As (III) and As (V) were prepared by dissolving weighed amounts of NaAsO_2 and Na_2HAsO_4 respectively in measured volumes of MilliQ water. The stock solutions were preserved with HNO_3 . 1ppm working solutions were then prepared from the stock for analysis.

The MWCNT was functionalized in a Microwave Accelerated Reaction System (Mode: CEM Mars) fitted with internal temperature and pressure controls according to an experimental procedures previously published by our laboratory[18]. Pre-weighed amounts of purified MWCNT was treated with a mixture of concentrated H_2SO_4 and HNO_3 solution by subjecting them to microwave radiation at 120°C for 20–40 min. This led to the formation of carboxylic groups on the surface along with some sulphonation and nitration. The resulting solid was filtered through a 10 μm membrane filter, washed with water to a neutral pH and dried under vacuum at 80°C to a constant weight. This product (f-MWCNT) was used in the subsequent synthesis of the MWCNT-ZrO₂ composite.

The MWCNT-ZrO₂ hybrid was synthesized by dispersing a weighed amount of the f-MWCNT in 0.008M ZrOCl₂[19]. The reaction was carried out in a Microwave Accelerated Reaction System (Mode: CEM Mars) fitted with internal temperature and pressure controls at 150°C for 1 hour. The product was vacuum filtered through a 10 µm membrane filter paper and thoroughly washed with DI water until all the unreacted ZrOCl₂·8H₂O was removed. The resultant product was dried in a vacuum oven at 80 °C for 12 hr.

The MWCNT-ZrO₂ was characterized using a scanning electron microscope (SEM) fitted with an Energy Dispersive X-ray spectrometer (EDS), Thermogravimetric analysis (TGA), X-ray diffraction (XRD), Fourier Transform Infrared spectroscopy (FTIR) and BET 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. TGA was performed using a Pyris 1 TGA from Perkin-Elmer Inc from 30°C to 900°C under a flow of air at 10mL/min, at a heating rate of 10°C per min. X-ray diffraction (XRD) was performed on a Philips X'Pert PW3040-MPD (Netherlands) diffractometer using Cu K α radiation (λ = 1.5406 Å) at 25°C. FTIR measurements were carried out in purified KBr pellets using a Perkin-Elmer (Spectrum One) instrument. Specific surface area, micropore volume, and average pore radius were measured using Quantachrome NOVA 3000 series (Model N32-11) High Speed Gas Sorption Analyzer at 77.40 K. Before each experiment, the samples were heated at 200°C and degassed at this temperature until constant vacuum for four hours. pH of Point of Zero Charge (pHpzc) was determined based on a previously published procedure[20].

2.2 Adsorption Studies

10 ml of 100µg l⁻¹ arsenic solution [As (III) and As (V)] was contacted with 0.01 g of the adsorbent in a series of conical flasks at pHs ranging between 5 and 8, and samples were collected at 5, 10, 15, 30, and 45 min 1, 3, 6, 12, 15 and 24 h for kinetic studies. Equilibrium contact time and pH were determined to be 6 h and pH 6 respectively. The mass of the adsorbent was varied from 0.01 to 0.1 g in the isothermal adsorption studies at pH 6 for 6 hours. The arsenic solutions and the adsorbents were mixed thoroughly at a speed of 175 rpm on a platform shaker, (Labsystems Wellmix). The mixture was filtered through a 0.45 µm membrane syringe filter.

Residual Arsenic was measured using Agilent 7500 ICP-MS. All standards were prepared from multi-element solution 2A, 10mg/L (Spex Certiprep) with addition of internal standard mix (Li6, Ge, Y, In, Tb, Bi). Buffer solution was used for all dilutions. Multi-element instrument calibration standard 1, 20 mg/L (Spex Certiprep) was used for the verification of calibration.

2.3 Effects of Competing Anions

To determine the effects of co-existing anions on arsenic adsorption, three types of the oxyanions (CO₃²⁻, SO₄²⁻ and NO₃⁻) were evaluated individually. The experiments were conducted at 25 °C and pH 6.0, for initial Arsenic concentration of 100 µg/L.. The concentrations of three oxyanions were controlled at three levels (0.1, 1 and 5 mM).

3. Results and Discussion

3.1 Characterization of Adsorbent

The BET surface area of MWCNT, f-MWCNT and the MWCNT-ZrO₂ hybrid were 110 m²g⁻¹, 162 m²g⁻¹ and 152 m²g⁻¹ respectively. BET surface area increased significantly after acid treatment as the value for f-MWCNT was an approximate 40% higher than that of original MWCNT. This increase may be due to defects on the surface of f-MWCNT as a

result of the acid treatment. BET surface area of the MWCNT-ZrO₂ hybrid was however not significantly different from f-MWCNT. Zirconia has a relatively small surface area which slightly decreased the surface area of the hybrid. The acid functionalization of the carbon nanotubes produced carboxylic groups on the surface enhancing zirconia loading. This increase in surface area was due to the presence of zirconia particles on the CNT surface. The pH at zero point charge (pH_{ZPC}) for MWCNT, f-MWCNT and the MWCNT-ZrO₂ hybrid were 6.8, 3.91 and 6.9 respectively. This is the point where the surface charge of the carbon nanotube is independent of the electrolyte concentration. Therefore it is evident that the carboxylic groups on the f-MWCNT had been replaced in the MWCNT-ZrO₂ hybrid.

SEM images of f-MWCNT and the MWCNT-ZrO₂ hybrid are shown in Figure 1a and 1b. Original MWCNTs had diameter in the range of 20–40 nm and the length was about 10–30 µm. There was no detectable change in tube morphology after acid treatment or zirconia loading, implying minimal damage to the tube structure. It is quite evident from figure 1b that the CNT surface was coated with zirconia.

The EDS data shown in figure 1c confirmed the presence of zirconia on the surface of the CNTs. Figure 2 shows the x-ray powder diffraction pattern of MWCNT, f-MWCNT and the MWCNT-ZrO₂ hybrid. The peak around 30.2° in 2θ in the XRD pattern of the MWCNT-ZrO₂ hybrid (Fig. 2c) indicated the presence of zirconia [21] which was clearly absent from the diffraction patterns of MWCNT and f-MWCNT (Fig. 2a and 2b). The intense peak around 26° in 2θ in all the XRD patterns was due to the MWCNT. TGA was used to quantify the zirconia loading in the MWCNT as shown in Figure 3(a). The resulting weight above 600 °C was attributed to the weight of residual metal or metal oxide. The MWCNT-ZrO₂ hybrid was found to contain 4.85 % zirconia.

The IR spectrum (Fig. 3b) confirmed the presence of functional groups in MWCNT, f-MWCNT, and MWCNT-ZrO₂. The carboxylic stretching frequency in f-MWCNT occurred at 1715 cm⁻¹ (C=O) and 1221 cm⁻¹ (C-O). The stretching (O-H) vibration occurred at 3424 cm⁻¹ in the f-MWCNT spectrum (Fig. 3b (iii)) which was clearly absent from the MWCNT spectrum [Fig. 2b(ii)]. In all the samples, the peak around 1576 cm⁻¹ was assigned to the C=C stretching of the carbon skeleton. From the MWCNT-ZrO₂ (Fig. 3b(i)) spectrum, it can be seen that the characteristic peaks of the carboxyl groups of the MWCNTs shifted from 1715 to 1701 cm⁻¹ and the relative intensity decreased significantly, the peak at 3440 cm⁻¹ belonging to the O-H vibration of carboxylic acid also disappeared. The disappearance of the peak of O-H vibration of carboxylic acid was attributed to fact that ZrO₂ is anchored to the MWCNTs through an esterification process forming C-O-Zr bonds, in line with previous observations[21].

3.2 Arsenic Removal by MWCNT-ZrO₂

It was found that no arsenic was adsorbed on the MWCNT and the carboxylated MWCNT; however the MWCNT-ZrO₂ hybrid was effective in removing arsenic from water. It occurred through a synergistic combination of chemisorption and physisorption processes on the Zr immobilized on the MWCNT backbone. Schmidt et al, (2008) have reported the surface speciation for Zirconium and arsenate adsorption using the GRFIT model, determining that they formed two surface complexes represented by equations 5 and 6, with reaction (5) being practically negligible [22].

Ion exchange and non-covalent H-bonding interactions may also play a role in the arsenic removal process [16]. This was somewhat different from the iron oxide coated MWCNTs where the former protonated forming OH_2^+ groups on the adsorbent surface at low pH values, and the arsenic species were removed by covalent ligand exchange with OH and OH_2^+ functional groups [9].

The kinetics of As uptake was investigated by the Lagergren[23] and Ho and McKay[24] kinetic models. The former models the rate of adsorption of pollutants on an adsorbent based on a pseudo-first order equation:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (1)$$

where q_e and q_t are the sorption capacity ($\mu\text{g g}^{-1}$) of the adsorbent at equilibrium and at time t (h), respectively and k_1 is the pseudo-first order sorption rate constant (h^{-1}). Ho and McKay proposed a pseudo-second order equation of the form:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (2)$$

where, k_2 is the pseudo-second order sorption rate constant ($\text{g (h } \mu\text{g)}^{-1}$) and t is time (h). Figure 5(a) shows As(III) and As(V) removal efficiencies as a function of time at the different pH values. After 10 mins of contact with the adsorbent over 50% of As (V) was removed as compare to 17% of As (III). 99% of As(V) and 92% of As(III) were removed after 60 minutes of contact. Relative to MWCNT-ZrO₂ nearly twice the amount of both As(III) and As(V) were removed in the presence Fe-MWCNT[9] after 10 mins of contact, with (80–99)% removed after only 30mins of contact. The kinetics of As(III) and As(V) adsorption using the MWCNT-ZrO₂ was relatively slower compared to that observed with iron oxide coated MWCNT[9].

Ho and McKay's pseudo-second kinetic equation was a better fit than the Lagergren's pseudo-first order equation for adsorption of both oxidation states of arsenic on MWCNT-ZrO₂. The pseudo-second order kinetic parameters at the pH range studied are presented in table 1. The R^2 values for both As (III) and As (V) were close to unity implying that their adsorption can best be described by the pseudo-second order kinetic model with chemisorption being the rate limiting step. This means that the adsorption rate is proportional to the amount of adsorbent and the square of the number of free sites. The latter corresponds to the term $(q_e - q_t)^2$ in the pseudo second order model.

The rate of As(V) removal was an order of magnitude faster than that of As(III) as shown by the pseudo-second order kinetic parameters in table 1 as was the removal efficiency(Fig. 4). This was similar to what was observed for arsenic adsorption on Fe-MWCNT. The higher removal rate of As(V) relative to As(III) may be due to the rate-limiting oxidation of As(III) to As(V) catalyzed by surficial carbon compounds preceded the adsorption reaction[22].

The optimum pH for As(V) removal was determined to be 6, the equilibrium adsorption q_e ($\mu\text{g g}^{-1}$) of both As(V) and As(III) was found to be fairly constant over the pH range studied as presented in figure 4(b). This was contrary to As(V) removal on Fe-MWCNT, where q_e was observed to decrease with increasing pH due to interference from dominant OH^- ions at basic pH. As(III) is dominant in the form of neutral species (H_3AsO_3) below pH 9.22, accounting for the relatively constant As(III) adsorption in both instances. This implies that

unlike Fe-MWCNT, MWCNT-ZrO₂ has the advantage of effective arsenic removal over a wide range of pH.

3.3 Adsorption Isotherms for As(III) and As(V) Removal

The capacity of arsenic removal by the adsorbent was evaluated with the [25], and Freundlich [26] isotherms. The linear form of Langmuir adsorption isotherm is presented below;

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{b q_m C_e} \quad (3)$$

where q_m (μg/g) is the maximum sorption capacity for monolayer coverage of the adsorbent, C_e (μg/L) is the equilibrium concentration of arsenic and Langmuir constant b (L/μg) is indirectly related to the enthalpy of adsorption. The linearized form of the Freundlich isotherm involves a plot of $\log q_e$ and $\log C_e$ with n and $\log k_f$ being the slope and y-intercept respectively.

$$\log q_e = \log k_f + n \log C_e \quad (4)$$

The Freundlich constants k_f and $1/n$ measure the adsorption capacity and intensity respectively. The bond energy increases proportionally with surface density for $n < 1$ and vice versa for $n > 1$. From the Langmuir isotherm parameters presented in Table 2, the maximum sorption capacity for monolayer adsorption (q_m) for the adsorbent in the removal of As(V) was much higher than that of As(III). The adsorption capacity, estimated by the Langmuir isotherm model was 2000 μg g⁻¹ and 5000 μg g⁻¹ for As(III) and As(V) respectively. These values were significantly higher than the q_m values obtained with Fe-MWCNT[9]. The Langmuir constant, b , the ratio of the adsorption rate constant to the desorption rate constant, is an indication of the affinity of the sorbent material toward arsenic[27]. The Langmuir b values for arsenic sorption by MWCNT-ZrO₂ as presented in Table 2 were approximately an order of magnitude lower than those observed for Fe-MWCNT[9] in the presence of both As(III) and As(V), indicating a higher affinity of Fe-MWCNT for arsenic. This also implies that the rate of desorption of adsorbed arsenic species during sorbent regeneration will be higher in the case of MWCNT-ZrO₂.

The adsorption of As(III) and As(V) fit both the Langmuir and Freundlich equations correlation coefficient R^2 value close to unity as was observed with Fe-MWCNT[9]. The applicability of the two isotherms to the arsenic sorption shows that both monolayer sorption and heterogeneous energetic distribution of active sites on the surface of the sorbent are possible.

The Freundlich constants $\log k_f$ and n were obtained from the y-intercept and slope respectively. The constants k_f (L μg⁻¹) and $1/n$ providing a measure of adsorption capacity and intensity respectively are presented in table 2. The bond energy increases proportionally with surface density for $n < 1$ and vice versa for $n > 1$ [26]. The adsorption capacity for the adsorbent in As(V) removal was much higher than As(III) as was the intensity. The Freundlich isotherm model effectively explained the removal of As(III) and As(V) by the adsorbent with correlation coefficients of 0.9999 and 0.9916 respectively. The value of the constant $1/n$ (0 – 1) is also indicative of the heterogeneity of the adsorbent surface, with $1/n$ closer to 0 implying heterogeneous surface. The values the freundlich isotherm parameter $1/n$ for arsenic adsorption on MWCNT-ZrO₂ were less than 1 for both As(III) and As(V) as was observed to the adsorption on Fe-MWCNT, indicating favorable adsorption on both

sorbents[27]. However the values were closer to zero in the case of Fe-MWCNT than MWCNT-ZrO₂, implying a more favorable process in the presence of the iron coated MWCNTs. This was consistent with the values Langmuir constant **b** observed. The Kinetic and Equilibrium data at pH 6 for As(III) and As(V) adsorption are shown in figure5.

3.4 Effect of Competing Anions

Sulfates, carbonates and nitrates are ionic components often present in many surface and subsurface aquatic systems, and have been reported to exert varied levels of influence on the adsorption of both arsenate and arsenite depending on pH and concentration of anions. In this study, the presence of these anions had negligible effects on the removal of As(V) over the concentration range investigated (0.1 mM – 5 mM) as presented in figure 6. Contrary to the above observation, the removal efficiency of As(III) decreased to various degrees by the presence of these anions. While the decrease in As(III) removal efficiency was not statistically significant in the presence of carbonate ions, sulfate and nitrate ions showed a statistically significant effect. The was contrary to what has been observed in literature for iron-modified sorbents, where the presence of sulfate and carbonate had negligible effects on the removal of both As(III) and As(V) at various pHs and ionic strengths[28–30]. An increase in anion concentration from 1mM to 5mM did not result in a corresponding larger decrease in removal efficiency indicating the saturation of sites accessible to the anions. The results suggest that the binding affinity of these anions for zirconia was weaker than As(V), but comparable to that of As(III).

4.0 Conclusion

The MWCNT-ZrO₂ was effective as a sorbent material for arsenic removal from drinking water. A major advantage of this material is that the sorption capacity was independent of pH over the range studied. The kinetics of As (III) and As (V) removal was explained by the pseudo-second order rate equation, and their adsorption by Langmuir and Freundlich models. Although the rate of Arsenic removal by MWCNT-ZrO₂ was two to three times slower than that for iron coated MWCNTs, the adsorption capacity was nearly two to five times higher. While the removal efficiency of As(V) was not affected by the presence of competing anions, As(III) removal was reduced by the presence of sulfate and nitrate ions.

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Highlights

Adsorptive removal of arsenic from water by MWCNT-ZrO₂.

MWCNT-ZrO₂ was effective in meeting drinking water standards of 10 µg L⁻¹.

As (III) and As (V) adsorption described by a pseudo-second order rate equation.

As (III) and As (V) adsorption fitted both the Langmuir and Freundlich models.

Higher adsorption capacities than those observed for iron oxide modified sorbents.

Figure 1. SEM Images of (a) carboxylated MWCNT, (b) the MWCNT- ZrO₂ Composite, (c) EDS spectra of the MWCNT-ZrO₂ Composite.

Figure 2.
X-ray powder diffraction patterns of (a) MWCNT (b) f-MWCNT, (c) MWCNT- ZrO₂ hybrid.

Figure 3.

(a) TGA data for MWCNT, f-MWCNT, and MWCNT-ZrO₂, and (b) FTIR spectra of (i) MWCNT-ZrO₂, (ii) MWCNT, and (iii) f-MWCNT

Figure 4. (a) Arsenic removal efficiency as a function of time, (b) Effect of pH on As(III) and As(V) adsorption.

Figure 5. (a) Kinetic, and (b) Equilibrium data at pH 6 for As(III) and As(V) adsorption by MWCNT-ZrO₂.

Figure 6.

Effects of oxyanions on Arsenic removal by MWCNT-ZrO₂ after 24 h at pH 6 and 25 °C for initial Arsenic concentration of 100 µg/L. (* difference significant at 95% confidence level).

Table 1

Pseudo-second order kinetic parameters for As (III) and As (V) adsorption

pH	As (III)				As (V)			
	q_e ($\mu\text{g g}^{-1}$)	k_2 ($\text{g (min } \mu\text{g)}^{-1}$)	h ($\mu\text{g (g min)}^{-1}$)	R^2	q_e ($\mu\text{g g}^{-1}$)	k_2 ($\text{g (min } \mu\text{g)}^{-1}$)	h ($\mu\text{g (g min)}^{-1}$)	R^2
5	95.4	2.5E-04	2.3	0.9987	101.1	1.0E-03	10.5	0.9999
6	98.6	3.1E-04	3.0	0.9993	100.5	1.3E-03	13.6	1.0000
7	95.4	4.1E-04	3.7	0.9997	101.1	1.7E-03	16.9	1.0000
8	97.5	3.6E-04	3.4	0.9999	101.7	7.0E-04	7.2	0.9999

Table 2

Adsorption isotherm parameters for removal of As(III) and As(V) by MWCNT-ZrO₂

	Langmuir			Freundlich		
	q_m ($\mu\text{g g}^{-1}$)	b ($\text{L } \mu\text{g}^{-1}$)	R^2	K_f ($\text{L } \mu\text{g}^{-1}$)	n	R^2
As(III)	2000	0.0049	1.0000	9.9	1.0204	0.9999
As(V)	5000	0.038	0.8801	274.09	1.2048	0.9916