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Sorption of ^{243}Am(III) to Multiwall Carbon Nanotubes

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Carbon nanotubes have attracted great interest in multidisciplinary study since their discovery. Herein, radionuclide ^{243}Am(III) sorption to uncapped multiwall carbon nanotubes (MWCNTs) was carried out at 20 ± 2 °C in 0.01 and 0.1 M NaClO$_4$ solutions. Effects of ^{243}Am(III) solution concentration, ionic strength, and pH on ^{243}Am-(III) sorption to MWCNTs were also investigated. The sorption is strongly dependent on pH values and weakly dependent on the ionic strength in the experimental conditions. The results show that MWCNTs can adsorb ^{243}Am(III) with extraordinarily high efficiency by forming very stable complexes. Chemisorption or chemicomplexation is the main mechanism of ^{243}Am(III) sorption on the surface of MWCNTs. MWCNTs can be a promising candidate for the preconcentration and solidification of ^{243}Am(III) or its analogue lanthanides and actinides from large volumes of aqueous solution, as required for remediation purposes, and perhaps also as a sorbent for the removal of heavy metal ions from the industry wastewater.

Introduction

Carbon nonotubes are a novel and interesting carbon material first found in 1991 by S. Iijima (*1, 2*). Carbon nanotubes include single-wall carbon nanotubes (SWCNTs) and multiwall carbon nanotubes (MWCNTs) depending on its amount of layers. Carbon nanotubes have attracted great attention since their discovery, because of their unique hollow nanosize tubes and their many outstanding and remarkable electronic, mechanical, and chemical properties (*3–10*). With the great progress in the methods of preparing carbon nanotubes, large efforts have been devoted to their fields of application, such as hydrogen storage, quantum nanowires, catalyst supports, chemical sensors, and so forth. With regard to the numerous possibilities of various technical applications, it is not surprising that their use for environmental purposes has also been considered. The large BET technique surfaces of the colloidal carbon nanotubes lying in a range of 100∼200 m^2/g suggest their use as sorbent for pollutants for environmental remediation purposes. Carbon nanotubes are reported to represent very effective sorbents for organic pollutants even at trace concentrations (*11–13*). Liu et al. (*8*) studied the sorption of Cu vapor on carbon nanotubes and found that carbon nanotubes can adsorb copper vapor with extra-

ordinarily high efficiency. Sorption of Cd^{2+} and Pb^{2+} to multiwall carbon nanotubes (MWCNTs) was investigated under aerobic conditions and the results indicate that MWCNTs have large sorption capability for metal ions (*14, 15*).

^{243}Am(III) contributes significantly to the radiotoxicity of nuclear waste and may be released into the environment during waste storage, processing, or disposal. The chemical behavior of radioamericium is very similar to lanthanides and actinides, and the understanding of radioamericium sorption is essential and necessary to know the other actinides' behavior in the environment.

To take full advantage of the unique properties of carbon nanotubes, it is necessary to attach them to other molecules or surfaces for fabricating composites. Functionalization of modification of carbon nanotubes has attracted increasing attention over the past years. To achieve this, it is essential to be able to functionalize the carbon nanotubes with chemical groups (*16*). Carboxylate groups have been introduced onto the surface of carbon nanotubes by reaction with strong oxidizing agents such as HNO$_3$ (*17*).

All of the facts mentioned above reveal that carbon nanotubes may have great potential use as an effective solid-phase extraction adsorbent for some metal ions, especially in high-level radioactive solutions. However, to the best of our knowledge, so far, there have been no reports on this topic in nuclear waste management. In the present paper, the applicability of carbon nanotubes as packing adsorbents for solid-phase extraction was investigated.

The aim of the present study is to examine the use of uncapped multiwall carbon nanotubes (MWCNTs) as adsorbents for radionuclide ^{243}Am(III). Effects of pH, ^{243}Am(III) concentration, and MWCNTs concentration on the sorption of ^{243}Am(III) to MWCNTs were also studied under aerobic conditions. The kinetic desorption of ^{243}Am(III) from MWCNTs was also measured by using chelating resin, which forms stronger complexes with ^{243}Am(III) than MWCNTs. Expermental results demonstrate that MWCNTs can adsorb radionuclide ^{243}Am(III) with extraordinarily high efficiency and be used as a promising sorbent in nuclear waste management.

Materials and Methods

Materials. MWCNTs were prepared by using chemical vapor deposition (CVD) of acetylene in hydrogen flow at 760 °C using Ni–Fe nanoparticles as catalysts (Fe(NO$_3$)$_2$ and Ni-(NO$_3$)$_2$ were treated by sol–gel process and calcinations to get FeO and NiO and then deoxidized by H$_2$ to get Fe and Ni) (*18*). The as-grown MWCNTs were added into the solution of 3 M HNO$_3$ to remove the hemispherical caps on the nanotubes (*17*). The mixture of 2 g MWCNTs and 400 mL 3 M nitric acid was ultrasonically stirred for 24 h. The suspension was filtrated and then rinsed with deionized water until the pH of the suspension reached about 6 and then was dried at 80 °C. Thus, prepared MWCNTs were calcined at 450 °C for 24 h to remove the amorphous carbon. The catalysts Ni and Fe in the treated MWCNTs were measured by ICP-MS and the results show that Ni and Fe are less than 0.01% and 0.03%, respectively.

The purified chelating cation exchanger (chelating resin, 3M Empore, Switzerland) was received from Karlsruhe Research Center of Germany as a gift. Purification of the cation exchanger and conversion into a mixed H$^+$/Na$^+$ form was made by first rinsing with 1 mol/L HNO$_3$, washing with 0.5 mol/L NaCl till the pH of the solution was near neutral, and finally percolating with Milli-Q water through the resin

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to remove excess NaCl (19). The purified chelating resin was dried at 45 °C.

The [243]Am(III) concentration was analyzed by liquid scintillation counting using a Packard 3100 TR/AB Liquid Scintillation analyzer (PerkinElmer). The scintillation cocktail was ULTIMA GOLD AB (Packard).

Methods. All solutions were prepared using Milli-Q water, and all experiments were conducted in polyethylene tubes at $T = 20 \pm 2$ °C in the presence of 0.1 M NaClO$_4$. The sorption behavior of [243]Am(III) on MWCNTs was investigated by using the batch technique and the ultracentrifugation method for the separation of liquid with solid phase for the varying [243]-Am(III) concentrations ($10^{-8} \sim 10^{-5}$ mol/L).

HClO$_4$ or NaOH was added to achieve the desired pH of the aqueous solutions. The test tubes were shaken for 4 days so as to get the equilibration states. The initial and final pH of the solutions were 7.0 ± 0.1 and 6.5 ± 0.2, respectively. The final pH of the suspension was a little lower than the initial one.

Kinetic desorption experiments of [243]Am(III) from MWCNTs were investigated after 30 days contact time of [243]Am(III) with MWCNTs (pH at 7.0 ± 0.1, in 0.1 M NaClO$_4$). A purified filter membrane coated with a resin containing iminodiacetic acid groups (Chelating Extraction Disk, 3M Empore) (19) was added to the solution after previous equilibration with the electrolyte at the given pH. 0.01 M HClO$_4$ or NaOH was added during the experiments to maintain the pH values. The concentration of [243]Am(III) on MWCNTs in the suspension was measured after different contact time with chelating resin.

Results and Discussion

Characterization of MWCNTs. Using the N$_2$–BET method, the specific surface area of the treated MWCNTs was 197 m^2/g. The main pore inner diameter of the treated MWCNTs is 3.6 nm (see Supporting Information). Li et al. (14, 15) measured the surface area of MWCNTs and found that the oxidized MWCNTs with HNO$_3$ have a larger specific surface area than that of untreated MWCNTs. The amorphous carbon, carbon nanoparticles introduced by the CVD preparation process, was removed during the treatment using HNO$_3$. Oxidation of carbon surface can offer not only more surface structure, but also a larger number of oxygen-containing functional groups, which increase the ion-exchange capability of carbon materials (20). The oxidization of MWCNTs with HNO$_3$ can offer a more hydrophilic surface structure and introduce adsorption oxygen-containing functional groups to the surface of nanotubes (16, 17, 20). The FT-IR studies of acid-treated MWCNTs indicated that this acid treatment generated functional groups on the MWCNTs: hydroxyl groups (3432 cm^{-1}), carboxyl groups (1729 cm^{-1}), and carbonyl groups (1588 cm^{-1}) (see Supporting Information). These functional groups are hydrophilic and MWCNTs are dispersed more easily in water.

The results of transmission electron microscopy images (TEM) reveal that the MWCNTs are about 1–10 μm long and 10–30 nm outer diameter (Figure 1).

The potentiometric titration of a MWCNTs suspension in 0.1 M NaNO$_3$ aqueous solutions with H$^+$ or OH$^-$ was performed by using a glass electrode for pH determination (21). The titrations were done under high pure N$_2$ at 25 °C. The surface charge was calculated from

$$\sigma_0 = F(\Gamma_{H^+} - \Gamma_{OH^-}) = F(C_A - C_B + [OH^-] - [H^+])/A \quad (1)$$

where F is the Faraday constant. Γ_{H^+} and Γ_{OH^-} are the excess surface concentrations of protons and hydroxide ions; their difference was calculated from the volumes and concentrations of titrants (acid, base) and the total area of MWCNTs in the experiments, where A is the total surface area of the
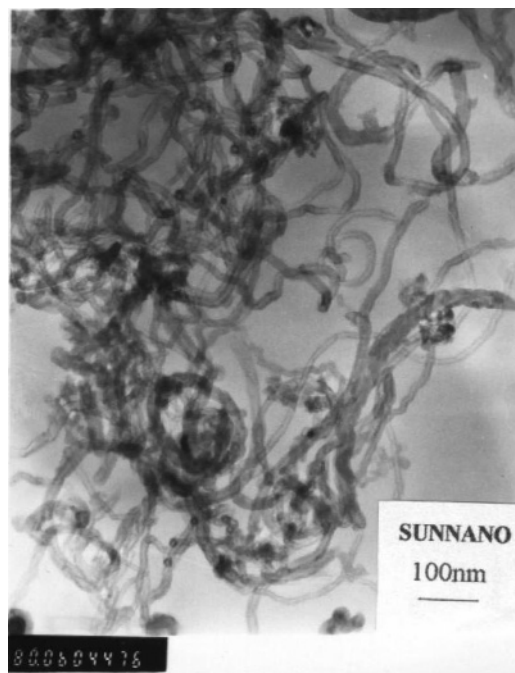

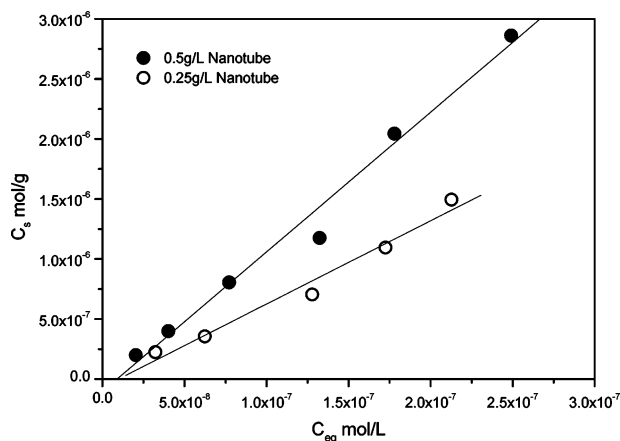
FIGURE 1. TEM images of the multiwall carbon nanotubes.

FIGURE 2. Sorption isotherms of [243]Am(III) to MWCNTs in 0.1 M NaClO$_4$. The contact time was 4 days. After the contact time, the MWCNTs solid phase was separated from the aqueous by centrifugation for 40 min at 18 000 rpm.

suspension (m^2/g), C_A and C_B are concentrations of acid or base after addition, and σ_0 has the unit Coulombs per square meter (C/m^2). The positive surface charge densities on the MWCNTs surface were found at pH < 5.5. (The information of surface charge density (σ_0) as a function of pH can be found in the Supporting Information.) Li et al. (14) had even measured the point of zero charge (pH$_{zpc}$) of the same method that produced MWCNTs and found it to be about 5. The result of our work is quite similar to that measured by Li et al. (14).

Sorption Isotherms. The isotherms of [243]Am(III) sorption onto MWCNTs are shown in Figure 2 (batch experiments, initial pH 7.0 ± 0.1, final pH (after equilibration) 6.5 ± 0.2, in 0.1 M NaClO$_4$, 0.26 and 0.5 g nanotube/L solution, respectively) after a contact time of 4 days. [243]Am(III) substitutes for H$^+$ of functional groups on the oxided MWCNTs. The H$^+$ is released from the MWCNTs into the solution and thus the pH values decrease after equilibration. From the kinetic study, 5–7 min is enough to get equilibration. From Figure 2, it is obvious that the sorption isotherms are linear. The distribution coefficient, K_d, is calculated from
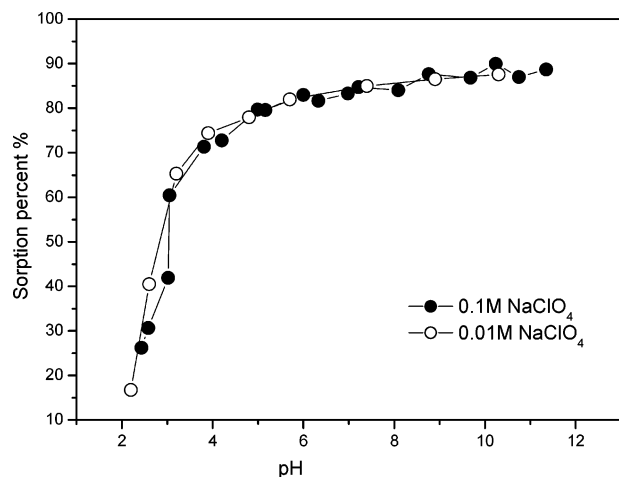
FIGURE 3. Effect of pH on the sorption of [243]Am(III) to MWCNTs. The contact time was 4 days. The initial [243]Am(III) concentration was 7.4 × 10^{−7}mol/L, MWCNTs concentration was 0.5 g/L.

$K_d = (C_0 − C_{eq})/C_{eq} \cdot v/m$, where C_0 and C_{eq} are the initial and equilibrium concentration of [243]Am(III) in the solution (mol/L) and m/v is the MWCNTs concentration in the solution (g/mL). The K_d values are $(1.04 ± 0.11) × 10^4$ mL/g (0.5 g nanotube/L) and $(1.21 ± 0.13) × 10^4$ mL/g (0.26 g nanotube/L), respectively. The ideal linear sorption isotherm demonstrates that the sorption of [243]Am(III) to MWCNTs is far from saturation although the concentration of MWCNTs is quite low and the initial concentration of [243]Am(III) is quite high (maximum to $3 × 10^{−6}$ mol/L). From the sorption isotherm, we can calculate that the sorption is still unsaturated when 1 g of nanotubes adsorbs at least 0.04 g [243]Am(III) under our experimental conditions. The removal percentage of [243]Am(III) from solution to MWCNTs is more than 85% although the concentration of MWCNTs is only 0.26 g/L. The results indicate that MWCNTs have a very large sorption capacity for radionuclide [243]Am(III).

The functional groups at the acid-treated carbon nanotubes surface can sorb [243]Am(III) via "chemisorption" or chemicomplexation (22−25). The strong sorption of [243]Am(III) to MWCNTs indicates that chemisorption or chemicomplexation is formed at the surface of MWCNTs. The hypothesis will be tested in the following part of kinetic desorption measurements.

Sorption of pH Dependence. The pH dependence of [243]Am(III) sorption by MWCNTs ranging from 2 to 12 at two different ionic strengths (0.1 and 0.01 M NaClO₄) is shown in Figure 3. In the low pH range, the sorption of [243]Am(III) shows a strong clear pH dependency suggesting the interaction with surface sites such as carboxylate groups being progressively deprotonated with increasing pH. About 80% [243]Am(III) is sorbed by MWCNTs at pH = 5 and then increases very weakly to $(88 ± 2)$% at pH ≈ 10. Sorption of the cationic species is explained by the generation of carbonyl and carboxylate groups at the MWCNTs surface because of oxidation with nitric acid. Chemisorption is assumed to account for the observed strong [243]Am(III) sorption onto MWCNTs in our experiments rather than physical attachment or electrostatic ion exchange reaction with carboxylate groups at the MWCNTs surface.

The weakly dependent sorption of [243]Am(III) to MWCNTs on ionic strength and strongly dependent sorption on pH values indicate that the sorption mechanism of [243]Am(III) is surface complexation (26). Strong chemicomplexation takes into account the sorption of [243]Am(III) on the surface of MWCNTs. The chemicomplexation is strong, while physical sorption or electrostatic ion exchange interaction of [243]Am-(III) with the functional groups at the MWCNTs surface is
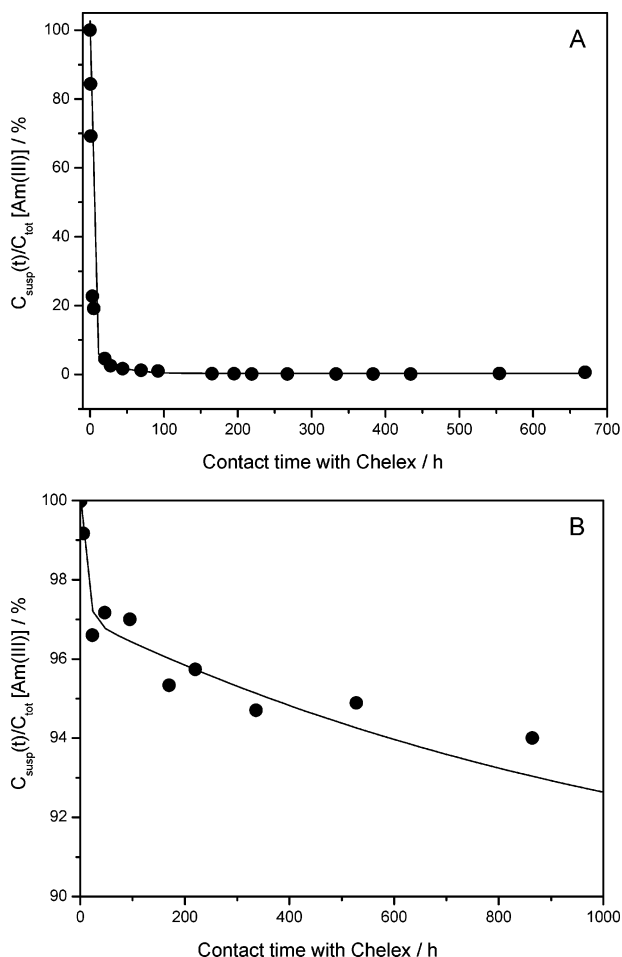

FIGURE 4. Fractions of [243]Am(III) species in MWCNTs suspension as a function of the contact time with a chelating resin in 0.1 M NaClO₄. The concentration of [243]Am(III) is 7.4 × 10^{−7} mol/L and that of MWCNTs is 0.5 g/L. (A) Free [243]Am(III) solution, pH 5.0 ± 0.2; (B) presence of MWCNTs, pH 7.0 ± 0.1.

weakly sorbed and the sorbed [243]Am(III) at the MWCNTs surface can be easily desorbed from the solid phase to the liquid phase when the experimental conditions change, such as the pH decreases, the ionic strength increases, or stronger complexes are formed in the solution or at other solid phases. To test whether the sorption mechanism of [243]Am(III) on MWCNTs surface is chemicomplexation or chemisorption or not, kinetic desorption experiments by adding chelating resin is applied in our works, and the results are discussed in the following part.

Kinetic Desorption Measurements. Fast reaction was found for the sorption/complexation of [243]Am(III) to the resin in the absence of MWCNTs (Figure 4A). More than 99% of [243]Am(III) forms strong complexation with the chelating resin; the results indicate that chelating resin forms stronger complexation with [243]Am(III) than MWCNTs with [243]Am(III), because only about $(88 ± 2)$% [243]Am(III) is sorbed to MWCNTs in the absence of the chelating resin. In the presence of MWCNTs, the initial [243]Am(III) concentration first drops rapidly to ≈96% of the initial concentration and then decreases very slowly (Figure 4B). The rapid decrease in the beginning is related to the free [243]Am(III) not complexed to MWCNTs in solution. The slow desorption kinetic of [243]Am-(III) is attributed to the very slow desorption kinetics of [243]Am(III) from the MWCNTs. Even after more than 2 months of contact time with the chelating resin, about 90% of [243]Am(III) still remains bound to MWCNTs. The experimental results suggest that [243]Am(III) forms kinetically stabilized

TABLE 1. Kinetic Parameters Obtained for Desorption Experiments by Fitting Experimental Data to the Kinetic Eq 4

system	C_{final}/C_{tot} (%)	τ_1 (h)	A_1 (%)	τ_2 (h)	A_2 (%)
Am−Chelex	0.3 ± 0.8	27.6 ± 7.3	8.1 ± 0.4	2.0 ± 0.3	94.2 ± 0.2
Am−MWCNTs−Chelex	89.4 ± 0.4	10.3 ± 1.7	3.2 ± 0.1	1166 ± 700	7.7 ± 0.8

chemicomplexation with MWCNTs and does not desorb from MWCNTs. This finding clearly proves the existence of strong chemical binding of ^{243}Am(III) to the nanotubes. Chemisorption or chemicomplexation of ^{243}Am(III) at the MWCNTs surface is formed rather than physical sorption or ion exchange.

The sorption/complexation reaction of ^{243}Am(III) with the chelating resin in the absence of MWCNTs according to

$$Am^{3+} + Na/H - chelax \Longrightarrow$$
$$Am - chelax + 3Na^+/H^+ \quad (2)$$
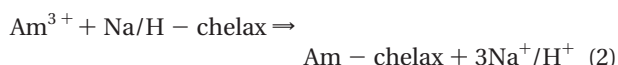
is rather fast. The desorption reaction of ^{243}Am(III) from MWCNTs is observed in the experiment.

$$Am - MWCNTs \xrightarrow{k_1} Am^{3+} + MWCNTs + Na/H -$$
$$Chelex \xrightarrow{k_2} Am - Chelex + 3Na^+/H^+ \quad (3)$$
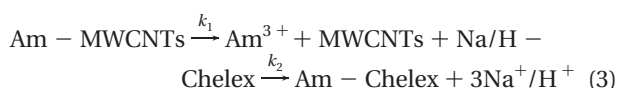
After the chelating resin is added to the MWCNTs suspension, eq 3 is the reaction of ^{243}Am(III) between the chelating resin and MWCNTs. In eq 3, k_2 is rather fast, while k_1 is very slow, compared to the reaction of free ^{243}Am^{3+} in solution to the chelating resin.

To quantify the differences in ^{243}Am(III) desorption behavior, the desorption rate of ^{243}Am(III) from MWCNTs is described by a pseudo-first-order kinetics (19, 27). At least two different ^{243}Am(III) complexation species, showing "fast" and "slow" desorption kinetics, are necessary to fit the experimental results:

$$\frac{C_{susp}(t)}{C_{tot}} = \frac{C_{final}}{C_{tot}} + A_1 \cdot \exp\left(\frac{-t}{\tau_1}\right) + A_2 \cdot \exp\left(\frac{-t}{\tau_2}\right) \quad (4)$$

where $C_{susp}(t)$ is the concentration of ^{243}Am(III) in the MWCNTs suspension at time t (h); C_{final} is the final concentration of ^{243}Am(III) in MWCNTs suspension after equilibration with the chelating resin; C_{tot} is the initial ^{243}Am(III) concentration in the system ($t = 0$); A_1 is the fraction of ^{243}-Am(III) MWCNTs desorbing with a time constant τ_1 (%); A_2 is the fraction of ^{243}Am(III) MWCNTs desorbing with a time constant τ_2 (%); and τ_1 and τ_2 are desorption time constants (h). The kinetic parameters obtained by fitting the experimental data to the kinetic eq 4 are listed in Table 1. Within the analytical uncertainty, almost 100% ^{243}Am(III) was sorbed to the chelating resin by forming strong complexation. In the system Am−MWCNTs−Chelex, after 2 months of contact time with the chelating resin, about 89.4% ^{243}Am(III) still remains on the MWCNTs surface. The fraction $A_2 = (7.7 \pm 0.7)\%$ with a long time constant $\tau_2 = (1166 \pm 700)$h is larger than $A_1 = (3.2 \pm 0.1)\%$ with a short time constant $\tau_1 = (10.3 \pm 1.7)$h. For the system Am−Chelex, the fraction $A_2 = (94.2 \pm 0.2)\%$ with a short time constant $\tau_2 = (2.0 \pm 0.3)$h is larger than $A_1 = (8.1 \pm 0.4)\%$ with a long time constant $\tau_1 = (27.6 \pm 7.3)$h. The experimental results suggest that ^{243}Am(III) forms kinetically stabilized complexes with MWCNTs and does not rapidly desorb into the solution. This finding clearly proves the existence of strong chemical binding of ^{243}Am(III) to the nanotubes.

About 85% ^{243}Am(III) is sorbed by MWCNTs after 4 days of contact time in batch experiments, and over 95% ^{243}Am-(III) is sorbed to MWCNTs after 1 month of contact time. Hummer et al. (28) studied the adsorption of H$_2$O by uncapped single-walled carbon nanotubes and found that water molecules can enter the central channels of the nanotubes by forming hydrogen-bonded chains. The removal percentage of ^{243}Am(III) by MWCNTs increases from 85% (4 days contact time) to 95% (30 days contact time); the slow increase may be explained by that ^{243}Am(III) enters the central channels and forms strong chemisorption in the central channels of the nanotubes. The exchange rate between H$_2$O in the central channels and ^{243}Am(III) is quite slow and thus causes the increase of ^{243}Am(III) removal percentage with increasing contact time. The very slow desorption kinetics of ^{243}Am(III) bound to MWCNTs could be an indication that the metal ions might as well be captured inside the nanotube. The finding needs further study to get more exact explanation and information. TEM or EXAFS measurements may be good methods to get this information.

In conclusion, carbon nanotubes may be a promising candidate in nuclear waste management.

Supporting Information Available

Figure of N$_2$−BET measurement; figure of surface charge density pH values; figure of FT-IR. This material is available free of charge via the Internet at http://pubs.acs.org.

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