Removal and sequestration of iodide from alkaline solutions using silver-doped carbon nanotubes

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The long-lived radioactive isotope iodine-129 that is associated with nuclear fuel cycle processes is becoming an increasing concern to human health and the environment due to difficulties in separating it from other nuclear wastes and the projected long-term risks. We have investigated the reaction of iodide in alkaline solutions with silver doped carbon nanotubes (Ag-CNTs) as a means of addressing concerns associated with this radioisotope. An in situ CNT doping technique, where the silver is added to the CNT during the chemical vapor deposition process, and a chemical filling process, where silver is added to the CNTs by solution contact followed by reduction under heat, were used to synthesize the Ag-CNTs. The iodide adsorption behavior of the Ag-CNTs appeared to be largely controlled by the silver content of the CNTs. In situ doping techniques resulted in silver contents of <0.0025 percent by weight, whereas chemical filling resulted in silver contents of almost 20 percent by weight. These chemically filled Ag-CNTs exhibited a sorption capacity of 458 ± 73 mg iodide/g CNT that was an order of magnitude greater than commercially available silver impregnated activated carbon tested in this study. Leaching of iodine from the reacted Ag-CNTs was below the method detection limit when a molar excess of silver was present and is consistent with an iodide release that is controlled by the sparingly soluble silver iodide solid. The properties of high sorption capacity and small iodine leaching of these Ag-CNTs make this material a potentially useful sorbent for application in nuclear waste separation processes and waste disposal systems.

Introduction

The element iodine occurs as three isotopes: ^{127}I (stable), ^{129}I (half-life 15.7×10^6 years), and ^{131}I (half-life 8 days). In the environment, iodine occurs primarily as the iodide (I^-) or iodate (IO_3^-) anion depending on pH and redox conditions.[1] While ^{129}I is produced naturally in the upper atmosphere by cosmic ray interactions with xenon and spontaneous fission of heavy elements like ^{238}U in the geosphere, measurements of isotopic ratios of $^{129}I/^{127}I$ clearly show that anthropogenic inputs from nuclear testing and the nuclear fuel cycle represent a significant input of the long-lived ^{129}I isotope into the biosphere ($^{129}I/^{127}I$ ratio: pre-nuclear[2] 10^{-12} and 10^{-10} and post nuclear[3] 10^{-9} and 10^{-8}). As further evidence of this trend, it has been recently reported that concentrations of ^{129}I in northern European precipitation and runoff are increasing [4]

Given the input of ^{129}I into the environment, its high mobility as an anionic specie, and its bio-uptake, ^{129}I is often one of the major long-term risk drivers for activities associated with the nuclear fuel cycle. For example, at many land-based nuclear waste disposal facilities at United States Department of Energy (DOE) sites like the Savannah River Site located on the coastal plain of western South Carolina, ^{129}I activity and its projected risk to human health and the environment is one of primary drivers for acceptance of low-activity solid radioactive waste.[5] With the importance of ^{129}I as a risk driver, efficient removal and sequestration technologies for ^{129}I are needed. "Getter materials," the engineering term applied to materials capable of sequestering specific contaminants, can provide a

solution to ^{129}I contamination problems. Ideally, a getter material should be capable of the sorption of large amounts of the target contaminant, be stable during treatment processes (e.g., must not produce or release other unwanted materials), and be suitable for long-term waste disposal (e.g., low leaching rates).

Previous work by the authors has shown that silver impregnated activated carbon (SIAC) and silver chloride impregnated activated carbon (SIAC-Cl) are effective materials for removal and sequestration of iodide from water through the formation of a silver iodide ($AgI_{(s)}$) surface precipitate (i.e., $Ag^+ + I^- \leftrightarrow AgI_{(s)}$ or $AgCl + I^- \leftrightarrow AgI_{(s)} + Cl^-$, AgI $K_{sp}=10^{-17}$).[6,7] Given the insoluble nature of $AgI_{(s)}$, leaching of iodide from the SIAC and SIAC-Cl was negligible. The modification of Ag(s) to AgCl(s) significantly reduced Ag release from the sorbent material without affecting the iodide removal characteristics of this material. Therefore, spent SIAC represents an improved secondary waste form for ^{129}I in land burial facilities. Even if the activated carbon backbone structure is destroyed with time, the release of ^{129}I to the subsurface is minimized by solubility control of $AgI_{(s)}$.

Since the discovery of carbon nanotubes (CNTs) in 1991,[8] they been produced and studied for their novel physical, chemical, and electronic properties. For example, applications of CNTs investigated include: chemical and biological sensors, transistors, hydrogen storage, and heterogeneous catalysts. CNTs have been evaluated for use in environmental remediation with the adsorption of ionic dyes[9] and phenols.[10] Functionalization of CNTs to include carboxyl moieties have

been evaluated as solid phase (micro) extractors for a range of heavy metals and this work has been reviewed by Pyrzynska.[11] These reviewed studies demonstrated high sorption capacities for heavy metals (Cu, Pb, and Zn) in the range from 40 to 80 mg metal per g CNT. Furthermore, the catalytic activity of CNTs can be modified through doping with B, N, and noble/transition metals. This topic has recently been reviewed and the summary conclusion was that this subject area is still not well understood.[12] While production of CNTs with or as a stable substrate has been slow in developing, membranes comprised wholly of CNTs and CNTs on porous inorganic substrates have recently been produced and evaluated for desalination and gas separation applications. The production of these membranes is often as simple as filtering suspensions of CNTs to create thin sheet membranes commonly referred to as "buckypaper."[13]

Given the recent advances in CNT application (e.g., substrate development and lowered production costs) and inherent reactivity (e.g., high surface area, large binding capacity, and tunable catalytic activity), we have investigated the synthesis of silver-doped carbon nanotubes (Ag-CNTs) and their application for aqueous separation and sequestration of radioactive iodine in nuclear fuel cycle processes and wastes. For the synthesis of Ag-CNTs two basic routes were investigated: in situ doping, where the silver was incorporated into the CNT structure during CNT formation; and post CNT production doping, where: in situ doped CNTs were reacted with a silver solution; separated from the solution; and silver associated with the CNTs reduced at elevated temperature under a gas mixture of H_2/Ar. As a baseline, the iodide sorption characteristics of both types of Ag-CNTs were compared to undoped CNTs and the analogous macro-scale silver carbon system (i.e., silver impregnated activated carbon).

Materials and Methods

Activated Carbon. A bituminous coal based silver impregnated activated carbon (SIAC) with a silver content of 1.05 percent by weight (TOG-NDS-20x50, Calgon Corporation) was used in this study. The characterization of this material and reactivity with iodide has been reported elsewhere.[6]

Carbon Nanotubes. A chemical vapor deposition (CVD) method was used to produce both doped and undoped CNTs using the method described by Andrews.[14] The CVD instrumental setup is illustrated in Figure 1. A quartz reaction tube is inside two tube furnaces placed in series. The first furnace serves as a preheater, volatilizing the 1 mL/h continuously pumped liquid reactants at 250 °C. The vapors are then swept further along the quartz tube into the second furnace by a mixture of 75 standard cubic centimeters per minute (sccm) hydrogen and 675 sccm argon gases. The nanotubes are produced at 750 °C, and then collected at the exit end of the quartz tube on a rectangular quartz slide approximately 1.0 by 3 inches in size.

For both types of materials, Ag-doped and undoped CNTs, the liquid reactants were a mixture of an aromatic carbon source (e.g., xylene) and ferrocene, an iron containing organometallic catalyst for nanotube growth. The CVD process is run for an hour to generate enough of the CNTs for further evaluation and the CNT product was removed from the

reaction tube after cooling. To produce samples of Ag-CNTs, xylene, ferrocene, and silver phthalocyanine were used as feed components. In this process, the iron in the ferrocene serves as a catalytic nucleation site for the growth of the CNTs. Other metals are incorporated in situ into the CNTs by adding an organometallic precursor into the xylene/ferrocene feed. In addition to CNTs doped with silver, we have been successful in doping other metals (e.g., titanium, iron, vanadium, platinum, palladium, and tungsten) into CNTs by this method.
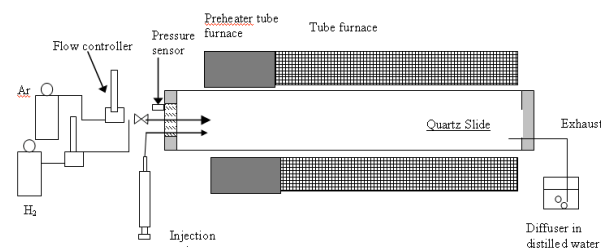

Fig. 1 Schematic of the chemical vapor deposition setup for synthesis of carbon nanotubes.

CNT Purification. To remove residual iron metal catalyst from the CNTs, the purification procedure described by Huang[15] was performed. In this procedure, approximately 200 mg dry CNTs were added to 40 mL of 2.6 M nitric acid and boiled for two days. The solution was centrifuged for 30 minutes at 2000 rpm to separate the CNTs from the acid and the solids rinsed with 2.6 M nitric acid two additional times. The CNTs were then rinsed with deionized distilled water (DDI H_2O) several times, centrifuging, and discarding the water between each wash to remove the residual nitric acid. After drying under vacuum in a nitrogen gas, the CNTs were ready for use.

Post CVD Doping of Carbon Nanotubes. Ex-situ doped CNTs were also synthesized by a chemical filling method described by Chu.[16] In this synthesis, Ag-CNTs produced by CVD and acid purified as described above were used as starting materials for the chemical filling. The doping process consisted of contacting the CNTs with aqueous metal solutions followed by drying under reducing conditions. About 170 mg Ag-CNTs in 350 mL of ~70% nitric acid were acid purified as described in the previous paragraph. Approximately ~40 mg of Ag-CNTs were contacted with solutions of 25% (w/w) silver nitrate in 50-mL beakers. The beakers of aqueous metal solutions and uncapped CNTs were placed on stir plates at room temperature and mixed at 550 rpm for 24 hours. The solutions containing the CNTs were filtered dropwise onto glass microfiber filters and the recovered solids placed in a ceramic reaction boat. The reacted CNTs were dried in a tube furnace for 10 hours at 150 °C under 97.2% argon gas / 2.8% hydrogen gas to reduce the silver. After cooling, the post CVD doped CNTs were ground in a mortar and pestle and heated again under the same conditions, except at a temperature of 240 °C.

Adsorption and Leaching Experiments. The constant-dose (i.e., constant sorbent dose) bottle-point sorption edge experiments were performed using completely mixed batch reactors as described in detail elsewhere.[6] A wide range of initial iodide concentrations (from 10^{-7} to 10^{-2} M) was

examined using stable (^{127}I) iodide made from potassium iodide in a pH-8, 50 mM each mono and dibasic phosphate, buffer. In these sorption experiments, one mL of the pH 8 iodide solution was contacted with 10 mg of CNTs in a 1.5-mL polypropylene centrifuge tube. Samples were contacted at room temperature on a shaker table for a period of one week. After contact, 0.74 mL of the liquid phase was diluted with 6.75 mL of pH 8 phosphate buffer and 0.15 mL of 5 M sodium nitrate (ionic strength adjuster). This provided an order of magnitude dilution and sufficient solution for ion selective electrode measurement of iodide. Iodide concentrations in aqueous solutions were measured using an ion selective electrode as described elsewhere.[6]

Leaching experiments were conducted at basic (pH 9.0) conditions with a mono and dibasic phosphate buffer solution containing no measurable amounts of iodide. Selected iodide-reacted samples (activated carbons and CNTs) from the sorption experiments were used in subsequent batch leaching experiments (at the same solids dose as the iodine contact) to examine the stability of iodide after sorption. A total of three sequential one-week leaching cycles were performed with the same contact and iodine analyses protocols described in the previous paragraph.

Characterization of Carbon Nanotubes. Characterization of the as-produced and purified CNTs was performed via scanning electron microscopy (SEM) (Hitachi 3200N), transmission electron microscopy (TEM) (JEOL JEM-2010) and micro-Raman spectroscopy (Jobin Yvon, LabRam HR, 532nm ex., 10 s, 4 accum.). In order to obtain a representative spectrum of the samples, Raman spectra were collected on different areas of the sample and averaged. Additionally, elemental mapping of the metal doping and reacted Ag-CNTs was conducted with an energy-dispersive x-ray (EDX) attachment on the TEM.

Brunauer-Emmet-Teller (BET) nitrogen adsorption analyses were run on a Micromeritics ASAP model 2010 (Accelerated Surface Area and Pore Analyzer). The samples were degassed at 300 °C for 6 hours and backfilled with N_2 (99.995%) to remove water and/or other absorbed contaminants from the sample prior to analysis. Next, a 19 point Nitrogen BET surface area analysis was conducted to measure the adsorption isotherms at liquid nitrogen temperatures. The first relative pressure point was 0.01 (P/P_o) and the last relative pressure point was 0.30.

In order to provide a non destructive analysis for silver, Cf-252 neutron-activation-analysis (NAA) was utilized at the Savannah River National Laboratory. The SRNL NAA facility holds six doubly encapsulated Cf-252 pods in a zircalloy source holder near the bottom of a de-ionized light water, 4-meter deep, 1.2-meter diameter tank. The inventory, approximately 55 mg of Cf-252, provided a flux of ~4×10^8 neutrons cm^{-2} s^{-1}. Silver content of Ag-CNTs was analyzed by activating Ag-109 to Ag-110 with a 1 minute exposure to the neutron flux. The Ag-110 decayed with a 24.6 second half-life, emitting a 657.8 keV gamma-ray, which was measured with a sodium iodide well gamma detector.

Results and Discussion

Iodine sorption to activated carbons (ACs) and carbon nanotubes (CNTs), with and without silver, was investigated in this study. The two activated carbons (i.e., undoped AC and silver impregnated activated carbon (SAIC)) were used and these samples have been extensively characterized and data published previously.[6] Three types of multiwalled CNTs were evaluated in this study: CNTs without any Ag (i.e., undoped CNTs); CNTs where the Ag was incorporated into the CNT structure during the chemical vapor deposition (CVD) process (i.e., in situ doped Ag-CNTs); and CNTs where Ag was added to CNTs made by CVD by solution addition and subsequent reduction (i.e., chemically filled Ag-CNTs). Characterization of the CNT samples as well as the results of iodide sorption studies to both the ACs and CNTs are presented below.

CNT Characterization. The characterization of CNTs produced for this work consisted of microscopy, elemental composition, surface area, and Raman spectroscopy.

Figure 2A, B, C are electron micrographs of CNTs produced by CVD without doping, in situ doping, and post CVD chemical filling, respectively. During the CVD process, CNTs were grown in vertically aligned arrays (Figure 2A) that were dispersed via sonication and acid refluxing during iron catalyst removal. A representative transmission electron microscopy (TEM) image of the in situ doped Ag-CNT, Figure 2B, shows several particles that are endohedral (i.e., constrained within) to the CNT structure and numerous iron inclusions which had been incorporated into the wall of the tubes during their CVD production of the CNT. In the back scatter electron micrograph shown Figure 2C, the chemically filled CNT contains several particles that are endohedral to the particle, but the majority of the particles are the light colored particles that exist on the external surface (i.e., exohedral) of the CNT. This structure is often referred to as a "decorated" CNT. Finally, TEM and EDX analyses of chemically filled CNTs (data not presented) show that only approximately half of the CNTs had been uncapped during the nitric acid reflux.
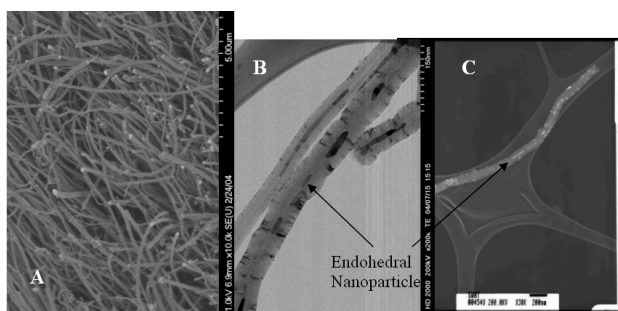

Fig. 2 (A) SEM of vertically aligned CNTs grown by CVD (scale bar 5 μm) (B) TEM of in situ filled Ag-CNT (scale bar 150 nm); (C) back scatter EM of metal nanocluster "decorated" CNT produced by chemical filling (scale bar 200 nm).

Neutron activation analysis (NAA) was performed on the Ag-CNTs. Although EDX analysis confirmed the presence of silver in the in situ doped Ag-CNTs, NNA quantified the silver content to be < 0.0025%. The first batch of chemically filled Ag-CNTs had a silver loading of 19.5 wt % (± 10%), while the second batch only contained 2.99 wt % (± 3.6%). Further work employing less-concentrated solutions for chemical metal

doping could be undertaken to optimize the metal nanoparticle filling process. Nevertheless, the microscopy and NAA results show that chemical filling can be an effective method for supplementing low metal nanoparticle concentrations from in situ doping.

The Raman spectra in the frequency range of 1200-2000 cm^{-1} of Ag-doped CNTs and undoped CNTs are shown in Figures 3 and 4, respectively. Each spectrum is an average of 3-points within the sample. For the Ag-doped CNT spectrum in Fig. 3, the main peak of the Raman-allowed phonon mode of graphitized carbon, E_{2g} or G-band, is observed between 1540-1560 cm^{-1}. This peak is downshifted from what is typically observed for undoped multi-walled carbon nanotubes (MWCNTs) (Fig. 4) or normal graphite[17] at 1580 cm^{-1}, which can be attributed to several factors including temperature, shape of the tube and the reduction reaction. Ando[17] observed a similar temperature dependence of the G-band of arc discharge processed MWNTs. Also, curvature of the graphene sheet due to nanotube formation causes an increased strain in the C-C bond which is observed as a shift in the frequency of the G-band in the Raman spectrum.

BET surface area analysis was used as a measure of surface area of the CNT samples produced by CVD in this work. Results for the CNTs ranged from 43.22 m^2/g for the in situ doped Ag-CNTs, up to 72.14 m^2/g for the single-walled carbon nanotubes (a purchased reference sample). These values correspond well with specific surface areas of multiwalled carbon nanotubes with 40 walls, 50 – 60 m^2/g, as predicted by Peigney.[19] The greater surface area of the single-walled nanotubes was expected, and is due to the smaller size of the tubes. The in situ doped Ag-CNTs were multi-walled, and the surface area of the Ag-CNTs (43.22 m^2/g) is comparable to that of the undoped multi-walled CNTs (54.80 m^2/g). In contrast, the surface area of SIAC was 960 m^2/g.[6] The smaller surface area of the CNTs compared to SIAC is thought to be due to bundling and agglomeration of the CNTs, which likely prevented interaction of the N$_2$ with many of the CNT surfaces, and probably does not represent the available surface area once they are dispersed in solution. Thus, in order to maximize reactivity of the metal-doped carbon nanotubes, physical separation (e.g., sonication) might be advantageous in creating a material with greater surface area and potentially greater reactivity.
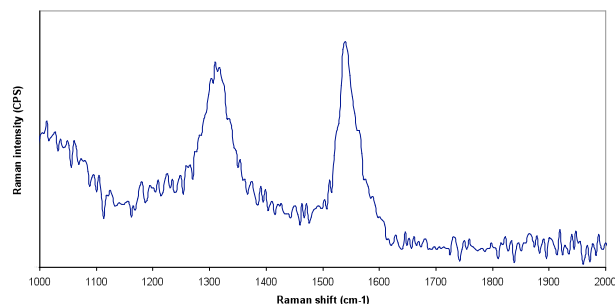

Fig. 3 Raman spectra of Ag-doped MWNTs showing the shift in the G-band around 1540cm^{-1}.

In situ doped Ag-CNTs were used as the solid phase in the first iodide sorption study. The reaction mechanism for the iodide sorption is as follows:
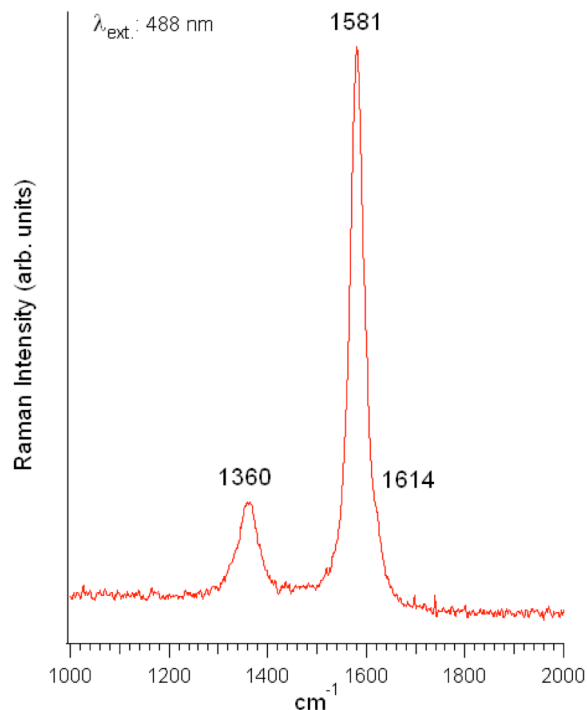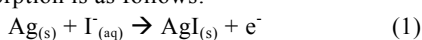
$$Ag_{(s)} + I^-_{(aq)} \rightarrow AgI_{(s)} + e^- \qquad (1)$$

Fig. 4 Raman spectra of undoped MWNTs showing the G-band at 1581cm^{-1}.

For carbon nanotubes which are not doped with silver, the mechanism for iodide sorption is based on physical rather than chemical sorption:

$$CNT_{(s)} + I^-_{(aq)} \rightarrow CNT\text{-}I^- \qquad (2)$$

The in situ doped Ag-CNTs which contained <0.025 wt. % silver did not adsorb detectable amounts of iodide (Figure 5); where the x-axis (Ce) is the dissolved concentration and the y-axis is the sorbed concentration normalized to mass of sorbent. Thus, unlike activated carbon, carbon nanotubes do not provide non-specific physical adsorption as in Equation 2. This is not surprising because although carbon nanotubes have hollow interiors, they do not contain the extensive pore structures characteristic of activated carbon.
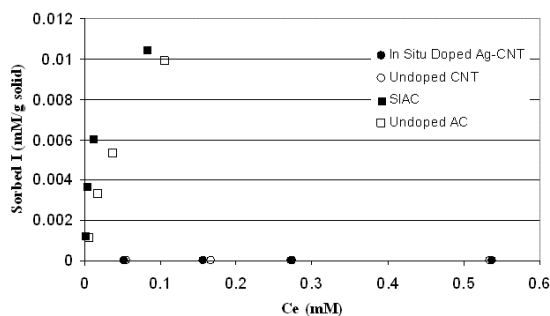

Fig. 5 Iodide sorption edge for undoped CNTs and in situ silver doped CNTs, undoped activated carbon (AC), and silver-impregnated AC.

A test batch contact of iodide solution with post-CVD chemically doped Ag-CNTs (containing 19.5 wt % Ag) showed iodide sorption, which was expected due to precipitation of AgI$_{(s)}$. Two iodide solutions were contacted with the first batch chemically filled Ag-CNTs, one with an iodide concentration below a 1:1 Ag:I ratio (4.5 mM I$^-$), and one

above (36 mM I⁻) (see Fig. 6). A full sorption edge was not performed due to the small amount of material synthesized during the first batch of chemically filled Ag-CNTs.
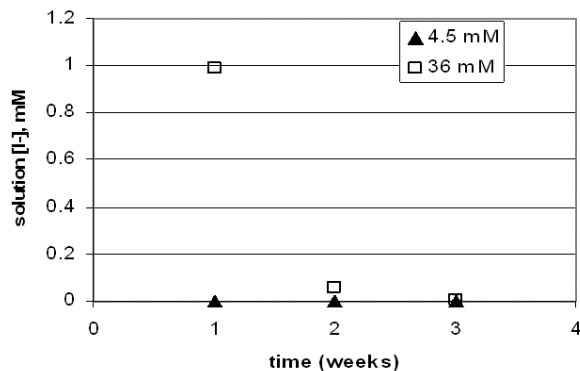

Fig. 6 Iodide leaching from carbon nanotubes (with 19.5% weight silver) initially contacted with 4.5 (excess silver) and 36 (excess iodide) mM iodide solution.

A full sorption edge was performed with the second batch of chemically filled Ag-CNTs, which allows comparison to the iodide sorption behavior of 1.05 wt % silver SIAC. The first seven points of the Ag-CNT iodide sorption edge of Figure 7 illustrate the loading capacity of the Ag-CNTs. The next four points show that the maximum iodide adsorbed was 458 ± 73 mg/g, which is over an order of magnitude more than the iodide adsorbed by 1.05% SIAC at 36 ± 4 mg/g. Stated in another way, the Ag-CNTs exhibited a sorption capacity an order of magnitude greater than that of the SIAC.
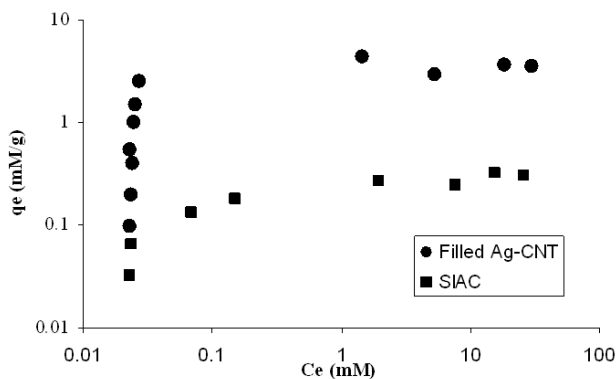

Fig. 7. Iodide sorption edge for chemically filled Ag-CNTs and 1.05% SIAC.

The shapes of sorption curves are also different between the two materials. The Ag-CNTs continually adsorbed iodide via precipitation with silver up until saturation, followed by a relatively steady increase in equilibrium solution iodide concentration. The SIAC, on the other hand, displayed a combination of surface precipitation and non-specific physical adsorption. At an excess of silver, iodide is removed by AgI(s) formation, whereas at an excess of iodide, the additional iodide is removed by the SIAC through non-specific sorption. The physically sorbed iodide in the SIAC is also readily desorbed and is, consequently not an attractive secondary waste form (i.e., waste to be disposed in a land based system).

Considering that iodide concentrations in the contaminated waste streams of interest are at the μg/L level, the large capacity of the Ag-CNTs means that small amounts of nanotubes are required to sequester iodine in nuclear waste leachates for long times while limiting the release of iodine by the solubility control of the AgI solid. As CNTs do not have the hydraulic properties of activated carbon,[9] an approach other than a packed column or cartridge would be necessary to implement their use. One possibility would be to flow iodide-containing waste through a thin filter (e.g., "buckypaper") of Ag-CNTs, which would exhibit much less back pressure than a long column. Like SIAC, chemically filled Ag-CNTs effectively sequestered iodide from solution. The production cost of carbon nanotubes is currently higher than that for activated carbons, but CVD syntheses have been scaled up to commercial levels and, therefore, CNT costs are falling. Further, the higher sorption capacity of the Ag-CNTs will help offset the higher material costs by reduced operation costs resulting from less frequent sorbent change outs and lower secondary waste disposal costs.

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