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Prussian blue caged in spongiform adsorbents using diatomite and carbon nanotubes for elimination of cesium

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Abstract

We developed a spongiform adsorbent that contains Prussian blue, which showed a high capacity for eliminating cesium. An *in situ* synthesizing approach was used to synthesize Prussian blue inside diatomite cavities. Highly dispersed carbon nanotubes (CNTs) were used to form CNT networks that coated the diatomite to seal in the Prussian blue particles. These ternary (CNT/diatomite/Prussian-blue) composites were mixed with polyurethane (PU) prepolymers to produce a quaternary (PU/CNT/diatomite/Prussian-blue), spongiform adsorbent with an *in situ* foaming procedure. Prussian blue was permanently immobilized in the cell walls of the spongiform matrix and preferentially adsorbed cesium with a theoretical capacity of 168 mg/g cesium. Cesium was absorbed primarily by an ion-exchange mechanism, and the absorption was accomplished by self-uptake of radioactive water by the quaternary spongiform adsorbent.

1. Introduction

Thousands of tons of water have been catastrophically contaminated with radioactive cesium-137 after the 9.0 magnitude earthquake, followed by the tsunami on March 11, 2011. Fukusima Daiichi nuclear power stations are equipped with systems constructed with zeolite as the absorbing material, and these are under maximum operation for eliminating radioactive elements from high-level radioactive water [1]. However, currently, there are no systems capable of eliminating radioactive elements from low-level radioactive water. In fact, in March, after the earthquake and tsunami, over 10,000 tons of low-level radioactive water had been dumped from the storage tanks into the ocean to address the more critical task of decontaminating high-level radioactive water [2]. Three major difficulties have been encountered in treating low-level radioactive water. First, the radioactive elements are very low in concentration (compared to co-existing abundant ions, sodium and potassium); thus, the adsorbing materials (adsorbents) must be highly selective for the targeted radioactive species. Second, the volume of low-level radioactive water is extremely large; thus, the treating systems must be able to operate without pumping all the water through the entire treating system. Third, low-level radioactive water is found in distant locations in Japan; thus, treating systems must be portable and easy to operate.

Prussian blue (ferric hexacyanoferrate), one of the first, man-made coordination compounds, widely known as "the blue pigment", has long been considered a potential adsorbent for radioactive cesium-137 [3]. However, due to its intrinsic property of forming a colloid in water, small sized Prussian blue particles (thereby the larger surface areas and the higher adsorbing capacity) can easily contaminate water; thus, practical applications have long been limited to medical and/or pharmaceutical treatments [4, 5]. Note that some Prussian blue analogs, like cobalt ferrocyanide [6, 7] and copper ferrocyanide [8], are highly water-insoluble; can be used directly as adsorbents for radioactive cesium eliminations. However, these analogs are costly compared to Prussian blue. Moreover, the procedures for isolating particles of desirable sizes are typically time-consuming, because impurities and smaller particles must be removed from the suitable particles. This is typically achieved by washing the mixtures with large amounts of water, followed by centrifugation.

For several years, we have been developing caged approaches to overcome the difficulties associated with colloidal dispersion. We have tested organic polymers (like alginate) and porous inorganic particles (like diatomite) as potential caging materials to create high-performance adsorbents [9, 10]. In this study, we demonstrated that the

caging approach can be applied to Prussian blue to create an absorptive structure with high efficiency for eliminating cesium-137 from low level radioactive water.

An *in situ* synthesizing process was used to synthesize Prussian blue within the cavities of diatomite. Highly-dispersed carbon nanotubes (CNTs) were used to form CNT-networks, which coated the surface of the diatomite and sealed in the Prussian blue particles. Prussian blue was finally immobilized in cell walls of polyurethane foam to produce a spongiform adsorbent. The resulting adsorbent showed high selectivity and high capacity for adsorption of radioactive cesium from low-level radioactive water. To the best of our knowledge, this is the first report to describe the packing of Prussian blue into foam (spongiform) for adsorbing cesium.

2. **Materials and methods**

2.1. *Prussian blue synthesized in the cavities of diatomite*

Prussian blue was synthesized within the cavities of diatomite with an *in situ* synthesizing process. Briefly, 750 g diatomite (MW-27, obtained from Eagle-Picher Filtration & Minerals, Inc., U.S.A.; average particle diameter, 13 μm; bulk specific gravity, 0.19 g/cm^3; as recommended by the manufacture) was mixed with an aqueous solution of 1000 mL 960 mM $FeCl_3 \cdot 6H_2O$ and 3000 mL de-ionized water

with a mixer (FM-L, Nippon Coke & Engineering Co., Ltd) for 2 hours. The resultant mixture (slurry) was heated at 90 °C in an oven to evaporate the water; the resulting fine powder (diatomite/FeCl$_3$ composite) was then slowly (approximately 30 minutes) added to an aqueous solution of 1000 mL 720 mM Na$_4$Fe(CN)$_6$ mixed with 3000 mL de-ionized water; the resulting slurry was then dried to fine powders at 90 °C. The standard Prussian blue fine powders were prepared with aqueous 960 mM FeCl$_3$·6H$_2$O and 720 mM Na$_4$Fe(CN)$_6$ solutions as the starting materials under the identical reaction conditions.

2.2. *Prussian blue sealed in with carbon nanotubes*

The diatomite/Prussian-blue fine powder was combined with 3000 mL of 2.0 wt% highly-dispersed CNTs and mixed gently for 10 min. The dispersed CNTs were prepared by dispersing multi-walled CNTs (trade name, Nanocyl-7000, Belgium; average diameter 9.5 nm, average length 1.5 μm and, surface area 250-300 m^2/g, as suggested by the manufacture) with a beads-milling system (Dyno-Mill, Basel, Switzerland) with zwitterionic surfactants as the wetting agent and sulfonated types of surfactants as the dispersants. The resulting slurry was then dried to a fine powder at 90 °C.

2.3. *Fabrication of the spongiform Prussian blue based adsorbent*

The ternary composite fine powders (diatomite with Prussian blue in the cavities sealed in with highly-dispersed CNTs) was mixed with polyurethane prepolymer NB-9000B to produce the spongiform, Prussian blue based adsorbent. NB-9000B is a typical polyurethane prepolymer, derived from poly(oxy C2-4 alkylene) diol and toluene diisocyanate. NB9000B has three isocyanate functionalities, and it is capable of forming spongiform structures when combined with water molecules. Pluronic L-62, a tri-block type of copolymer, was used to strengthen the cell walls of the polyurethane foam (i.e., spongiform structure). The ratio of ternary-composite-powder/NB-9000B/Pluronic-L-62 was optimized at 10/100/1.

2.4. Adsorption experiments

Elemental, inactive cesium (cesium-133) was used to study adsorption behaviors. The quaternary spongiform matrix (polyurethane polymer, CNTs, diatomite, and Prussian blue), Prussian blue based adsorbent (in this paper, denoted as PUP/CNT/DM/PB) was cut into small pieces (approximately 0.1 g, dry weight) and then immersed in 40 mL aqueous cesium nitrate solution. The test tubes were then shaken on a vortex shaker. The amount of cesium that remained in solution was quantified with inductively-coupled plasma, atomic emission spectrometry

(ICP-AES; ICP-AES-9000, Shimadzu). In addition, radioactive cesium-137 was used as the targeted species at low concentrations. The adsorption of each sample was tested in triplicate, and averages were used to evaluate adsorbent capabilities.

3. Results and discussion

3.1. *Caging Prussian blue*

The diatomite used in this study had a cylindrical shape and ultra-high porosity; its maximum capacity for absorbing aqueous $FeCl_3 \cdot 6H_2O$ solution was 2.5 ml solution/g diatomite. This was found to be optimal, irrespective of the $FeCl_3$ concentration. Figure 1A shows typical scanning electron microscope (SEM) images of the pristine diatomite used for capturing iron (III) chloride. Figure 1B shows typical SEM images of Prussian blue. The Prussian blue particles were mostly found in diatomite cavities (very few Prussian blue particles were observed on the diatomite surface). Prussian blue particles had diameters of 10–150 nm, measured with transmission electron microscopy (TEM, data not shown). Prussian blue particles packed in diatomite cavities were analyzed with X - ray diffraction (XRD). Figure 1C shows a typical XRD diffractogram; four main peaks were observed at scattering angles (2θ) of 17.44, 24.78, 35.34, and 39.54. Prussian blue is typically specified as either "soluble" or "insoluble" [11]. This

distinction is related to the presence or absence of an alkaline moiety (denoted as A'; in this study, A' = Na) in the structural formula. Thus, A'FeFe(CN)$_6$ represents the soluble Prussian blue, and Fe$_4$[Fe(CN)$_6$]$_3$ represents the insoluble Prussian blue. The term "insoluble" is applicable only to Prussian blues with a large particle size and a highly crystallized structure. These properties can be obtained by very slowly diffusing water vapor into a solution of Fe^{3+} and Fe(CN)$_6^{4-}$ in concentrated hydrochloric acid; however, this process is very time-consuming (generally, a few weeks are required) [12]. In this study, Prussian blues with structural formulas identical to the "insoluble" Prussian blues were produced in very short reaction times (30 min for 120 mmol Prussian blue); they were much smaller in diameter than the typical insoluble Prussian blues, and therefore, they had a tendency to readily disperse in water.

The highly dispersed CNTs formed dense networks through their intrinsic self-assembly properties that coated the diatomite surfaces based on physical sorption (Figure 2A). As a result, Prussian blue particles were prevented from diffusing out of the diatomite cavities. CNTs used in this study with the diameters possibly penetrate into the diatomite cavity. Few portions of the CNTs might undergo in this manner. The ratio of diatomite/Prussian-blue to CNT (2.0 wt%) was optimized at 300 g/L.

The ternary (CNT/DM/PB) composite was finally immobilized in the cell walls of the polyurethane matrix. Figure 2B shows typical SEM images of the PUP/CNT/DM/PB spongiform, Prussian-blue based adsorbent. This was confirmed by washing the PUP/CNT/DM/PB quaternary spongiform adsorbent with de-ionized water, and then analyzing the wash water for released Prussian blue with a UV-vis spectrometer. Prussian blue was not detected in the wash water; this indicated that Prussian blue was firmly immobilized in the spongiform adsorbent.

3.2. Effects of CNTs and diatomite on cesium adsorption

Adsorption experiments were conducted in duplicate with aqueous solutions that contained 10.0 ppm cesium-133 as the targeted species. The adsorbents were the PUF/CNT/DM/PB quaternary composite and the ternary (PUF/DM/PB) composite, with and without the CNT-based coating, respectively. Figure 3 shows the levels of cesium-133 detected in the solution after the adsorption. The PUP/CNT/DM/PB adsorbent showed an elimination efficiency of 57.7%. Elimination efficiency was calculated as $(C-C_0)/C_0$, where C denotes the concentration of residual free cesium after adsorption, and C_0 denotes the initial cesium concentration. The PUP/DM/PB adsorbent gave an elimination efficiency of 47.2%. Thus, the elimination efficiency of the PUP/CNT/DM/PB adsorbent was

10.5% higher than that of the PUP/DM/PB adsorbent under identical experimental conditions. Moreover, the PUP/CNT/DM/PB adsorption equilibrated within 2 h, and the PUP/DM/PB adsorption required 5 h for equilibration. The surface roughness of the spongiform adsorbents was analyzed with a surface morphological analyzer (a Keyence VK-X 100/X 200 system). Figure 4 shows that the PUP/CNT/DM/PB adsorbent had a rougher surface than the PUP/DM/PB adsorbent. Because the rougher surface of the PUP/CNT/DM/PB adsorbent might have provided more contact areas for the distribution of cesium into the spongiform structure, this may have contributed to the higher elimination efficiency. Furthermore, a previous study showed that, when CNTs penetrated into a vegetable organism, they enhanced plant growth by enhancing water absorption [13]. In the present study, the PUP/CNT/DM/PB absorbent was coated with a homogenous distribution of CNTs. Thus, like the plant system, this coating most likely enhanced water uptake into the spongiform matrix [13]. Note here that the entire CNTs in the powder form were tested as adsorbent for absorption of cesium from the water samples; a significant change (> 3%) in cesium concentration was not observed. In other words, the entire CNTs were found to have no or very little ability for the cesium adsorption.

For the diatomite, their filtration characteristics are particularly significant. In

a previous study, a naturally occurred diatomite after being ground into 60 mesh fine powders were used for adsorption of three radionuclides (Cs-137, Cs-134 and Co-60) [14]. A pilot-scale, column-type device was established; it was found to be capable of reducing the radioactivity from the initial 2.60 Bq/ml to 0.40 Bq/ml within about 8 days, for a certain liquid waste sample. In our study, the diatomite was used to serve as micro-meter sized containers for the storage of the Prussian blue particles. Diatomite once being embedded in the spongiform materials showed very little ability ($< 2\%$) for absorbing cesium.

3.3. Adsorption isomers

Adsorption isotherms were plotted to evaluate the PUP/CNT/DM/PB adsorption of cesium. A Langmuir model was used, because it fit well to the experimental data. The expression of the Langmuir model in this study is:

$$\frac{1}{q_A} = \frac{1}{QK_A}\frac{1}{C_A} + \frac{1}{Q} \tag{1}$$

This was derived from the following Langmuir equation:

$$q_A = \frac{QK_AC_A}{1 + K_AC_A} \tag{2}$$

where q_A is the amount of cesium (mg) absorbed per gram of Prussian blue in the

PUP/CNT/DM/PB adsorbent (mg/g); C_A is the equilibrium concentration (mg/L) of

cesium in aqueous solution; Q is the theoretical adsorption saturation capacity for a

monolayer of the adsorbent (mg/g); and K_A is the Langmuir constant that relates to the

affinity of the adsorptive sites (i.e., Prussian blue) for cesium. Figure 5 shows a typical

adsorption isotherm. The Q value was found to be 166.67 mg/g, which was comparable

or better than the Q value (158.47 mg/g) obtained from the Langmuir isotherm plotted

from adsorption data with Prussian blue alone as the adsorbent. In other words, after

immobilizing Prussian blue in the spongiform matrix with our caging approach in

diatomite and coating with highly dispersed CNTs, its function improved for adsorbing

cesium. The linear coefficient (R^2) of the Langmuir isotherm exceeded 0.99; this

suggested that the PUP/CNT/DM/PB adsorbed cesium according to the Langmuir

adsorption model. Adsorption isomers were also plotted with the q_A as a function of the

amount of cesium absorbed per gram of spongiform matrix (i.e., the overall weight of

the quaternary PUP/CNT/DM/PB adsorbent). This showed that the quaternary

spongiform matrix that contained 1.79 wt% Prussian blue had a Q value of 2.94 mg/g.

In other words, one gram of the PUP/CNT/DM/PB-1.79% adsorbent was capable of

adsorbing 2.94 mg of cesium. K_A, the Langmuir constant, was found to be 0.8814 for

PUP/DM/PB, and 0.8841 for PUP/CNT/DM/PB, indicating a fact that Prussian blue is

the essential adsorptive sites for cesium.

3.4.   *Elimination efficiency*

The elimination efficiency of the quaternary spongiform adsorbent was evaluated

as a function of the amount added (mg); Table 1 summarizes the experimental data.

Different amounts of PUP/CNT/DM/PB-1.79% adsorbent were tested at an initial

cesium concentration of 10.0 ppm. Cesium was eliminated with an efficiency of

95.96% by adding 0.3 g of PUP/CNT/DM/PB-1.79% adsorbent to 40 mL of the 10.0

ppm cesium solution. Similar results were also observed for the samples prepared by

dissolving cesium in seawater.

3.5.   *Mechanism of adsorption*

The PUP/CNT/DM/PB adsorbent takes up cesium from the aqueous solution based

on ion-exchange. We analyzed the amount of absorbed cesium and the amount of

released sodium (Table 2). Cesium was exchanged for sodium almost

stoichiometrically. Prussian blue is a cubic, lattice-based, crystal with ferrous and

ferric atoms occupying alternate corners of the cubic lattice, and cyanide groups on

the edges [15]. The alkali atoms, which are exchangeable with cesium ions, are

located at the centers of alternating cubes. Among the alkali ions, cesium ion has the highest affinity for occupying the centers of these alternating cubes of Prussian blue. Therefore, the exchange of sodium and/or potassium for cesium is nearly irreversible. This unique affinity of cesium for Prussian blue confers a high selectivity and a high elimination efficiency for removing radioactive cesium from saline water, like seawater and body fluids.

3.6.   Elimination of radioactive cesium-137

Simulated radioactive water samples were prepared by adding cesium-137 into deionized water and seawater. We chose a cesium-137 activity of 1.50 Bq/ml. The simulated water samples (10 ml) were taken up into the spongiform absorbents (approximately 0.25 g of each adsorbent). After about 10-hours of water/spongy contacting, the water was squeezed from the spongy and the residual radioactivity in the water was analyzed. Table 3 shows that the elimination efficiency for cesium-137 was 99.93% in deionized water and 99.47% in seawater.

4.   Conclusion

This study showed that low-levels of radioactive cesium could be selectively eliminated from water with a spongiform adsorbent that incorporated Prussian blue

as the functional moiety. Prussian blue was caged within the cavities of diatomite and sealed in with highly dispersed carbon nanotubes. Prussian blue caged in this manner preferentially absorbed radioactive cesium, despite its permanent immobilization on the cell walls of polyurethane foam (i.e., the spongiform matrix). Carbon nanotubes were able to seal in Prussian blue particles and they enhanced the adsorption of cesium. It is important to note that another advantage of these spongiform adsorbents is that, after adsorbing radioactive cesium, the adsorbent can be condensed into very small volumes with carbonization. This provides a desirable, practical approach for reducing the final volumes of radioactive waste. Currently, our research groups have used this spongiform, Prussian blue-based adsorbent for the elimination of radioactive cesium from low-level radioactive water in Fukushima areas, and preliminary results have been highly satisfactory. For the actual *in-situ* applications, the ratio of water/spongiform-adsorbent was chosen at 1/1 (volume/volume); after the radioactive cesium being adsorbed, the water was squeezed from the adsorbent using machine arms.

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Development Center for detecting the concentrations of ^{137}Cs in the simulated samples.

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Table 1 Cesium elimination efficiency as a function of the amount (mg) of spongiform adsorbent, PUP/CNT/DM/PB-1.79%.

Weight	100 mg	150 mg	300 mg	500 mg
Efficiency [a]	57.72%	90.62%	95.96%	ND*
Efficiency [b]	56.82%	89.66%	94.82%	N.D*

Samples were tested in 40 mL aqueous solutions containing 10.0 ppm cesium. [a]The elimination efficiency for the sample prepared by dissolving cesium nitrate in deionized water and [b]that for the samples prepared by dissolving cesium nitrate in seawater. ND*: Residual cesium was not detected in the solution after adsorption (10 h for each sample).

Table 2 Cesium uptake by the PUP/CNT/DM/PB adsorbent and the amount of the released sodium ions.

Cesium absorbed	57.6 μmol	78.3 μmol	97.5 μmol
Sodium released	59.8 μmol	79.7 μmol	99.7 μmol

Table 3 Radioactive cesium-137 in simulated samples, before and after adsorption.

Adsorbent	PUP/CNT/DM/PB	PUP/DM/PB	PUP/DM
Cs-137 in DW; Bq/ml	$1.50 \rightarrow 0.001$	$1.50 \rightarrow 0.17$	$1.50 \rightarrow 1.47$
Elimination ratio*	99.93%	88.67%	2.00%
Cs-137 in SW; Bq/ml	$1.50 \rightarrow 0.008$	$1.50 \rightarrow 0.27$	$1.50 \rightarrow 1.47$
Elimination ratio*	99.47%	82.00%	2.00%

Each 10.0 ml of deionized water (DW) or seawater (SW) contained cesium-137 (initial radioactivity, 1.50 Bq/ml) sample was taken up (absorbed) with 250 mg of PUP/CNT/DM/PB, PUP/DM/PB, or the polyurethane polymer combined with diatomite (PUP/DM). *The elimination efficiency was calculated from the initial (C_0) and final (C) cesium-137 concentrations: $(C_0-C)/C_0 \times 100\%$.
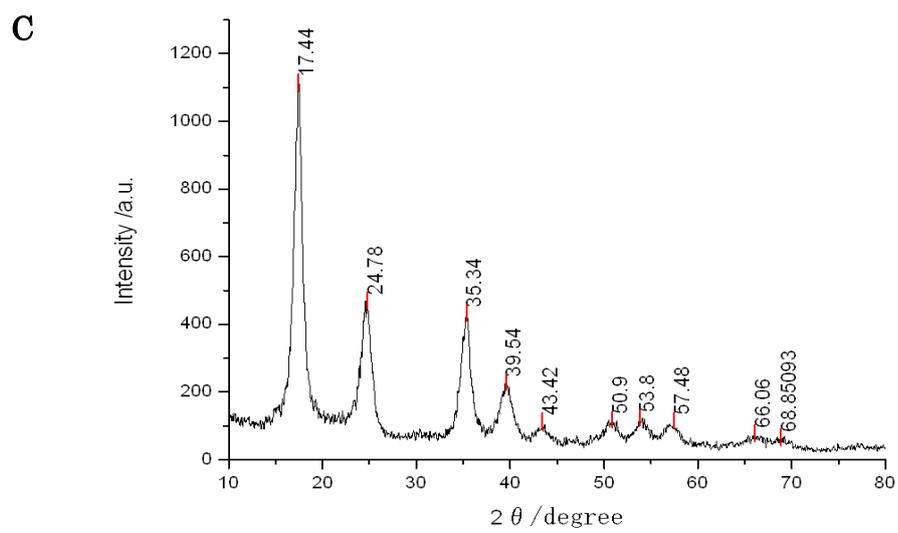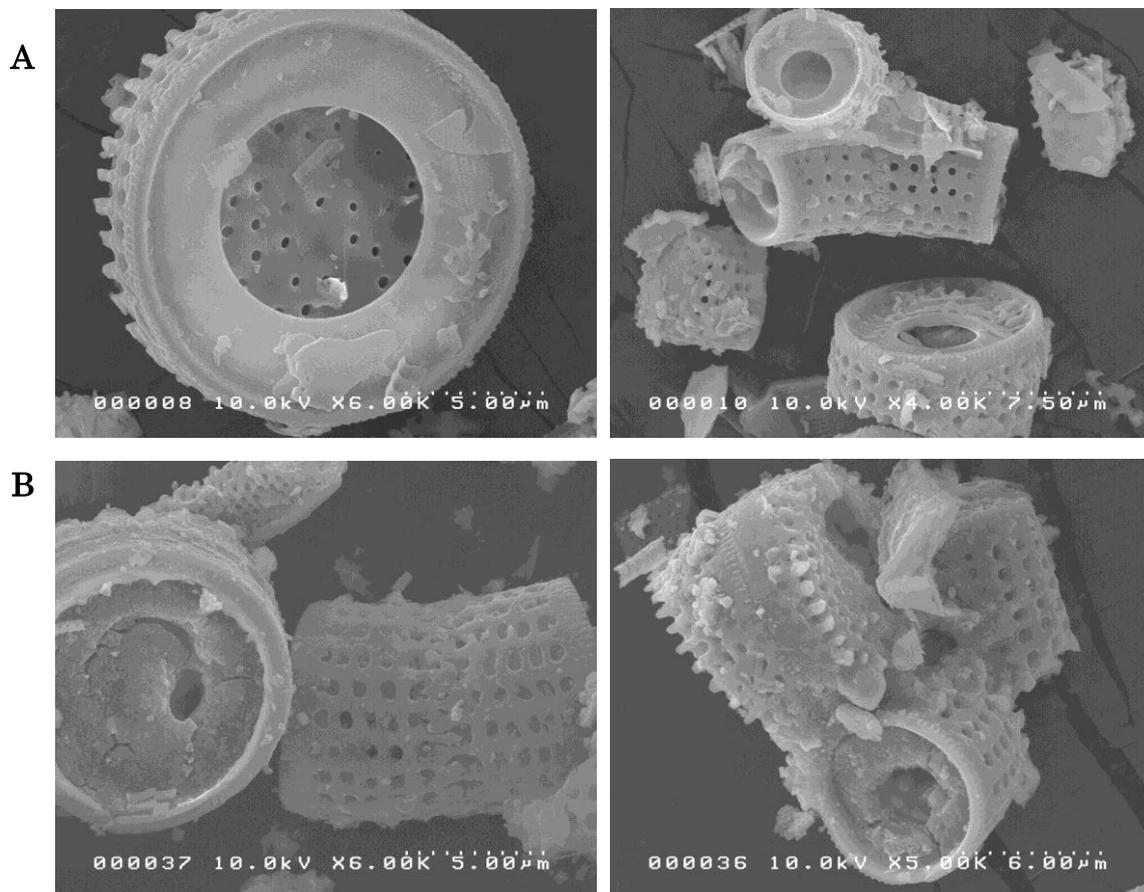
Figure 1 Prussian blue particles were synthesized in diatomite cavities. (A, B)

Representative SEM images show (A) pristine diatomite and (B) Prussian blue particles produced in the cavities of diatomite. (C) Typical XRD diffractogram of Prussian blue packed in the cavities of diatomite (a.u. arbitrary units)
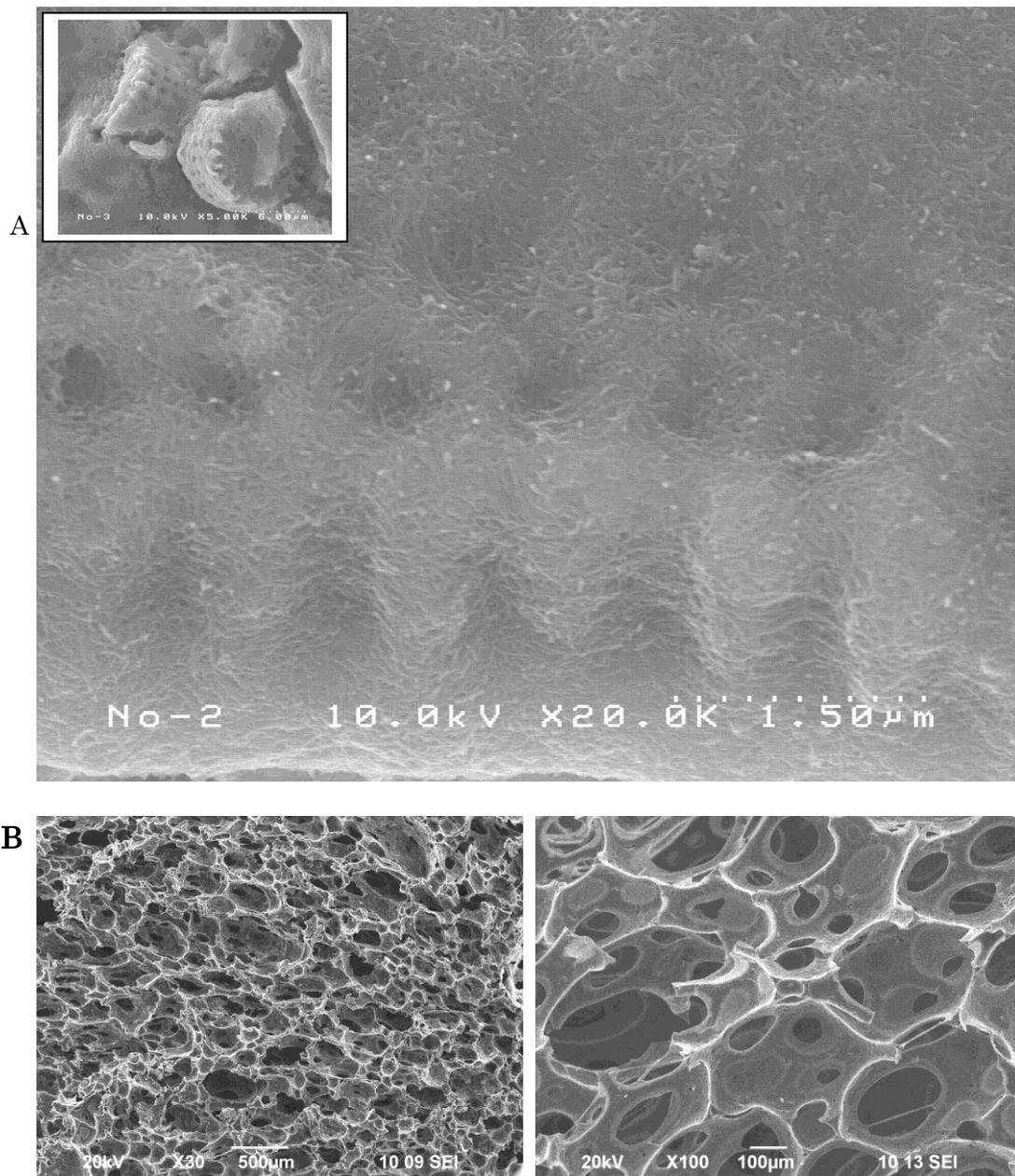
Figure 2 (A) Prussian blue was sealed into the cavities of the diatomite (upper, lower resolution). The diatomite surfaces were coated with highly dispersed multi-walled CNTs (upper, high resolution). The CNTs formed a continuous, interconnected network that prevented the diffusion of Prussian blue particles. (B) Representative SEM images of the quaternary (polyurethane polymer, CNTs, diatomite, and Prussian blue ,

PUP/CNT/DM/PB), spongiform, Prussian blue based adsorbent (left, ×30

magnification; right, ×100 magnification).
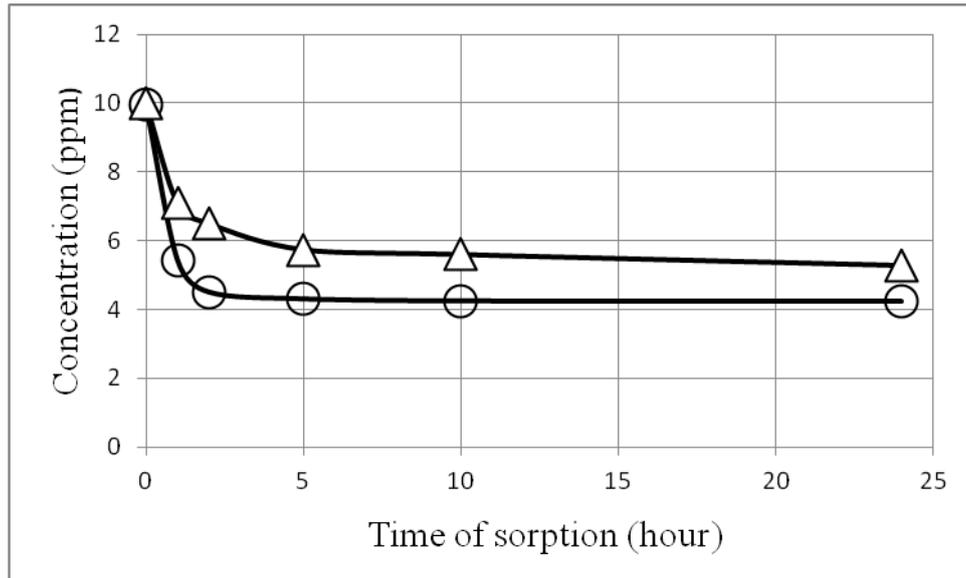
Figure 3 Concentrations of residual cesium-133 in the aqueous solution as a function of

the time of adsorption. Circles represent adsorptions conducted with PUP/CNT/DM/PB;

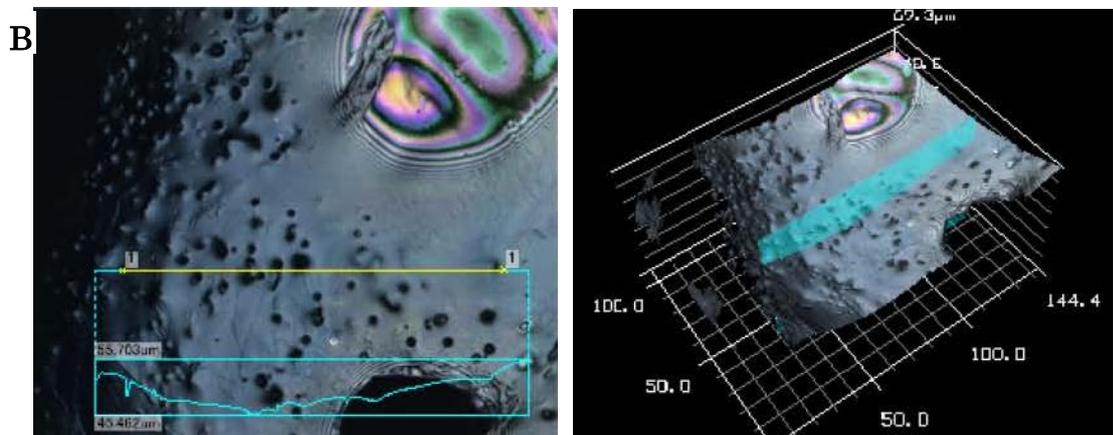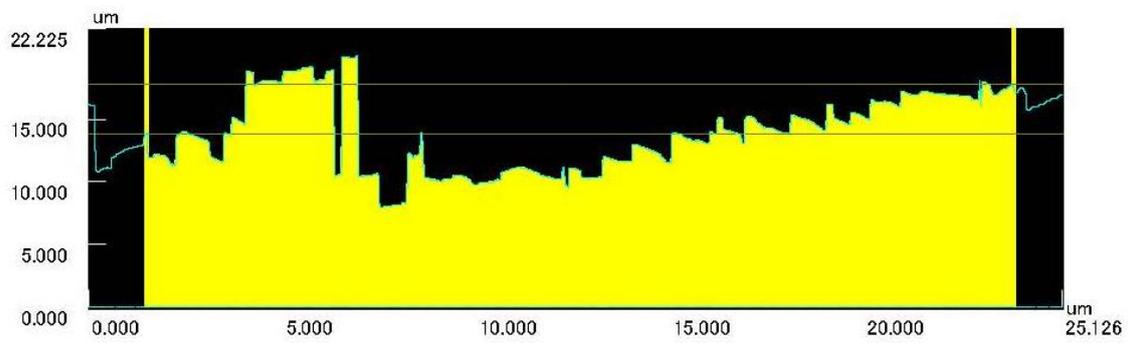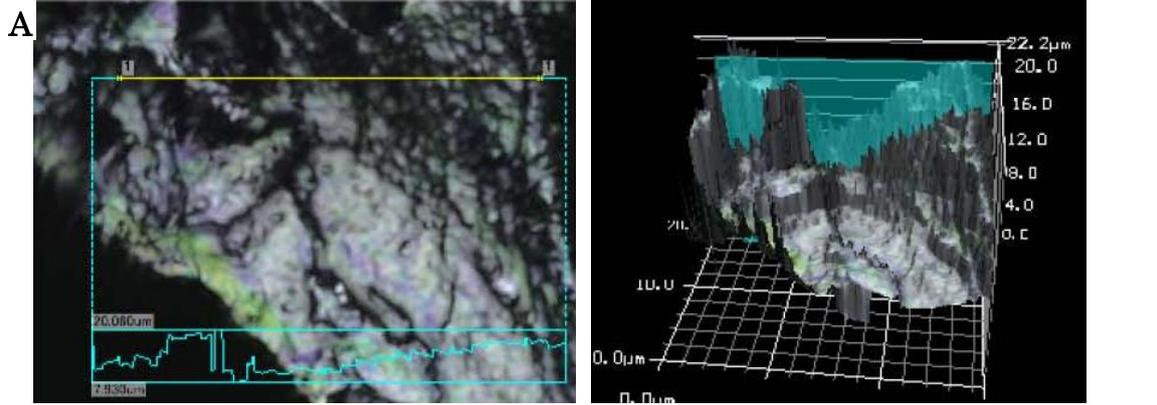triangles represent adsorptions conducted with PUP/DM/PB.
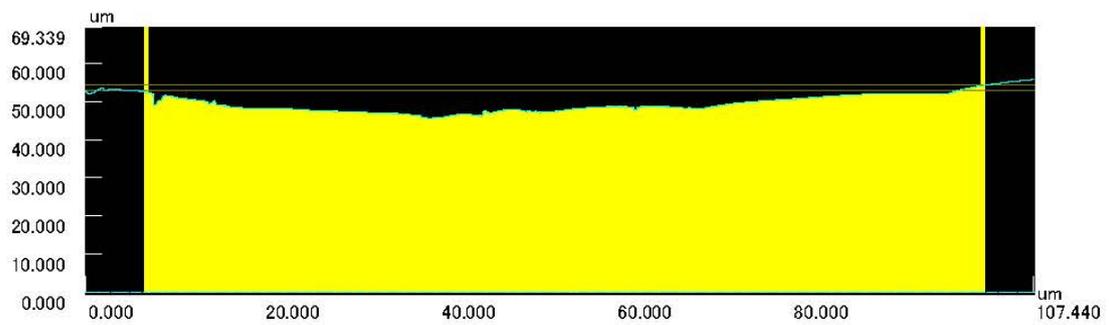
Figure 4 Surface roughness of adsorbents with (quaternary) and without (ternary) a CNT coating. The surface roughness was analyzed in the selected areas (areas boxed in top left panels). (A) The quaternary PUP/CNT/DM/PB adsorbent had a surface roughness of 3.88 ± 0.78 µm, and (B) the ternary PUP/DM/PB adsorbent had a surface roughness of 3.08 ± 0.23 µm.
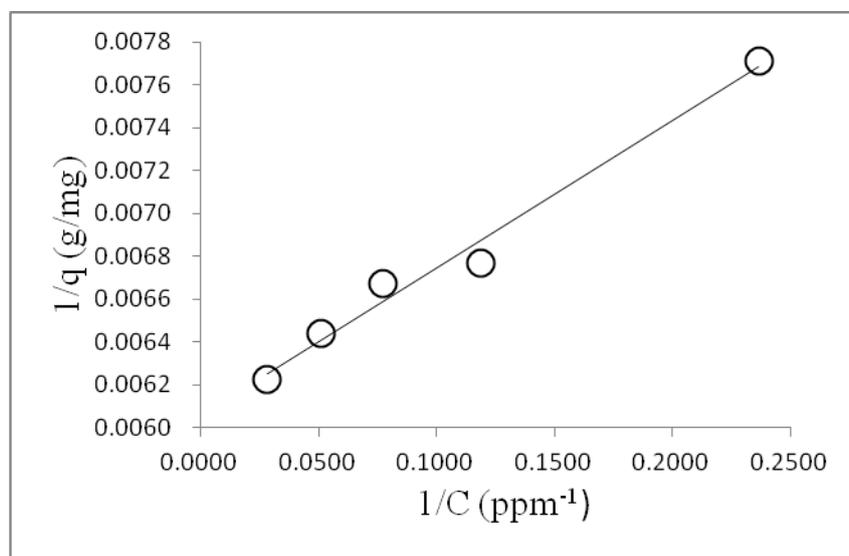
Figure 5 Langmuir isotherm for cesium-133 adsorption by the PUP/CNT/DM/PB

adsorbent; temperature was maintained at 25 °C during the experiments.