Chapter 14
CNT Applications in the Environment and in Materials Used in Separation Science

Contents

14.1 Overview

CNTs have been considered for use in *environmental applications* and in *materials used in separation science*. Such applications include, e.g., filters, membranes, and water treatment.

14.2 Environmental Applications

In recent work [402] a porous "nanosponge" was constructed via a CVD process that used ferrocene as the catalyst precursor and added sulfur. This "nanosponge" was then used to absorb *o*-dichlorobenzene and oils from a water sample; the oils absorbed were more than 100x the weight of the sponge. In similar, earlier work, B-doped CNT "nanosponges" were fabricated from CVD-deposited CNT forests that were shown to behave somewhat like surfactants but with very high oil absorption capabilities [403].

A comparative study of the water treatment capability of granular activated-C, activated-C-fiber, and CNTs [404] found that the absorption capabilities of the CNTs (including SWCNTs as well as MWCNTs) for three aromatic organic compounds tested were somewhat better than those of the activated-C materials. Other work in water treatment has shown that molecular sieves constructed from CNTs have the potential of being activated and deactivated via an external electrostatic field [405]. CNTs have also been shown to be usable in a variant of *reverse osmosis* methods but operating at lower pressures, lower temperatures, and higher

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flow rates than conventional (e.g., polycarbonate membrane based) reverse osmosis methods, although it also appears that only very specialized and very small-diameter SWCNTs function well in this application [406, 407]. In one study of desalination of water using self-supporting CNT membranes, a 99% salt rejection rate was claimed at a flux rate of water of about 12 kg/m^2 h [408].

In other work, CNT filters have been demonstrated that electrochemically oxidize organic contaminants, bacteria, and viruses or remove them through simple microfiltration mechanisms [409–413].

A company called Seldon Water (formerly Seldon Technologies and now owned by CB Tech) markets *Seldon Nanomesh*-brand portable water filters for water purification and claimed to "remove bacteria, viruses, and cysts, such as Cryptosporidium and Giardia, to US EPA Drinking Water Standards (99.9999% of bacteria, 99.99% of viruses, and 99.9% of cysts) also reduce sediment, total organic carbon (TOC), chlorine, color, bad taste, and odors also removes significant levels of harmful chemical contaminants, including: Lead and Cadmium, Organophosphates (pesticides and herbicides), Disinfection byproducts, radioactive contaminants such as cesium-137" [414].

14.3 Applications in Separations and Related Fields

CNTs have been studied for use in solid-phase extraction, as microextraction sorbents, in chromatography, and as laser desorption/ionization substrates [415].

One of the important parameters that must be considered in the use of CNTs in separation-related applications is the *point of zero charge* (*isoelectric point*), at which CNTs' surface has *zero net charge* [415]. When the pH is higher than this point, the CNT surface is negatively charged; electrostatic interactions can be established to adsorb cationic species. Conversely, when the pH decreases below the point of zero charge, protons compete with cations for the same sites on CNTs, and the subsequent neutralization of CNTs provides a decrease in the adsorption. This fact can be used, for example, to retain at a certain pH value, in metals, and to later elute them using acidic solutions, allowing for facile separation of such materials. On the other hand, it is also estimated that the CNTs' covalent functionalization must not exceed about 10% of their surface [415, 416].

The use of CNTs in chromatographic stationary phases has been documented for the separation of the following analytes, as summarized succinctly by Herrera-Herrera et al. (type of CNT, if applicable, given in parentheses, and technique used given in brackets) [415, 417–442]: Ar and CO_2 (SWCNTs) {GC-TC}; alkanes and aromatic hydrocarbons (MWCNTs functionalized with –COOH and $CONH_2$) {GC-FID}; methanol, hexane, ethanol, carbon tetrachloride, benzene, six other alcohols, and two other esters (CNTs) {GC-FID}; benzene, toluene, dichloromethane, trichloromethane, acetonitrile, propanol, toluene, 1-butanol, m-Xylene, phenol, and naphthalene (SWCNTs functionalized with COCl, diameter < 2 nm) {GC-FID}; nine esters, nine aromatics, two alcohols, two ketones, and two alkanes

(MWCNTs with NH_2-R functionalization) {GC-FID}; chloro-substituted PCBs and terpenes (MWCNTs with NH_2 functionalization) {HPLC-DAD}; polyaromatic hydrocarbons (PAHs), aromatics, and amines (silica-MWCNT composites, CNT diameter < 8 nm) {HPLC-UV}; one nucleobase with seven benzene derivatives (variously functionalized MWCNTs) {HPLC-UV}; 12 peptides (MWCNTs with NH_2 functionalization) {HPLC-UV}; five nucleosides, a nucleobase, and four tetracycline antibiotics (silica-MWCNT composites, CNT diameter 20–40 nm) {CEC-UV}; five nucleobases, five nucleosides, eight flavonoids, and six phenolic acids (COOH-functionalized MWCNTs, diameter 20–40 nm) {CEC-UV}; five vitamins (COOH-functionalized SWCNTs, diameter about 1.2 nm) {CEC-DAD}; clenbuterol enantiomers (brominated MWCNTs, diameter 10–20 nm) {TLC}; thioamides (MWCNTs, diameter 8 nm) {micro-CEC-UV}; six nonsteroidal anti-inflammatory drugs (MWCNTs, diameter ca. 10–15 nm {CE}; and four flavonoids, four phenolic acids, and two saponins (MWCNTs, diameter 3–20 nm, and SWCNTs, diameter 0.7–1.1 nm) {CE} (Table 14.1).

CNTs have also begun to be studied for applications in laser desorption/ionization (LDI) time-of-flight mass spectrometer (TOFMS). These CNT-derived materials have been used as substrates in both matrix-assisted LDI (MALDI) [207–211] and surface-assisted LDI (SALDI) [415, 443–451]. However, this incipient work is still very much in the development phase, with no conclusive results as of this writing.

14.4 Problems and Exercises

1. Briefly describe the principles and practical construction behind the following applications of CNTs: water treatment and "nanosponges." Rate the applications using CNTs against the corresponding, more established applications using non-CNT materials (in terms of such parameters as performance, cost, size, and closeness to the market).
2. Enumerate and describe CNT applications in separations. Enumerate at least ten (10) chemicals whose mixtures have been separated using CNT-based materials. Define *isoelectric point*.
3. Describe the principles of the use of CNTs in mass spectrometry. What are their relative advantages and drawbacks in this application?

Table 14.1 After ref. [415]

Analyte	Methodology	Recovery (%)	LODs
Ag (I)	Flame atomic absorption spectrometry	96–108	0.35 μg L^{-1}
As (V)	Hydride generation-atomic fluorescence spectrometry	94–104	2 ng L^{-1}
As (III), As (V), Sb (III), Sb (V) (as APDC complex)	Hydride generation-double channel atomic fluorescence spectrometry	92–107	2.1–4.3 ng L^{-1}
As (III), As (V), Sb (III), Sb (V) (as APDC complex)	ETAAS	94–104	0.02–0.05 μg L^{-1}
Au (III), Mn (II)	Flame atomic absorption spectrometry	94–102	0.01–0.03 μg L^{-1}
Au (III)	Flame atomic absorption spectrometry	>95	0.3 μg L^{-1} for PANI/MWCNTs and 0.5 μg L^{-1} for PEDOT/MWCNTs
Au (III)	Flame atomic absorption spectrometry	>96	0.15 μg L^{-1}
Cd (II)	Flame atomic absorption spectrometry	98	0.22 μg L^{-1}
Cd (II)	ETA-AAS	97–100	0.010 μg L^{-1}
Cd (II)	ICP-OES	–	1.03 μg L^{-1}
Cd (II), Pb (II), Ni (II)	Flame atomic absorption spectrometry	97–104	0.04–0.23 μg L^{-1}
Cd (II), Co (II), Cu (II), Cr (VI), Pb (II), V (V), As (III)	ICP-MS	92–110	0.4–3.4 ng L^{-1}
Cd (II), Co (II), Ni (II), Pb (II), Fe (III), Cu (II), Zn (II) (as 8-hydroxyquinoline complexes)	Flame atomic absorption spectrometry	88–104	1.0–5.0 μg L^{-1}
Cd (II), Pb (II)		96–109	0.15 and 0.44 μg L^{-1}
Cd (II), Pb (II)	Flame atomic absorption spectrometry	97–101	0.3 and 1 μg L^{-1}
Co (II)	Flame atomic absorption spectrometry	101	50 ng L^{-1}
Co (II), Cu (II), Pb (II)	ETAAS	96–109	1.2–39 ng L^{-1}
Co (II), Cu (II), Ni (II), Pb (II), Fe (III), Mn (II)	Flame atomic absorption spectrometry		
Cu (II), Ni (II)	Flame atomic absorption spectrometry	81–100	0.31–0.63 μg L^{-1}
Cu (II), Ni (II), Zn (II)	Flame atomic absorption spectrometry	–	40–60 μg L^{-1}
Cu (III, Fe (III), Mn (II), Pb (II)	Flame atomic absorption spectrometry	23–106	3.5–8 μg L^{-1}

(continued)

Table 14.1 (continued)

Analyte	Methodology	Recovery (%)	LODs
Cu (II), Fe (III), Pb (II)	ICP-OES	97–105	0.15–0.26 μg L^{-1}
Cr (III), Fe (III), Pb (II)	ICP-OES	99–100	0.19–0.33 μg L^{-1}
Cr (VI)	UV spectrometry	98–12	8.5 ug kg^{-1}
F-, Br-, Cl-, No_2^-, BrO_3^-, NO_3^-, CO_3^-, PO_4^{3-}, SO_4^{2-}	HPLC conductivity detector	72–118	0.41–3.17 μg L^{-1}
BrO3-, NO3-, CO3-, PO43-, SO42-	HPLC conductivity detector	84–120	1.54–10.02 μg L^{-1}
Ga (III)	Flame atomic absorption spectrometry	87–94	3.03 μg L^{-1}
Hg (II)	Batch adsorption experiments	88–95	0.0123 μg L^{-1}
Ni (II), Pb (II)	ETAAS	–	10–30 ng L^{-1}
Pb (II)	ICP-OES	96–100	0.27 μg L^{-1}
Pb (II)	ICP-OES	99–109	0.32 μg L^{-1}
Pb (II)	Atomic absorption spectrometry	99–113	0.30 μg L^{-1}
Pd (II)	Flame atomic absorption spectrometry	99	0.3 μg L^{-1}
Pd (II)	Flame atomic absorption spectrometry	81–91	0.3 μg L^{-1}
Rh (III) (as PAN complex)	Flame atomic absorption spectrometry	96–105	0.010 μg L^{-1}
Total Tl, Tl (III)	STPF-ETAAS	>98	150 ng L^{-1}
Zn (II)	Flame atomic absorption spectrometry	>98	0.07 ng L^{-1}
Pesticides 8 multiclass pesticides	GC-MS	79–105	1.5–3.0 μg L^{-1}
Carfentrazone-ethyl	GC-ECD	74–80	10 ng L^{-1}
5 sulfonylurea herbicides	HPLC-DAD (236 nm)	79–102	1.1–7.2 ng L^{-1}
3 chloroacetanilide herbicides	GC-MS	89–1106	2–6 ng L^{-1}
7 OPPs and 1 thiadizine	GC-NPD	54–91	2.97–31.6 ng L^{-1}
Atrazine, methidathion on propoxur	UV–Vis spectrometry (200–300 nm)	84–104	0.31–0.41 mg L^{-1}
6 pyrethroids	HPLC-UV (210 nm)	71–118	1.3–5.0 ng L^{-1}
4 chloroacetanilide herbicides	GC-ECD	81–88	0.01 μg L^{-1}
11 triazines	UPLC-MS	73–98	<0.1 ng L^{-1}
4 triazines	μ-LC-UV (220 nm)	55–71	0.2–0.5 μg L^{-1}
3 triazines	GC-MS	–	–
Chlorpyrifos and phosalone	HPLC-UV (288 nm)	85–100	4.02 and 1.02 ng L^{-1}
Chlorsulfuron and metsulfuron	CE-UV (231 nm)	86–108	0.36 and 0.40 μg L^{-1}
Atrazine and simazine	GC-MS	87–110	2.5 and 5.0 ng L^{-1}

(continued)

Table 14.1 (continued)

Analyte	Methodology	Recovery (%)	LODs
Mefenacet and three photolysis degradation products	UPLC-UV-MS (220 nm)	70–120	0.02–0.04 μg L^{-1}
7 sulfonylurea herbicides	LC-MS/MS	82–110	0.01–0.20 ng L^{-1}
3 triazines and 2 dealkylated metabolites	HPLC-UV (220 nm)	86–102	4–30 ng L^{-1}
9 multiclass pesticides	Nano-LC-UV (200 nm)	36–101	16–67 ng L^{-1}
Pharmaceuticals			
Chloramphenicol	HPLC-MS/MS	96–102	Egg, 0.004 μg kg^{-1}; honey, 0.003 μg kg^{-1}; milk, 0.003 μg kg^{-1}
10 quinolones	UPLC-UV (279 and 319 nm)	70–100	5.8–14.5 μg L^{-1}
11 quinolones	Ce-DAD (250 and 280 nm)	62–114	0.028–0.094 μg L^{-1}
3 macrolides	HPLC-UV (210 nm)	85–96	–
Ursolic acid	HPLC-UV (210 nm)	80	–
Miscellaneous biological compounds			
Bovine hemoglobin and serum albumin	UV–Vis spectrophotometry (190–500 nm)	90	1.0 mg L^{-1}
Bovine serum albumin	Bradford assay	–	–
3 estrogens	MEKC-DAD (196 nm)	90–100	0.1–0.2 μg L^{-1}
3 estrogens	HPLC-FD (λ_{ex}/λ_{em} = 280/310 nm)	88–112	1.21–2.35 μg L^{-1}
3 biogenic thiols	HPLC-FD (λ_{ex}/λ_{em} = 360/510 nm)	92–113	0.004–0.080 nM
4 cobalamins	HPLC-DAD (265, 351 and 361 nm)	76–102	0.35–29 μg L^{-1}
3 albumins, bovine hemoglobin, and lysozyme	HPLC-UV (280 nm)	92–97	–
3 neurotransmitters	HPLC-FD (λ_{ex}/λ_{em} = 326 nm/412 nm)	88–94 for SWCNTs; 82–94 for MWCNTs	–
PAHs			
3 PAHs	HPLC-FD (λ_{ex}/λ_{em} = 274 nm/412 nm), 266 nm/436 nm, 270/416 nm	89–98	5–8 ng L^{-1}
16 PAHs	GC-MS	72–93	0.001–0.15 μg L^{-1}
16 PAHs	GC-MS	70–127	2.0–8.5 ng L^{-1}
8 PAHs	GC-MS	88–122	0.10–0.88 ng L^{-1}

(continued)

Table 14.1 (continued)

Analyte	Methodology	Recovery (%)	LODs
16 PAHs	GC-MS	72–99	4.2–46.5 ng L^{-1}
Chemical warfare agents			
9 chemical warfare agents	GC-MS	63–110	0.01–1 μgL^{-1}
9 chemical warfare agents	GC-FPD	55–96	0.05–1 μg L^{-1}
6 acidic degradation products of chemical warfare	GC-MS	48–112	0.05–0.08 μg L^{-1}
Other			
2 polychlorophenols and 2 tetrahalogenated biphenyls	GC-ECD	55–100	1.0–6.0 μg L^{-1}
2-Nitrophenol, 2,6-dichloroaniline and, naphthalene	HPLC-UV (-)	–	0.1–3 μg L^{-1}
27 amines, 2 anilines, 12 chloroanilines, 10 N-nitrosamines, and 3 aliphatic amines	GC-MS	–	–
8 low-molecular-mass aldehydes	LC-MS/MS	–	–
4 parabens	HPLC-C-CAD	85–104	0.5–2.1 mg L^{-1}
Sudan IV	HPLC-UV (510 nm)	89–95	2.3 ng L^{-1}
Pentachlorophenol	GC-ECD	92 for MWCNTs; 43–78 for o-MWCNTs	–
Trans- and cis-resveratrol	LC-MS/MS	95–108	0.02 μg L^{-1}
Melamine	HPLC-UV (240 nm)	90–93	0.3 μg L^{-1}
4 linear alkylbenzene sulfonates	HPLC-UV (224 nm)	82–110	0.02–0.03 μg L^{-1}
4 linear alkylbenzene sulfonates	HPLC-UV (224 nm)	87–106	0.013–0.021 μg L^{-1}
16 phthalate acid esters	GC-MS	63–119	0.0031–0.0038 μg L^{-1}