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2 **SUPPORTING INFORMATION:**

3 **Mobility of Multi-walled Carbon Nanotubes in Porous Media**

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FIGURE S-1. Transmission Electron Microscope (TEM) image of Multi-walled Carbon Nanotubes (MWCNT).

Characterization and Preparation of the MWCNTs

Thermal gravimetric analysis (TGA) of the MWCNTs did not indicate the presence of amorphous carbon impurities and confirmed removal of the metal catalysts, with a carbon content ranging from 99.6 to 99.9% (n=3). X-ray photoelectron spectroscopy (XPS) analysis indicated that the elemental oxygen content of the MWCNTs increased by almost a factor of 6 following acid treatment (from 1.57% to 9.25%). Transmission electronic microscope (TEM - Philips CM10) images of CNTs indicate that the MWCNTs are a mixture of carbon nanotubes and some impurities (metal catalysts). The diameter of the carbon nanotubes typically ranged from 7 nm to 70 nm (Figure S-1). An average MWCNT length of 407 nm (ranging from 100 nm to 2 μ m) was determined using a Philips/FEI XL30 FEG scanning electron microscope operating at an accelerating voltage of 15.0 kV [1].

Electrophoretic mobility measurements of the two MWCNT suspensions (ZetaPALS, Brookhaven Instruments Corporation, Holtsville, NY) indicate that the suspensions were

negatively charged in the measured pH range (5 to 11). At pH 10, the mean electrophoretic mobility was $-3.80 \times 10^{-8} \text{ m}^2/\text{V/s}$ for suspensions in stock solution I (SS I). For the low ionic strength solution (SS II), the mean electrophoretic mobility was $-3.76 \times 10^{-8} \text{ m}^2/\text{V/s}$.

Aqueous suspensions consisting of 100 mg/l MWCNT were used in all experiments. The first aqueous phase solution (SS I) had an ionic strength of 10 mM and was buffered to pH 10 with 2.8 mM NaHCO_3 and 2.1 mM Na_2CO_3 . One mM NaBr or NaCl was added to SS I as a conservative tracer. For the low ionic strength aqueous phase solution (SS II), sodium hydroxide (NaOH) was added to deionized water to make a 0.1 mM ionic strength solution with a pH around 10. No conservative tracer was added to SS II. MWCNTs were added to 100 ml, 150 ml or 200 ml of aqueous phase stock solutions and sonicated for 30 or 45 minutes using an ultrasonic homogenizer at 210 watts. These suspensions were stable in the aqueous phase in excess of twelve months. Concentrations of aqueous phase MWCNT suspensions were quantified using a UV-spectrophotometer (Cary 50) at a wavelength of 400 nm. Dilutions of the 100 mg/L MWCNT suspension were used to develop an absorbance/concentration calibration curve. This procedure had a detection limit of 0.1 mg/L.

Column Experiments.

Columns were dry packed in 10-cm long aluminum columns with an inner diameter of 5.0cm. A stainless steel mesh (pore size: 150 μm) was placed at both ends of the column to support the sand and glass beads. Dry sand or glass beads were added in layers of approximately 0.5 cm. Each layer was mixed and surface scoured with a spatula prior to the addition of subsequent layers following the procedure of Oliviera et al. [2] to ensure porous media homogeneity. The average porosity of the columns was calculated using the difference in the column weight before and after packing, the total column volume and the specific gravity of the media. The mean porosity of the sand packed columns was 0.35 (ranging from 0.344 to 0.368) and 0.38 for the glass bead columns. Carbon dioxide gas was flushed upwards through the packed column for 15 minutes to displace air in the column. De-ionized water was then introduced at the bottom of the carbon dioxide saturated column to completely saturate the column with water (about 30 pore volumes).

The column experiments were flushed with at least 40 pore volumes of stock solution (i.e., SS I or SS II) vertically upward and the effluent UV absorbance continually monitored to ensure clean

effluent conditions. The flow direction was then switched to vertically downward and the effluent UV absorbance again continually monitored to ensure clean effluent conditions prior to injecting the MWCNT suspension.

Numerical Model Development

A numerical model was developed to simulate the transport of MWCNTs in porous media. The aqueous phase mass balance is represented as [e.g., 3, 4]:

$$\frac{\partial C}{\partial t} + \frac{\rho_b}{n} \frac{\partial S}{\partial t} + v \frac{\partial C}{\partial x} - D \frac{\partial^2 C}{\partial x^2} = 0 \quad (S1)$$

where C is the concentration of multiwalled carbon nanotubes in the aqueous phase, t is time, ρ_b is the solid phase bulk density, n is porosity, S is the amount of carbon nanotubes associated with the solid phase, v is the pore water velocity, x is the spatial dimension in the column and D is the dispersion coefficient ($D = v * \alpha_l$, where α_l is the longitudinal dispersivity).

The solid phase mass balance equation is represented as [e.g., 3, 4]:

$$\frac{\rho_b}{n} \frac{\partial S}{\partial t} - k_{att} \psi C + \frac{\rho_b k_{det}}{n} S = 0 \quad (S2)$$

where k_{att} is the removal rate constant associated with mechanisms typically associated with colloid filtration theory (ie: diffusion, sedimentation and interception), ψ is an adsorption site blocking term and k_{det} is the rate constant for the detachment of MWCNTs associated with the solid phase. The adsorption site blocking term is defined as [e.g., 3, 5]:

$$\psi = \left(1 - \frac{S}{S_{max}} \right) \quad (S3)$$

where S_{max} is the maximum adsorption capacity of the solid phase for the removal of MWCNTs due to mechanisms typically associated with colloid filtration theory,

The removal rate constant k_{att} is defined as [6]:

$$k_{att} = \frac{3 \alpha \eta_o v (1 - n)}{2 d_c} \quad (S4)$$

1 where α is the attachment efficiency, η_0 is the theoretical single collector efficiency and d_c is the
2 mean diameter of the collector (grain). The attachment efficiency is typically fit to experimental
3 data whereas the theoretical single collector efficiency is based on theoretical considerations.

5 **Determination of the Theoretical Collector Efficiency**

7 Given that the particles used in this study are non-spherical, the model proposed by Yao et al. [6]
8 to predict the collector efficiency of spherical particles approaching a large spherical collector is
9 inappropriate. As a result, new relationships are developed to determine the collector efficiency
10 for carbon nanotubes in a spherical collector system. For this analysis it is assumed that the
11 carbon nanotubes are uniform cylinders with a diameter d_p and length l , with the exception of the
12 friction factor in the derivation of diffusive and gravitational collector efficiencies when the
13 carbon nanotubes are assumed to be prolate ellipsoids.

15 **i) Interception for Cylindrical Particles**

16 In this analysis the theoretical collector efficiency is assumed to be the sum of three distinct
17 collision types, collision due to MWCNT interception, gravity sedimentation, and diffusion. For
18 interception, two cases will be considered for this analysis: either the end or the side of the
19 MWCNT cylinder makes contact with the collector surface. This will be referred to as “end-
20 contact” and “side-contact”, respectively (Figure S-2).

Figure S-2. Interception Mechanisms for Cylindrical Particles in Spherical Collector System (adapted from [7])

Following the procedure of Yao et al. [6], consider a spherical grain collector in the flow path of suspended nanoparticles. The total flux of suspended nanoparticles approaching the collector, J , can be expressed as:

$$J = v_o C_o \frac{\pi d_c^2}{4} \quad (\text{S5})$$

where v_o is the undisturbed uniform flow velocity; C_o is the concentration of suspended nanoparticles in bulk solution; d_c is the diameter of the grain collector.

The flux of suspended particles that strike the collector due to interception alone is determined by assuming that all particles flowing within a stream tube, S_o or S_o' (ie: streamlines containing cylindrical particles that touch the collector surface) will contact the collector and be removed from the aqueous phase. The flux of MWCNT removed due to end-contact interception can be expressed as:

$$J_I = \frac{1}{2} v_o C_o \frac{\pi l^2}{4} \left(3 - \frac{l}{l + d_c} \right) \quad (\text{S6})$$

and for side-contact it can be expressed as:

$$J_I = \frac{1}{2} v_o C_o \frac{\pi d_p^2}{4} \left(3 - \frac{d_p}{d_p + d_c} \right) \quad (S7)$$

By definition, the end-contact single collector efficiency of a cylindrical particle due to interception alone, η_I , is:

$$\eta_I = \frac{J_I}{J} = \frac{1}{2} \left(\frac{l}{d_c} \right)^2 \left(3 - \frac{l}{l + d_c} \right) \quad (S8)$$

Similarly, η_I for side-contact of a cylindrical particle is:

$$\eta_I = \frac{1}{2} \left(\frac{d_p}{d_c} \right)^2 \left(3 - \frac{d_p}{d_p + d_c} \right) \quad (S9)$$

ii) Sedimentation

The theoretical collector efficiency due to sedimentation is a function of the settling velocity of the MWCNTs. A force balance approach is used to determine the settling velocity of the MWCNTs:

$$\begin{aligned} ma &= F_g - F_B - F_D \\ &= (\rho_p - \rho)gV_p - f v \end{aligned} \quad (S10)$$

where F_D is the drag force; F_B is the buoyant force; F_g is the gravitational force, m is the mass of the particle; a is the acceleration of the particle; ρ_p is the density of the particle; ρ is the density of the fluid; V_p is the volume of the particle; f is the friction coefficient (friction factor); v is the settling velocity of the particle. When particles reach their ultimate settling velocity, $a = 0$, and:

$$(\rho_p - \rho)gV_p = \frac{1}{2} f v \quad (S11)$$

Since friction factors for non-spherical particles are unavailable, Hiemenz and Rajagopalan [8] suggest the following equation to estimate the effect of nonsphericity and solvation on the friction factor:

$$\frac{f}{f_0} = \frac{f}{f^*} \cdot \frac{f^*}{f_0} \quad (\text{S12})$$

Where f_0 is the friction factor for an unsolvated spherical particle; f^* is the friction factor for a spherical particle having the same volume as the solvated particle of mass m ; f^*/f_0 measures the increase in f due to solvation; f/f^* measures the increase in f due to asymmetry.

Since carbon nanotubes are not solvated particles:

$$\frac{f}{f_0} = \frac{f}{f^*} \cdot \frac{f^*}{f_0} = \frac{f}{f^*} \quad (\text{S13})$$

In order to determine the ratio f/f^* for the MWCNTs it is necessary to assume that the MWCNTs are prolate ellipsoids with $a \gg b$ (a , b are the semi major and minor axes, respectively) (Figure 6) as a friction factor for cylinders has not been developed, to our knowledge.

Figure S-3. Ellipsoids of Revolution (Formed By Rotating an Ellipse about Either Its Major Axis (Prolate) or Minor Axis (Oblate)) (Adapted from [9])

The ratio f/f^* for prolate ellipsoids ($b/a < 1$) is [10]:

$$\frac{f}{f^*} = \frac{\left[1 - \left(\frac{b}{a}\right)^2\right]^{1/2}}{\left(\frac{b}{a}\right)^{2/3} \ln \left(\frac{1 + \left[1 - \left(\frac{b}{a}\right)^2\right]^{1/2}}{\frac{b}{a}} \right)} \quad (\text{S14})$$

The friction factor of the unsolvated spherical particle which has the same volume as the cylindrical particle is:

$$f_0 = 3\pi\mu d_o = 3\pi\mu \left(\frac{3}{2} d_p^2 l \right)^{1/3} \quad (\text{S15})$$

Where d_o is the diameter of the equivalent unsolvated spherical particle. The ultimate settling velocity is therefore:

$$v = \frac{0.146(\rho_p - \rho)g(d_p^2 l)^{2/3}}{\frac{\mu \left[1 - \left(\frac{d_p}{l}\right)^2\right]^{1/2}}{\left(\frac{d_p}{l}\right)^{2/3} \ln \left(\frac{1 + \left[1 - \left(\frac{d_p}{l}\right)^2\right]^{1/2}}{\frac{d_p}{l}} \right)}} \quad (\text{S16})$$

And the theoretical collector efficiency due to sedimentation is:

$$\eta_G = \frac{0.146(\rho_p - \rho)g(d_p^2 l)^{2/3}}{\mu v_o \left[1 - \left(\frac{d_p}{l} \right)^2 \right]^{1/2} \left(\frac{d_p}{l} \right)^{2/3} \ln \left(\frac{1 + \left[1 - \left(\frac{d_p}{l} \right)^2 \right]^{1/2}}{\frac{d_p}{l}} \right)} \quad (\text{S17})$$

iii) Diffusion

The final mechanism considered for MWNCT removal from the bulk fluid is diffusion across the thin liquid boundary layer adjacent to the collector surface for subsequent removal at the collector surface. The flux across this boundary layer has been determined by solving the convective/diffusion equation [11]

$$J_D = 7.98 C_0 D^{2/3} v_o^{1/3} \left(\frac{d_c}{2} \right)^{4/3} \quad (\text{S18})$$

Where J_D is the diffusive flux of particles through the boundary layer to the collector and D is the diffusion coefficient of the particle which is defined as [8]:

$$D = \frac{kT}{f} \quad (\text{S19})$$

Where k is Boltzmann's constant and T is temperature. Solving yields a theoretical collector efficiency due to diffusion for the MWCNTs of:

$$\eta_D = \frac{4.03 \left[kT \ln \left(\frac{1 + \left(1 - \left(\frac{d_p}{l} \right)^2 \right)^{1/2}}{\frac{d_p}{l}} \right) \right]^{2/3}}{\left(3\pi \mu d_c v_o \left(\frac{3}{2} d_p^2 l \right)^{1/3} \left(\frac{l}{d_p} \right)^{2/3} \left(1 - \left(\frac{d_p}{l} \right)^2 \right)^{1/2} \right)^{2/3}} \quad (\text{S20})$$

In summary, particle filtration theory is based on the assumption that retained particles are spherical, however many particles are far from spherical (eg: bacteria, nanotubes). New relationships for the theoretical collector efficiencies due to interception, gravity sedimentation and diffusion were developed for cylindrical particles to broaden the applicability of colloid filtration theory.

1 Table S1: Fitted parameter and RMSE

	QUARTZ SAND								
	Fitted Parameters				RMSE				
	α	$S_{\max}$ (mg/g)	$k_{\det}$ (s^{-1})	α_l (m)	$v = 43$ m/d	$v = 21$ m/d	$v = 4$ m/d	$v = 0.42$ m/d	Total
CFT only (high IS)	5.05×10^{-2}	N/A	N/A	1.12×10^{-3}	0.56	0.60	0.16	0.86	2.18
CFT with detachment (high IS)	6.02×10^{-2}	N/A	1.19×10^{-5}	1.10×10^{-3}	0.54	0.56	0.20	0.72	2.02
CFT with blocking term (Smax) (high IS)	1.21×10^{-1}	1.18×10^{-5}	1.57×10^{-11}	1.15×10^{-3}	0.41	0.41	0.31	0.24	1.36
CFT with blocking term (Smax) (low IS)	5.97×10^{-2}	1.18×10^{-5}	6.41×10^{-12}	8.30×10^{-4}	N/A	N/A	N/A	0.15	0.15
	GLASS BEADS								
	Fitted Parameters				RMSE				
	α	$S_{\max}$ (mg/g)	$k_{\det}$ (s^{-1})	α_l (m)	$v = 0.42$ m/d (low IS)				
CFT only (high IS)	2.34×10^{-2}	N/A	N/A	5.97×10^{-4}	0.36				
CFT with detachment (high IS)	2.34×10^{-2}	N/A	7.43×10^{-11}	5.97×10^{-4}	0.36				
CFT with blocking term (Smax) (high IS)	7.22×10^{-2}	5.38×10^{-6}	7.95×10^{-12}	7.43×10^{-4}	0.042				
CFT with blocking term (Smax) (low IS)	1.89×10^{-2}	3.55×10^{-6}	1.98×10^{-11}	1.45×10^{-5}	0.085				

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