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Effect of hydrodynamic diameter on the sieving of waterborne carbon nanotubes by porous membranes

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ABSTRACT

Carbon nanotubes (CNTs) are rapidly influencing the development and applications of membrane technology for water treatment. Passage of CNTs through membrane pores is becoming a fundamental question to water industries, as the toxicity and environmental fate of waterborne CNTs are largely unknown. This study utilized CNTs and membranes with known properties to investigate the applicability of the Ferry–Renkin sieving equation to the rejection of CNTs by porous membranes. The results demonstrate that the hydrodynamic size of CNTs is more important than their physical dimensions for rejection. Moreover, the classical sieving equation provided reasonable predication of the experimental results. Important for water industries, current membranes used in drinking water treatment should be efficient barriers for waterborne CNTs leached from composite membranes or released from wastewater effluents. Further, process streams containing CNTs may be treated using membrane filtration for CNT recovery. However, micron-pore-size membranes used in previous studies for CNT-membrane fabrication may not be efficient in protecting CNT breakthrough. Since the hydrodynamic diameters of waterborne CNTs are usually above 150 nm, as a general rule of thumb, membranes with pore size smaller than 100 nm need to be used to ensure the safety of CNT membranes.

1. Introduction

Carbon nanotubes (CNTs) are increasingly being studied for their potential application into a variety of technologies, including drinking water treatment. CNTs are organic materials with fiber-like geometry and consist of graphene sheet(s) rolled into single- or multiple-layer tubes, i.e. single-walled CNTs (SWCNTs) and multi-walled CNTs (MWCNTs) [1]. Since their first discovery in 1991 and the subsequent establishment of the method for large-scale synthesis [1,2], the production and use of CNTs in industrial and consumer products has increased dramatically due to their superb electrical, mechanical, thermal, and chemical properties [3,4]. Currently, their annual production has increased to several hundreds tons per year, resulting in a decrease of their market prices to as low as $100 per kilogram and registered uses in 36 types of consumer products [3,5].

Waterborne CNTs may be produced during the separation and purification phase of CNT manufacturing [3,6,7], or during dispersion of CNTs for the manufacturing of CNT composites [3]. Use of CNT products, such as during manufacturing of consumer products [8] and water treatment [9–14], may also lead to the formation of waterborne CNTs. These waterborne CNTs will be released into aquatic environments and adsorb natural organic matter (NOM) and counter-ions, becoming stabilized by repulsive steric and/or electrostatic forces [15–18]. If these repulsive forces are not strong enough to overcome the attractive forces between hydrophobic CNT surfaces, the CNTs will aggregate, settle, and finally accumulate into the sediment phase or into soil during subsurface infiltration. As a result, the environmental concentrations of CNTs in surface water is often predicted at relatively low levels [19,20]. However, actual environmental concentrations of CNTs are likely to increase faster than expected due to the increasing number of available CNT-containing commercial products and because novel

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techniques for the dispersion of CNTs are quickly developed to facilitate industrial applications (i.e., oxidation, functionalization, etc.) [3,21]. These modified CNTs with enhanced colloidal stabilities may remain in the aqueous phase longer than pristine (or unmodified) CNTs after entering the environment [22].

The advance in CNT-related products is rapidly influencing the development and application of membrane technology to control the release of CNTs into the environment in three ways. First, wet production is favorably adopted by CNT factories over dry production to minimize the workers' exposure to airborne CNTs, given the proven toxic effects of inhaled CNTs on the human respiratory system [23,24]. Consequently, membrane filtration has been used by the factories to efficiently recover or separate waterborne CNTs from the process streams [3].

Second, even at relatively low levels, water pollution by CNTs is still a serious concern to water industries due to uncertainties in the health effects associated with long-term human exposure to waterborne CNTs [3,24]. Removal of stabilized CNTs by conventional coagulation treatment has been considered, but the efficiency is dependent on source water quality, particularly the level of NOM [25,26], thereby making it difficult to manage in full-scale water treatment. Consequently, utilizing the sieving effects of porous membrane is potentially a better choice for the treatment of water and wastewater contaminated by colloidal-stable CNTs.

The third aspect has more direct impacts on membrane science and technology. Recently, a vast number of studies have been reported on the synthesis and laboratory testing of CNT-enabled membranes or filters for water treatment and desalination [27–33]. Despite the promising performances obtained with these membranes, leaching of CNTs (even at low levels) into the treated water or during membrane cleaning is a major concern to the membrane industry and the general public. This has hindered full-scale applications of CNT-membranes in drinking water systems. In order to eliminate this concern, a fundamental question needs to be answered, i.e., why would CNTs pass through one membrane but be rejected by another or practically, what relevant criteria can be used to design a membrane filtration system without the concern of CNT breakthrough? The answer to this question is critically important to the application of porous membranes to the recovery and removal of waterborne CNTs as described above.

Currently, little information is available in the literature on the filtration of waterborne CNTs by porous membranes. As elucidated below, application of existing knowledge on membrane sieving to waterborne CNTs has been in doubt due to the extreme length to diameter ratio of CNTs (>100). Numerical models for packed bed filtration of CNTs have been developed by incorporating straining effects into classical physicochemical filtration models [34,35]. However, adaption of these models to membrane filtration is difficult due to the differences in dominant rejection mechanisms between packed bed filtration and membrane sieving. Therefore, this study aimed to fill this research gap by using a modified CNT filtration model. The objectives of this study were three fold: 1) experimentally determining major characteristics of CNTs and membranes that influence the passage/rejection of stabilized CNTs by porous membranes; 2) modeling the rejection of CNTs using the sieving equation; and 3) based on experimental and modeling results, identifying suitable conditions for the control of CNT breakthrough during membrane filtration.

It was hypothesized that hydrodynamic sizes, instead of geometric sizes, of CNTs play a primary role in CNT rejection by porous membranes. We therefore expected porous membranes with pore sizes smaller than the hydrodynamic sizes of CNTs to be effective for CNT rejection and recovery. Solution chemical conditions unfavorable to CNT aggregation and physicochemical filtration were chosen to ensure the dominant effects of membrane sieving on CNT filtration.

2. Theory

2.1. Physical and hydrodynamic sizes of waterborne CNTs

CNTs possess needle-like geometry with nano-sized diameters (d, m) and micro-sized lengths (L, m) [1,3]. As a result, aspect ratios of CNTs ($\psi = L/d$, dimensionless) are normally between 100 and 1000. These high ψ values substantially deviate from the spherical particle condition previously used in the development of the sieving model for porous membranes. An equivalent diameter (d_0, m) may be calculated by assuming a spherical particle with the same volume as a CNT. Since a CNT may be approximated as a cylinder, we obtain:

$$d_0 = \sqrt[3]{1.5 d^2 L} \tag{1}$$

The physical sizes described above do not account for interactions between water molecules and CNTs. Like spherical particles, CNTs dispersed in water will undergo random Brownian motions due to the collisions with water molecules [36]. By measuring temporal variations in the intensity of the light scattered by CNTs under Brownian motion, the diffusion coefficient of CNTs (D_t, $\mathrm{m^2\,s^{-1}}$) can be determined experimentally by dynamic light scattering (DLS). Subsequently, the hydrodynamic diameter of CNTs (d_H, m) can be estimated using the Stokes–Einstein equation:

$$D_t = \frac{kT}{3\pi\eta d_H} \tag{2}$$

where k [J/K] is the Boltzmann constant, T [K] is the absolute temperature, and η [Pa s] is water viscosity. In addition to the DLS analysis, the following expression has been established by [37] for computing the diffusion coefficient of SWCNTs.

$$D_t = \frac{kT}{3\pi\eta L}(\ln\psi + 0.32) \tag{3}$$

A generalized relationship for nanotubes has also been validated [38]:

$$D_t = \frac{\left(\frac{kT}{3\pi\eta L}\right)}{\sqrt{1-\left(\frac{1}{\psi}\right)^2}} \ln\left[\frac{1+\sqrt{1-\left(\frac{1}{\psi}\right)^2}}{\left(\frac{1}{\psi}\right)}\right] \tag{4}$$

Since $\psi > 100$ for most CNTs, Eq. (4) may be simplified as:

$$D_t = \frac{kT}{3\pi\eta L}\ln(2\psi) \tag{5}$$

Eq. (5) yields D_t values less than 6% above those computed using Eq. (3), and therefore, provides a reasonably good approximation for SWCNTs. Combination of Eqs. (5) and (2) yields:

$$d_H = \frac{L}{\ln(2\psi)} \tag{6}$$

According to Eq. (6), L has a stronger impact on d_H than ψ because the values of $\ln(2\psi)$ vary in a narrow range of 5.3–7.6 for common CNT samples ($1000 > \psi > 100$), while those of L change from a few tenths of a micron to dozens of microns. Consequently, the values of d_H calculated by Eq. (6) range approximately from a few hundred nanometers for short SWCNTs to a few microns for long MWCNTs.

2.2. Particle filtration by porous membranes

Filtration of particles by a clean porous membrane involves particle-membrane collisions induced by convective flow and particle attachment on membrane surfaces by favorable physicochemical interactions. During these processes, spherical particles