

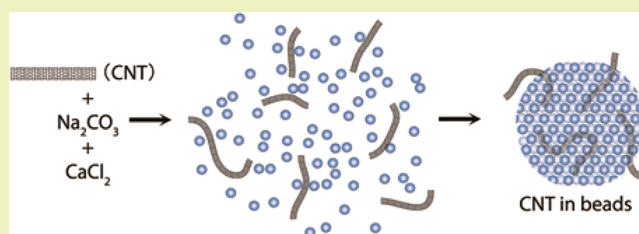
# Entrapment and Removal of Carbon Nanotubes and Fullerenes by Coprecipitation with Calcium Carbonate Beads

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## S Supporting Information

**ABSTRACT:** Production, growth, and obvious health and environmental concerns about engineered nanomaterials (ENM) require development of methods for their entrapping/removal. Here, we propose a facile method for removal of carbon nanomaterials from water solutions based on coprecipitation with vaterite ( $\text{CaCO}_3$ ) beads.  $\text{CaCO}_3$  beads are formed by an aggregation of initially formed amorphous  $\text{CaCO}_3$  nanoparticles that efficiently incorporate nanomaterials in solution into the growing beads so that can be finally removed by settling. We show that by using this approach, a high percentage of fullerenes and carbon nanotubes (typically over 95%) can be removed in a broad range of ENM concentrations. We also discuss potential applications of the method for treatment of contaminated water.

**KEYWORDS:** Nanomaterials pollution, Nanomaterials removal, Coprecipitation, Calcium carbonate beads



## INTRODUCTION

The amount of produced engineered nanomaterials (ENM) has been progressively increasing since the beginning of the 21st century,<sup>1</sup> therefore, the environmental fate of nanomaterials requires our close attention.<sup>2</sup> As a result of greater use and disposal of ENM-containing products, the concentrations of ENM in surface waters are believed to grow over time.<sup>3</sup> On the other hand, studies on ENM toxicity over two past decades revealed numerous cases of their adverse effects on living organisms.<sup>4</sup> The behavior of nanomaterials in the environment and in biological samples, i.e., chemical and physical transformations of ENM and their transport properties, was also intensively studied, and an overall complexity of the pathways associated with ENM transformations was revealed.<sup>5</sup> Anticipating an increase in the ENM amount in the environment<sup>6</sup> makes development of strategies for removal of ENM pollutions important.

Although the problem of nanocontamination is currently well recognized, the removal of nanomaterials is still poorly addressed, and the number of relevant reports is limited. For example, it was shown that conventional protocols used for wastewater as well as drinking water treatments to remove inorganic nanoparticles are generally not efficient for decontamination of water sources due to a substantial “breakthrough” of inorganic nanoparticles.<sup>7–10</sup> Treatments of carbon nanotubes by inducing their aggregation and separation by filtration<sup>11</sup> or by complexation with magnetic nanoparticles and removal in a magnetic field<sup>12</sup> were successful only in

removal of relatively high concentrations of carbon nanomaterials with residual concentrations of ENM as high as 0.5 mg/L. Several treatment techniques were proposed for removal of water-soluble fullerenes. It was shown that biomass concentration plays an important role in both  $\text{C}_{60}$  biosorption and successive removal efficiency.<sup>13,14</sup> In solutions of natural organic matter, fullerene was shown to form water-stable aggregates that can be removed from water in a series of alum coagulation, flocculation, sedimentation, and filtration processes<sup>15,16</sup> until about 10  $\mu\text{g/L}$  levels. Because ENM's fate during wastewater treatment is dramatically influenced by chemical and physical transformations such as dissolution and aggregation, biodegradation, sorption of ENM on biomass, etc., further systematic research is still required.<sup>17</sup> On the other hand, risk of potential accidental exposure of a large amount of ENM into the environment demands low-cost efficient methods for nanomaterials entrapping to prevent spreading of ENM pollution.

In general, a simple but robust strategy for ENM removal from liquids is to induce ENM aggregation into particles of micrometer size or larger to further separate them by settling or filtration. Such coprecipitation treatment was earlier applied in removal of low molecular weight chemicals having affinity to precipitating solids, for example, in arsenic removal,<sup>18</sup> and in

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incorporation of polymeric substances such as NOM into precipitates of  $\text{CaCO}_3$  during water softening.<sup>19</sup> Coprecipitation strategy is particularly suitable for nanomaterials having a high surface energy and tendency to aggregate with each other or adsorb on surfaces of other colloids in solution. Recently, we proposed a method for entrapment of various ENM using a pair of oppositely charged polyelectrolytes that assemble into a three-component water-insoluble precipitate.<sup>20</sup> However, the method had a number of practical limitations, such as poor performance toward small (<10 nm) ENM (quantum dots, fullerenes) and relatively high cost.

Herein, we report a novel facile method based on coprecipitation of water-dispersed nanomaterials with calcium carbonate beads. We tested this method for removal of carbon nanomaterials, such as carbon nanotubes and fullerenes that are among most widely used classes of nanomaterials present. We tested the proposed method over a wide concentration range of the nanomaterials to address its practicality for fast removal from heavily contaminated liquids (such as wastewater) as well as moderately contaminated samples containing environmentally relevant concentrations of nanomaterials.

## EXPERIMENTAL SECTION

**Materials.** Hydroxyfullerene, ( $\text{C}_{60}(\text{OH})_n$ ,  $n = 6-12$ , Nanom spectra D100) was purchased from Frontier Carbon, Japan. Multiwalled carbon nanotubes MWCNT-OH containing hydroxyl surface groups (outer diameter, 10–20 nm; length, 0.5–2  $\mu\text{m}$ ) and multiwalled carbon nanotubes MWCNT-COOH containing carboxyl surface groups (outer diameter, 10–20 nm; length, 0.5–2  $\mu\text{m}$ ) were purchased from Nanostructured & Amorphous Materials, Inc. (U.S.A.).  $\text{Na}_2\text{CO}_3$  and  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  were purchased from Kanto Chemical Co., Inc. (Japan) and Wako (Japan), respectively. Either Milli-Q water or a sample from Kagami Lake (Nagoya, Japan, coordinates 35°15'73"63, 136°96'36"02, pH 7.8 (25 °C), 28 mg/L suspended solids) was used as media for dispersing of nanomaterials and removal tests.

**Methods. UV–Vis Spectroscopy.** UV–vis spectra of nanomaterials were recorded on a Jasco J-630 spectrophotometer in 1.0 cm  $\times$  1.0 cm  $\times$  5.0 cm quartz cells at a room temperature. The amount of nanomaterials was calculated from the absorbance intensity at  $\lambda = 330$  nm.

**Light and Fluorescence Microscopy.** Light microscopy (LM) and fluorescence microscopy (FM) observations were performed using an ECLIPSE TE2000-U (Nikon, Japan) microscope equipped with an oil-immersed 100X lens and a Nikon DS-R1i digital camera (Micron Optics, Cedar Knoll, NJ). Digital color pictures were obtained using an image-analysis system, a Nikon Eclipse 80i microscope (Micron Optics, Cedar Knoll, NJ), and NIS-Elements BR 3.1 software (Micron Optics, Cedar Knoll, NJ).

**Transmission Electronic Microscopy (TEM).** TEM observations were performed at room temperature using a HITACHI H-800 microscope (Japan) at 200 kV acceleration voltage. A drop of a solution containing  $\text{CaCO}_3$  beads after 10 min settling and triple washing with large volumes of water was placed onto a 3 mm copper grid covered with a collodion film. The blotted solution was removed after 3 min of incubation with a filter paper, and the sample was dried at room temperature before observation.

**Zeta Potential Analysis.** Zeta potential measurements of nanomaterials were performed on a Zetasizer Nano ZS (Malvern, England) in Milli-Q water at pH 7.4 for MWCNT and 6.8 for  $\text{C}_{60}\text{-OH}$ .

**Sample Preparation. Hydroxyfullerene ( $\text{C}_{60}\text{-OH}$ ).** Hydroxyfullerenes ( $\text{C}_{60}(\text{OH})_n$ ) were dispersed in water at 0.1 g/L concentration and sonicated for 15 min. Insoluble fullerenes were separated by centrifugation at 15,000 rpm for 15 min, and the supernatant was used as a stock solution for further investigations. To determine the concentration of fullerene in solution, a small amount of hydroxyfullerene was completely dissolved in 1,4-dioxane, and the

resulted solution was diluted 50 times by water, upon which no precipitation was observed. The absorbance at 500 nm was measured by UV–vis spectroscopy, and the extinction coefficient of hydroxyfullerene was determined. Finally, using the extinction coefficient, the concentration of the fullerene in aqueous stock solution used for further experiments was calculated from its UV–vis spectra to be 3.2 mg/L.

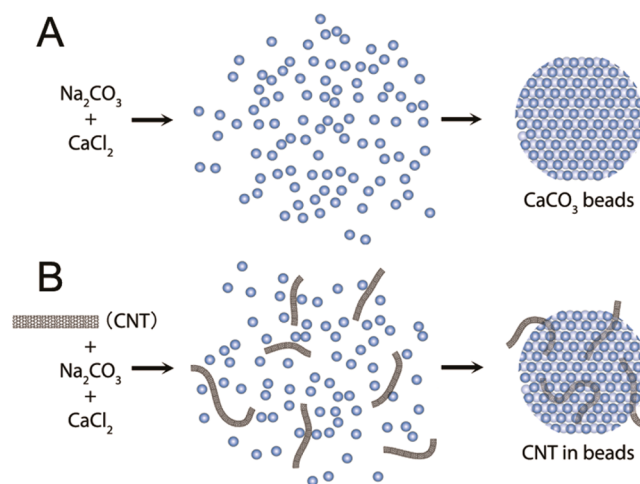
**Hydroxylated and Carboxylated Carbon Nanotubes (MWCNT-OH and MWCNT-COOH).** About 0.1 g of multiwalled carbon nanotubes MWCNT-OH or MWCNT-COOH was moistened with 2 mL of Milli-Q water for 1 day, and the resulted slurry was added to 30 mL of Milli-Q water containing 200  $\mu\text{L}$  of 0.5 NaOH solution and sonicated at 20 kHz for 2.5 h. The resulted suspension was centrifuged at 11,000 rpm for 30 min to remove nondispersed nanotubes. The concentration of MWCNT-OH and MWCNT-COOH in the resulted sample was determined gravimetrically by drying 1 mL of a carbon nanotube solution sample at 100 °C for 3 h and weighing the residue on Sartorius balances with readability to 0.1 mg. The concentration of nanotubes in solutions before and after treatment correlated with UV–vis absorbance intensity linearly according to the Lambert–Beer law within a range of MWCNT concentrations between 0.05 mg/L and 5 mg/L (Supporting Information). For fluorescence microscopy analysis, hydroxyl groups of MWCNT-OH were labeled with fluorescein using a 5-DTAF reagent (Funakoshi, Japan).

**General Protocol for Removal of Nanomaterials.** To a solution with a dispersed nanomaterial either in Milli-Q water or in lake water, equal volumes of  $\text{Na}_2\text{CO}_3$  and  $\text{CaCl}_2$  solutions of equal molar concentrations were added and stirred for 5 min, after which the mixture settled for 20–30 min. A mother liquid was separated by decantation and analyzed by spectroscopy. Precipitates were collected, washed by Milli-Q water, and observed by microscopy techniques.

## RESULTS AND DISCUSSION

According to earlier reports, mixing of equimolar solutions of  $\text{Na}_2\text{CO}_3$  and  $\text{CaCl}_2$  results in a formation of about 5  $\mu\text{m}$ -sized  $\text{CaCO}_3$  (vaterite) microbeads.<sup>21</sup> These beads, for instance, were successfully utilized as a template for layer-by-layer (LbL) fabrication of polyelectrolyte capsules having many potential applications in biological and medical fields.<sup>22,23</sup> Importantly, formation of  $\text{CaCO}_3$  microbeads proceeds through an aggregation of amorphous  $\text{CaCO}_3$  nanoparticles into larger  $\text{CaCO}_3$  particles,<sup>24</sup> as schematically illustrated in Figure 1A.

This mechanism suggests that during assembly of  $\text{CaCO}_3$  nanoparticles into  $\text{CaCO}_3$  microbeads, the nanosized matter in



**Figure 1.** (A) Mechanism of  $\text{CaCO}_3$  beads formation.<sup>25</sup> (B) Proposed mechanism of entrapment of a nanomaterial (carbon nanotubes) into  $\text{CaCO}_3$  beads.

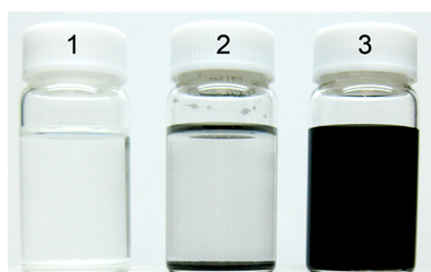
Table 1. General Characteristics of Investigated Nanomaterials

nanomaterial	C <sub>60</sub> -OH	MWCNT-OH
size (nm)	~1 nm (theoretical)	<i>d</i> (outer) = 10–20 nm, length = 0.5–2 μm (manufacturer)
ξ potential (mV) <sup>a</sup>	-20 ± 5	-50 ± 18
saturated stock solution concentration	3.2 mg/L	1.5 g/L

<sup>a</sup>In Milli-Q water at pH 7.4 for MWCNT and 6.8 for C<sub>60</sub>-OH.

solution can be efficiently entrapped into the body of CaCO<sub>3</sub> beads as schematically shown in Figure 1B, and such a system can be potentially useful for removal of nanomaterials from aqueous solution by coprecipitation with CaCO<sub>3</sub>. To test this hypothesis, we utilized the above reaction and focused on the removal of two types of carbon nanomaterials, hydroxylated multiwalled carbon nanotubes (MWCNT-OH) and hydroxyfullerenes (C<sub>60</sub>-OH). The main characteristics of the nanomaterials, i.e., their size and charge, are summarized in Table 1. We investigated both concentrated regimes between mg/L and g/L of nanomaterials relevant to wastewaters of plants or accidentally polluted aquatic systems as well as diluted solutions of ENM containing μg/L concentrations of nanomaterials relevant to drinking water treatment. The concentration of nanomaterials varied between saturated concentrations (0.5 g/L for MWCNT-OH and 0.11 mg/L for fullerenes) and the concentrations exceeding about 100 times the detection limit of spectrometer.

A mixing of equal volumes of 0.33 M CaCl<sub>2</sub> and 0.33 M Na<sub>2</sub>CO<sub>3</sub> solutions results in the formation and settling of a white precipitate of CaCO<sub>3</sub> (Figure 2, sample 1). Next, this

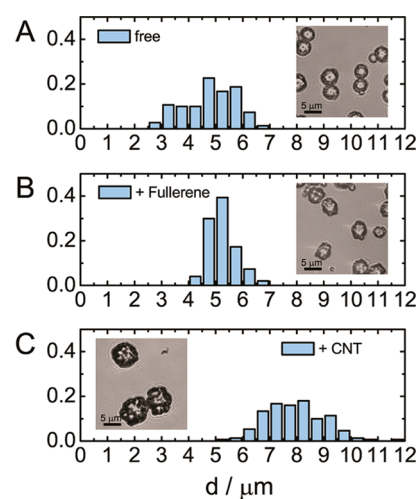


**Figure 2.** Photographic images of (sample 1) aqueous solution of Na<sub>2</sub>CO<sub>3</sub> (final concentration 0.11 M) and CaCl<sub>2</sub> (0.11 M), after CaCO<sub>3</sub> precipitation during 30 min of settling, (sample 2) solution of 0.5 g/L MWCNT-OH coprecipitated by mixing with Na<sub>2</sub>CO<sub>3</sub> (0.11 M) and CaCl<sub>2</sub> (0.11 M) after 30 min of settling, and (sample 3) original solution of MWCNT-OH diluted three times (final concentration, 0.5 g/L).

protocol was applied to solutions containing nanomaterials. Addition of only CaCl<sub>2</sub> at 0.33 M concentration to MWCNT-OH had no effect on the stability of MWCNT-OH (clear solution). Addition of only Na<sub>2</sub>CO<sub>3</sub> at 0.33 M concentration caused a slight aggregation of MWCNT-OH when MWCNT-OH concentration was high. Yet the precipitate of MWCNT-OH did not settle, and centrifugation was necessary for its separation. Successive addition of CaCl<sub>2</sub> and Na<sub>2</sub>CO<sub>3</sub> into the MWCNT solution caused immediate formation of dark gray precipitates that gradually settled down within about 10–20 min as shown in Figure 2, sample 2. For comparison, the original solution of MWCNT-OH, diluted three times to adjust its final concentration to conditions of the MWCNT-OH coprecipitation experiment, is shown in Figure 2, sample 3. The original solution of MWCNT-OH had a thick black color, while

after treatment with Na<sub>2</sub>CO<sub>3</sub> and CaCl<sub>2</sub>, the solution became almost colorless (slightly gray), indicating inclusion of most of the MWCNT-OH content into calcium carbonate precipitate. Similar solution color changes were observed during treatment of hydroxyfullerenes.

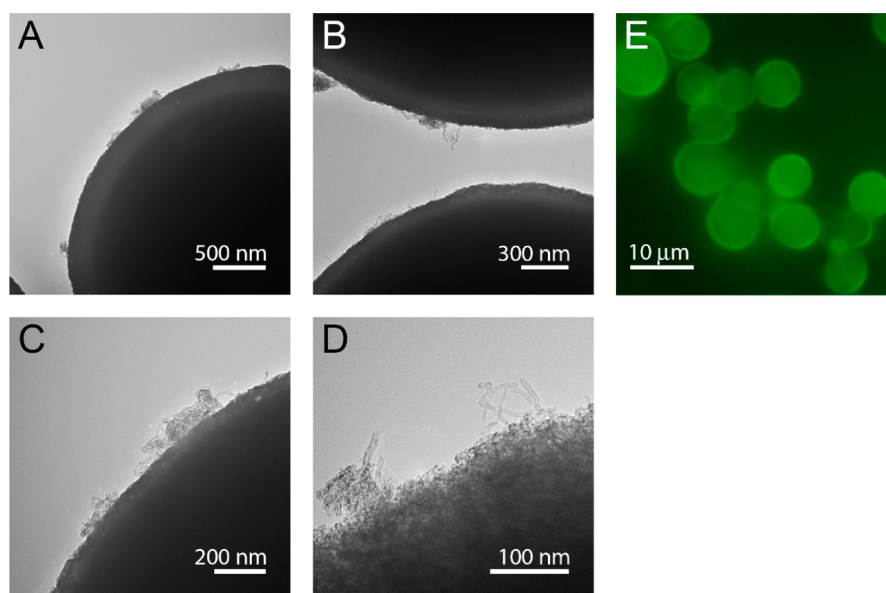
To investigate the influence of entrapped nanomaterials on CaCO<sub>3</sub> precipitate morphology, we employed light microscopy (LM). LM images of beads formed in solution without nanomaterials and in the presence of either 50 mg/L MWCNT-OH or 0.11 mg/L C<sub>60</sub>-OH are shown in Figure 3



**Figure 3.** Light microscopy images and corresponding size distributions of CaCO<sub>3</sub> beads formed in solutions of Na<sub>2</sub>CO<sub>3</sub> and CaCl<sub>2</sub> (A) and in the presence of either fullerenes (0.11 mg/L) (B) or carbon nanotubes (50 mg/L) (C). The scale bar on LM images is 5 μm. Size distributions were built by measuring 150 beads for each sample.

together with size distributions. An average size of CaCO<sub>3</sub> beads formed in water solutions was  $4.8 \pm 0.9 \mu\text{m}$ , in agreement with earlier studies.<sup>23</sup> The size of beads depended slightly on CaCl<sub>2</sub> and Na<sub>2</sub>CO<sub>3</sub> concentrations. In particular, the size of beads increased to 10–25 μm at 10-fold lower CaCl<sub>2</sub> and Na<sub>2</sub>CO<sub>3</sub> concentrations (0.011 M).

After formation of beads in solutions of either nanomaterial, the spherical morphology of the beads was preserved in both cases. At low concentrations of nanomaterials, the average size of the beads did not change during entrapment of nanomaterials. For example, the size of beads containing hydroxyfullerenes entrapped from 0.11 mg/L solutions was  $5.3 \pm 0.5 \mu\text{m}$ . At higher concentrations of nanomaterials, the size of the beads slightly increased, for example,  $7.9 \pm 1.1 \mu\text{m}$  beads were formed after coprecipitation with nanotubes from 50 mg/L MWCNT-OH solutions. The latter increase is ascribed to a higher concentration of MWCNT-OH than fullerene used for observations. Due to solubility limitations of fullerenes (Table 1), the influence of a higher concentration of fullerenes on beads size cannot be verified.



**Figure 4.** (A–D). Typical TEM images of  $\text{CaCO}_3$  beads with MWCNT-OH. The sample was prepared by coprecipitation of 50 mg/L MWCNT-OH with  $\text{Na}_2\text{CO}_3$  (0.11 M) and  $\text{CaCl}_2$  (0.11 M). (E) Fluorescence microscopy image of  $\text{CaCO}_3$  beads with fluorescein-labeled MWCNT-OH. The sample was prepared by coprecipitation of 5 mg/L fluorescein-labeled MWCNT-OH with  $\text{Na}_2\text{CO}_3$  (0.11 M) and  $\text{CaCl}_2$  (0.11 M).

The surface of the beads was observed by transmission electron microscopy (TEM). Figure 4 shows typical TEM images of  $\text{CaCO}_3$  beads formed in a 50 mg/L solution of MWCNT-OH. In contrast to the original beads with a smooth surface structure (data not shown), the surface of the beads formed in a solution containing carbon nanotubes was decorated with a nanotube protruded outward bead surface (Figure 4A–D). TEM observations of beads with fullerenes were not useful due to the small size of the fullerenes ( $\sim 1$  nm).

To analyze the spatial distribution of nanotubes inside beads, we labeled MWCNT-OH with a fluorescent dye (fluorescein) and entrapped them into  $\text{CaCO}_3$  beads by coprecipitation. Figure 4E shows fluorescence microscopy images of beads containing labeled MWCNT-OH. Fluorescence intensity of the beads was evenly distributed over the beads' volume, which is in a good agreement with the mechanism of nanomaterial coprecipitation illustrated in Figure 1B, i.e., the nanomaterials were entrapped due to coaggregation with  $\text{CaCO}_3$  nanoparticles at the stage of microbead formation rather than by adsorption of nanomaterials onto a surface of formed beads.

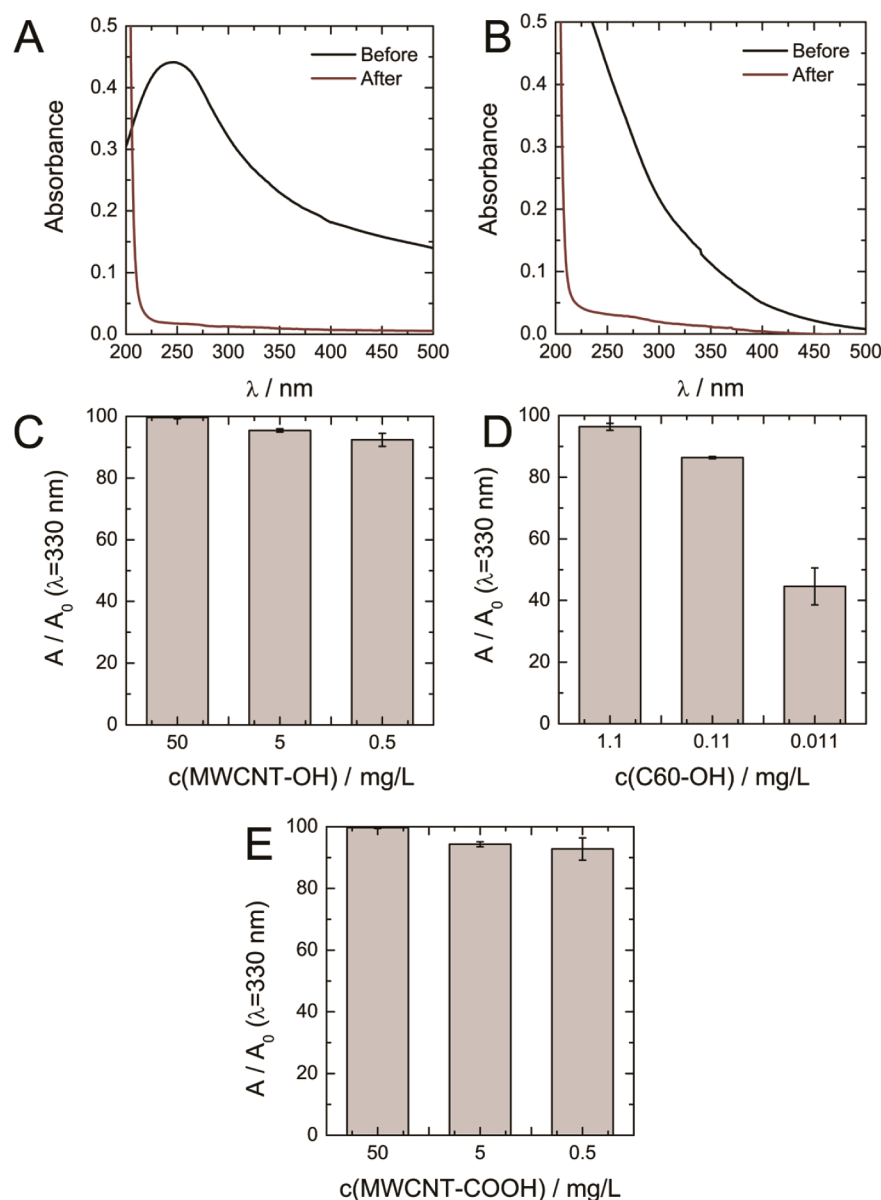
For a quantitative analysis of carbon nanomaterials entrapment efficiency, the concentrations of MWCNT-OH and  $\text{C}_{60}$ -OH in solution were monitored by UV–vis spectroscopy at  $\lambda = 330$  nm for both MWCNT-OH and  $\text{C}_{60}$ -OH. Figure 5A and B show UV–vis spectra of MWCNT-OH and  $\text{C}_{60}$ -OH, respectively, in Milli-Q water before and after coprecipitation with  $\text{CaCO}_3$ , and it is clear that after coprecipitation of MWCNT-OH and  $\text{C}_{60}$ -OH with  $\text{CaCO}_3$  beads the absorbance intensity of both carbon nanomaterials dramatically decreased.

Figures 5C and D show the data of the removal efficiency of carbon nanomaterials from solutions with different MWCNT-OH and  $\text{C}_{60}$ -OH content based on three independent experiments. The concentration regimes chosen for MWCNT-OH and  $\text{C}_{60}$ -OH were different, which is, on one hand, due to the limitation in nanomaterials solubility and on the other hand due to the detection limit of nanomaterials by UV–vis spectroscopy. Figure 5C shows that removal of carbon nanotubes was higher than 90% at any concentration of

MWCNT-OH. Due to a more diluted concentration regime for  $\text{C}_{60}$ -OH, the highest studied concentration of fullerenes was about 1 mg/L (Figure 5D). At this concentration, similar to 5 mg/L MWCNT-OH, the entrapment efficiency was high ( $>95\%$ ). However, in 10- and 100-times diluted solutions, fullerenes entrapment efficiency decreased to about 80% and 40%, respectively. The entrapment efficiency of the fullerenes is noteworthy because it is advantageous in comparison to the earlier proposed method of nanomaterials removal by a pair of polyelectrolytes, which was not efficient for the entrapment of fullerene without ultracentrifugation.<sup>20</sup> To address the effect of the surface groups of nanomaterials, the uptake efficiency of carbon nanotubes with carboxylic surface groups (MWCNT-COOH) was studied under the same conditions as MWCNT-OH (Figure 5E). The uptake of MWCNT-COOH by  $\text{CaCO}_3$  beads was very similar to that of MWCNT-OH, indicating that the proposed method works equally well in spite of the different nature of functional groups on the nanotube surface.

Although the linearity of UV–vis absorbance of both nanomaterials against ENM concentration was confirmed (Supporting Information), it should be mentioned that the presence of nano- or microparticles in solution can affect the absorbance intensity of nanomaterials. However, the aggregation phenomenon during coprecipitation can only cause an increase in the absorbance intensity due to light scattering caused by aggregates. In such a case, it would lead to overestimation of the remaining nanomaterial concentration in solution, i.e., underestimation of the removal efficiency; therefore, the actual data of ENM uptake percentage can be even higher.

The capacity of microbeads for nanomaterial uptake in terms of ENM weight per weight of beads was calculated at different experimental conditions, and the highest, about 1% (w/w), entrapment capacity was found for high concentrations of MWCNT-OH (0.5 g/L). As will be shown later, 1% ENM uptake limitation might be caused by a repulsion between charged nanomaterials destabilizing microbeads. However, despite the low capacity,  $\text{CaCO}_3$  precipitate can be solubilized,



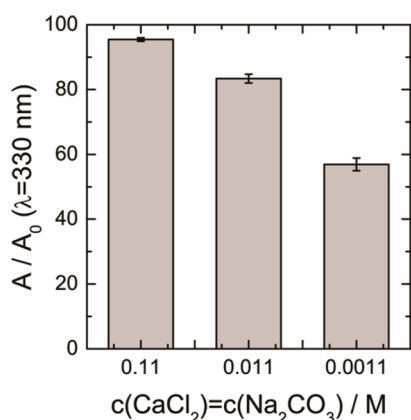
**Figure 5.** Removal efficiency of carbon nanomaterials by coprecipitation with  $\text{CaCO}_3$  beads. (A) UV-vis spectra of 50 mg/L MWCNT-OH before and after coprecipitation. (B) UV-vis spectra of 0.11 mg/L  $\text{C}_{60}$ -OH before and after precipitation with  $\text{CaCO}_3$  beads. (C–E) Removal efficiency of MWCNT-OH (C),  $\text{C}_{60}$ -OH (D), and MWCNT-COOH (E) at various concentrations by precipitation with  $\text{CaCO}_3$  beads. The removal efficiency was calculated as a ratio between absorbance intensities at  $\lambda = 330$  nm before and after coprecipitation with beads. The data for removal of MWCNT-OH from 0.5 g/L solution ( $97.9 \pm 1.1\%$ ) are not shown. Error bars show a standard deviation from the mean value of three independent measurements.

separated from nanomaterials, and reused; thus, the required amount of  $\text{CaCO}_3$  in this method can be substantially reduced.

Although the proposed method was mainly designed to target heavily polluted water and wastewater treatment, in some cases, for example, for drinking water treatment, a high ionic strength of cleared water after treatment might require further post-treatment. Therefore, it was important to determine whether lower concentrations of  $\text{CaCl}_2$  and  $\text{Na}_2\text{CO}_3$  can be utilized in the proposed method. From earlier studies, it is known that under moderate alkalinity (pH 10) spherical particles of vaterite ( $\text{CaCO}_3$ ) can be formed by the mechanism in Figure 1A even at as low as 15 mM of  $\text{CaCl}_2$  and  $\text{Na}_2\text{CO}_3$  concentrations.<sup>26</sup> To verify the efficiency of ENM removal at lower ionic strengths, we used 10- and 100-times diluted solutions of  $\text{CaCl}_2$  and  $\text{Na}_2\text{CO}_3$ , i.e., 11 mM and 1.1 mM final

concentrations of precipitate-forming reactants to treat 5 mg/L MWCNT solutions. The results in Figure 6 indicate that at 10-fold decrease in  $\text{CaCl}_2$  and  $\text{Na}_2\text{CO}_3$  concentrations the efficiency of MWCNT removal remained high, over 80%, and even at 100-fold lower concentrations, over 50% of the nanomaterials could be removed by coprecipitation. Therefore, the ionic strength of water after treatment by the proposed method can be decreased to mM monovalent ions concentration but multiple coprecipitation runs should be necessary to achieve higher removal ratios of the dispersed ENM.

It is well known that without stabilization, either electrostatic or steric, nanoparticles in solution are unstable and aggregate into bulky precipitate.<sup>27</sup> In the present study, fullerenes and carbon nanotubes are stabilized due to their electrostatic charge of either carboxylic or hydroxyl groups on the surface of



**Figure 6.** Removal efficiency of carbon nanotubes (5 mg/L) by coprecipitation with  $\text{CaCO}_3$  beads formed by mixing  $\text{CaCl}_2$  and  $\text{Na}_2\text{CO}_3$  at different concentrations. Error bars show a standard deviation from the mean value of three independent measurements.

nanomaterials. Electrostatic charge causes repulsion between nanoparticles and stabilization in solution. On the other hand, at short distances, the particles attract each other by van der Waals forces, and without the stabilization explained above, the dispersion of nanoparticles coagulates. For example, it was experimentally demonstrated in recent numerous studies<sup>28,29</sup> that due to overweighing of electrostatic repulsive forces by van der Waals attractive forces ENM strongly aggregate at high ionic strength. In our method, coagulation occurs between nanoparticles of  $\text{CaCO}_3$  and targeted nanomaterials, although the driving force is essentially van der Waals attraction, which becomes predominant at high ionic strengths, i.e., at high concentrations of  $\text{Na}_2\text{CO}_3$  and  $\text{CaCl}_2$ .

Formation of beads from  $\text{CaCO}_3$  nanoparticles and nanomaterials is driven by a high surface energy of nanoscale particles, but in aqueous solutions, nanomaterials are substantially charged (Table 1). This may affect the stability of beads due to repulsion between ENM. Such repulsion interactions might be a reason for an increase in the size of the beads incorporating large amounts of nanomaterials, which was observed during uptake of MWCNT from their concentrated solutions (Figure 3C). On the other hand, it may be a reason for a decrease in nanomaterials uptake efficiency at lower concentrations of  $\text{CaCO}_3$  beads (Figure 6) due to about a 1% upper limit of entrapped nanomaterial weight to bead weight explained above.

To address the applicability of the coprecipitation method to an environmental sample, we tested the same removal method using a lake water sample. The results of the carbon nanomaterial removal are compared in Table 2. It is clear that the removal efficiencies of carbon nanomaterials are similar for ENM treatment in distilled water (Milli-Q) and in an environmental sample. Interestingly, an unexpectedly high uptake percentage was found in the lake sample compared to the Milli-Q water solution. Although the stabilization of fullerenes in solution containing natural organic matter was reported,<sup>15</sup> in our experiments, the enhanced uptake of fullerenes from the lake water sample might be caused by a simultaneous adsorption of NOM on both fullerenes and  $\text{CaCO}_3$  nanoparticles of high concentration promoting efficient coagulation and resulting in higher uptake of fullerenes during bead formation.

**Table 2.** Comparison of  $\text{C}_{60}\text{-OH}$  and MWCNT-OH Removal Efficiency from Milli-Q Water and from a Lake Water Sample Calculated as a Ratio between Fullerene or Nanotube Absorbance at  $\lambda = 330 \text{ nm}$  before and after Coprecipitation with  $\text{CaCO}_3$  Beads

nanomaterial	$\text{C}_{60}\text{-OH}$	MWCNT-OH		
initial concentration	0.11 mg/L	50 mg/L	5 mg/L	0.5 mg/L
removal efficiency in Milli-Q water	96.3 ± 1.1%	99.6 ± 0.4%	95.4 ± 0.5%	92.4 ± 2.1%
removal efficiency in lake water	>99.9%	94.4%	98.0%	84.6%

The above results show that solutions with high (g/L and mg/L) concentrations of nanomaterials can be decontaminated by coprecipitation with  $\text{CaCO}_3$  beads decreasing ENM concentrations by 10–50 times. This process is particularly relevant for treatment of plant wastewaters containing high concentrations of ENM as well as for separation of nanomaterials from complex mixtures of chemical waste. Although, we originally designed the proposed method for treatment of high concentrations of accidentally exposed ENM to prevent their spread, the process can be also considered for wastewater as well as drinking water treatment as described below.

(1) Accidental contamination. In case of accidental contamination of environmental water, the coprecipitation method can be used as a primary step for entrapment of nanomaterials to avoid their spread in the environment by, for example, simultaneous injection of  $\text{Na}_2\text{CO}_3$  and  $\text{CaCl}_2$  solutions of equal concentrations into the contaminated area. It should be mentioned that applicability of this method might be limited under acidic conditions, at which  $\text{CaCO}_3$  beads can slowly dissolve, and thus, entrapped nanomaterials can be released.

(2) Water treatment plant (WTP). Typical wastewater and drinking water treatment relies on water cleaning by using traditional coagulation, flocculation, and sedimentation operations. Because the installation of a new facility for treatment of nanomaterials by the described method is not economically reasonable, the proposed method can be incorporated into or combined with existed WTP treatment scheme. The proposal in this study method is predominately based on a precipitation of nanomaterials embedded into microsized beads, large fractions of which precipitates upon settling and can be also filtered out using an existing filtration facility of WTP. Therefore,  $\text{Na}_2\text{CO}_3$  and  $\text{CaCl}_2$  can be added to entrap ENM either before or after adding alum or another coagulant. Further flocculation, sedimentation, and filtration operations should not be influenced by the presence of  $\text{CaCO}_3$  beads with ENM; thus, all the precipitates can be removed simultaneously.

Alternatively, taking advantage of naturally occurring alkalinity and calcium ion in natural waters and supplementing with soda ash ( $\text{Na}_2\text{CO}_3$ ) or lime ( $\text{CaO}$ ) entrapment of ENM by the  $\text{CaCO}_3$  precipitate can be further developed as a more practical approach, which resembles lime softening, a process commonly used in conventional treatment of surface waters with high hardness.

In the case of drinking water, treatment of highly contaminated samples using submolar concentrations of  $\text{Ca}^{2+}$  and other ions results in a high ionic strength water that needs to be further treated before potable use.

Conventional water cleaning methods can partially remove inorganic and carbon ENM by standard procedures. Zhang et al. studied TiO<sub>2</sub> nanoparticles removal from ultrapure and tap water by alum coagulation and reported >60% removal efficiency and emphasized a correlation between removal efficiency and ionic strength of the aqueous solution.<sup>30</sup> Later, Schwab et al. studied removal of ENM from natural waters and evaluated nanomaterials “breakthrough” during drinking water treatments also using a conventional alum-based process including coagulation, flocculation, and sedimentation of fine particles.<sup>10</sup> Westerhoff et al. monitored nanomaterial removal and release from wastewater treatment plants<sup>8</sup> and concluded that 10–100 µg/L concentrations of Ti of TiO<sub>2</sub> nanoparticles remained in effluents. Removal of fullerenes from wastewater by standard techniques such as alum coagulation was also reported,<sup>15,16</sup> where the remained concentration of fullerenes was generally about 10–100 µg/L depending on the initial concentration. The research on the carbon nanotubes fate during wastewater treatment has not been yet reported. In most of studied systems, the remained concentrations of nanomaterials after conventional water treatment was significantly higher than the “no effect” concentration level of ENM, which is on the order of 1 µg/L;<sup>31</sup> it is clear that in both cases for waste waters and drinking waters that a method for a deeper removal of nanomaterials is still required to decrease ENM concentrations to “no effect” levels.

Using the proposed method of coprecipitation with CaCO<sub>3</sub> beads, we succeeded in decreasing the concentration of fullerene to about 1–5 µg/L, which is near “no effect” concentrations. After treatment of MWCNT-OH with this method, the remained concentration of MWCNT-OH (50 µg/L) was still quite high to satisfy the standards of drinking water. However, the lower concentrations were not analyzed due to instrumental limitations, and it is believed that a deeper removal is possible.

## CONCLUSIONS

In summary, we have shown that coprecipitation of carbon nanomaterials with calcium carbonate beads results in their efficient entrapment and removal from the aqueous phase. The mechanism of such an effective entrapment is obviously based on van der Waal’s interactions between initially formed CaCO<sub>3</sub> nanoparticles (Figure 1) and nanoscale matter driven by a high surface energy of nanomaterials that causes their coaggregation to reduce the surface area exposed in solution. In this report, we demonstrate only one possible procedure for ENM decontamination; however, the concept of coprecipitation in general should be further developed toward more efficient (in terms of concentration and cost) protocols for ENM removal.

## ASSOCIATED CONTENT

### Supporting Information

Dependence of UV–vis absorbance of MWCNT-OH on its concentration. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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