



Influence of ions on the coagulation and removal of fullerene in aqueous phase



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HIGHLIGHTS

- The coagulation removal efficiency of fullerene was investigated.
- Multivalent anions and humic acid can enhance C₆₀ removal due to bridging effects.
- Monovalent anions have slight effect on fullerene removal.
- Na⁺ or Ca²⁺ is not essential for flocs formation and effective C₆₀ removal.

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ABSTRACT

Increased attention has been paid to the transportation and removal efficiencies of nanoparticles during water treatment. Here, C₆₀ was selected as nano-pollutant to investigate its removal efficiency in the process of coagulation by Al³⁺ in regard to different ions. Negatively charged C₆₀ tends to adsorb hydrated Al³⁺ to form positively charged C₆₀-Al(OH)_n^{(m-6)+} particles, leading to the restabilization of C₆₀. Multivalent anions, i.e., CO₃²⁻, SO₄²⁻, HPO₄²⁻, and humic acid (HA), were shown to bridge the C₆₀-Al(OH)_n^{(m-6)+} particles together and induce the formation of flocs, resulting in enhanced C₆₀ removal (>80%). Monovalent anions, such as OH⁻, NO₃⁻ and the surfactant SDS, were not able to bridge the C₆₀-Al(OH)_n^{(m-6)+} particles together; hence, they had no effect on the C₆₀ removal. The addition of Na⁺ and Ca²⁺ increased the ionic strength of the aqueous solution, which compressed the electric double layer and induced the C₆₀-Al(OH)_n^{(m-6)+} particles to aggregate. However, they are not the essential factors for flocs formation. This is the first study to report the bridging phenomena between multivalent anions and C₆₀-Al(OH)_n^{(m-6)+} in water treatments, and it highlights that the presence of multivalent anions and cations in raw water are important for the effective removal of C₆₀.

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1. Introduction

With increasing commercial interest in its unique chemical and physical properties, fullerene (C₆₀) has been widely used in various products, such as new high-strength materials, electronics, optics, biomedicines and catalysts (Innocenzi and Brusatin, 2001; Jensen et al., 1996; Sherigara et al., 2003; Tenne and Seifert, 2009). As the use of C₆₀ continues to grow rapidly, it is inevitable that fullerene particles will enter natural aquatic systems if they are not properly controlled during their production, use and disposal. C₆₀ suspensions can cause

oxidative damage to human cell membranes, DNA damage and human cell death, partially due to the production of reactive oxygen species and uptake by cells (Dhawan et al., 2006; Isakovic et al., 2006; Sayes et al., 2004). Moreover, because of their large surface areas, C₆₀ nanoparticles are more likely to bind metals, such as Pb²⁺, Cd²⁺ and other contaminants, such as polycyclic aromatic hydrocarbons, which serve to enhance the mobility of these substances (Li et al., 2002, 2003; Yang et al., 2006). Drinking water is a direct pathway for humans to exposure to nanoparticles. The risk for humans to ingest the nanoparticles in drinking water is determined by the efficiencies of water treatment processes, which generally include coagulation, flocculation, sedimentation and filtration. Therefore, it is necessary to understand the behaviors of nanoparticles during the process of water treatment to ensure safe drinking water.

Coagulation is one of the most effective operations for removing colloidal particles and dissolved organic matter (DOM) during the treatment of surface water. Recent research has investigated the removal

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of nanoparticles in the process of coagulation. Zhang et al. (2008) reported that 20–60% of the total mass of commercial metal oxide (TiO₂, NiO, Fe₂O₃, and ZnO) nanoparticles could be removed by coagulation followed by sedimentation. Hyung and Kim (2009) examined the fate of C₆₀ nanoparticles during conventional water treatment and found that aggregated C₆₀ could be effectively removed in the operation units, while the efficiency of C₆₀ removal depended on various parameters, such as pH, alkalinity and coagulant dosage. Moreover, it was reported that ions such as Ca²⁺, Mg²⁺, and humic acid (HA) affected the coagulation behavior of the colloids (Nathalie and Gregory, 2003; Peter et al., 2007). However, how exactly these substances affected the coagulation behavior of the nanoparticles is not fully understood, though they were confirmed to alter the stabilities of the nanoparticles (Chen and Elimelech, 2006, 2007; Mashayekhi et al., 2012; Zhang et al., 2009). Furthermore, some anions, such as HCO₃⁻ and H₂PO₄⁻, were ubiquitous in the natural water and their impacts on the coagulation of nanoparticles were not known.

The aim of this work was to examine the coagulation removal efficiency of C₆₀ under different water conditions that had been adjusted by various types of ions (both monovalent and multivalent cations and anions), macromolecules (HA) and surfactants (sodium dodecylsulfate, SDS). In addition, the mechanisms of the C₆₀ removal efficiency by these cations, anions, HA and SDS are discussed.

2. Materials and methods

2.1. Preparation of C₆₀ aqueous solutions and HA solution

C₆₀ powder was purchased from MER Corp. (Tuscan, AZ). Approximately 50 mg of 99.9% pure C₆₀ was dissolved in 25 mL of HPLC-grade toluene (Sigma–Aldrich, St. Louis, MO) by shaking for more than 12 h, resulting in a clear dark-purple mixture. The mixture was gently introduced into a solution of 750 mL deionized distilled water with the pH adjusted to 10 with NaOH. Then, the mixture was sonicated with a sonicating probe (450 Sonifier, Branson Ultrasonics Corporation, Danbury, CT) in a fume hood for 1–1.5 h to evaporate the toluene. Next, nitrogen was allowed to flow through the solution for 10 min to further remove any soluble toluene in the solution. The final solution was filtered using a vacuum filter setup, first through a 0.45 μm cellulose acetate membrane filter, followed by a 0.20 μm nylon membrane filter (Fisher Scientific). The resulting clear yellow filtrate containing the fullerene nanoparticles was collected and stored in the dark at 4 °C. Through high temperature oxidation at 680 °C (TOC-L CPH, Shimadzu, Kyoto, Japan), the fullerene nanoparticle stock suspension was determined to have a total organic carbon content of 16.035 mg/L.

Commercial Aldrich HAs were purified according to a previous report (Pan et al., 2006). Briefly, a solution containing 0.1 M NaOH and 0.1 M Na₄P₂O₇ was mixed with Aldrich HA (50:1, v:w) to extract the HA. The supernatants were filtered and collected, and the HAs were precipitated with HCl. The precipitated HAs were washed using distilled water until a chloride test using AgNO₃ was negative for chloride, freeze-dried and ground to <500 μm particles. An aliquot of the purified HAs was dissolved into deionized water, and the mixture was adjusted to pH 12 with 0.5 mol/L NaOH. After 10 h stirring, the solution was filtered through a 0.20 μm cellulose acetate membrane filter, and the

supernatant was collected. The concentration of HA in the filtrate was quantified by TOC and stored at 4 °C.

2.2. Jar test procedure

Jar tests were performed by diluting 50 mL of the C₆₀ solution with 200 mL deionized water in 400 mL beakers using a Jar Mixer (Phipps & Bird, Inc., Richmond, VA). One milliliter NaCl (1 M) solution was added to the solution to adjust the ionic strength unless otherwise stated. The pH values of the water samples were maintained from 8–9. After adding a predetermined amount of alum (Al₂(SO₄)₃·18H₂O) (Aldrich, Milwaukee, WI) from a 0.01 M stock, the solution in the jar was mixed at a paddle speed of 120 rpm for 5 min, followed by 30 min slow mixing at 40 rpm. After 1 h of quiescent settling, the supernatant was removed for analysis.

When investigating the effect of Ca²⁺ on C₆₀ removal, 4 mM NaCl was replaced by 1 mM CaCl₂. Correspondingly, HCO₃⁻, HPO₄²⁻, SO₄²⁻, NO₃⁻, macromolecular substances such as HA and surfactants such as SDS were added to the water samples when investigating the effects of bridging functions by anions on C₆₀ removal.

2.3. Analytical methods

The sizes of the C₆₀ particles were analyzed by dynamic light scattering (DLS) using a Zetasizer ZS90 (Malvern Instruments, Bedford, MA) equipped with a folded capillary cell at 25 °C. The zeta potential was analyzed using a Zeta 90 Plus Zeta Potential Analyzer (Brookhaven Instruments Co., Holtsville, NY). The concentration of C₆₀ in organic-free water was determined by UV absorption at 268 nm using an Agilent 8453 UV–Vis Spectroscopy System (Palo Alto, CA). The coagulation removal efficiency of C₆₀ were then calculated by $(1 - \text{UV}_{268\text{-end}} / \text{UV}_{268\text{-initial}}) \times 100\%$. All samples were run in triplicate.

3. Results and discussion

3.1. Characterization of C₆₀ in different aqueous solutions

The zeta potential and particle sizes (PS) of the C₆₀ particles measured in the background solution with different ions are shown in Table 1. The measurements were performed after the jar tests in the absence of coagulant. The zeta potential of the C₆₀ particles in the deionized water was negative, similar to data from previous studies (Chen and Elimelech, 2007; Dhawan et al., 2006). The addition of cations caused the zeta potential to increase in the following order: Ca²⁺ > Na⁺, while the addition of anions decreased the zeta potential in the order of: HCO₃⁻ < HPO₄²⁻ < HA < SDS⁻. Cations neutralized the negative charge on the surface of the C₆₀, while the anions imparted a negative charge. The hydrodynamic diameter of C₆₀ varied from 57.9 to 148.58 nm. More than 60% of the nanoparticles were less than 100 nm, and the mean diameter was approximately 97.0 nm. Slight variations in the PS were observed in the presence of Na⁺ and Ca²⁺ and other ions. The inconsistency of the PS in the presence of Na⁺ and Ca²⁺ compared to previous studies (Chen and Elimelech, 2007) could be attributed to the lower concentrations of Na⁺ (4 Mm) and Ca²⁺ (1 mM) in this work, which did not reach the critical coagulation concentration (CCC) of 160 mM Na⁺ and 40 mM Ca²⁺.

Table 1
Characterization of C₆₀ in different aqueous solutions.

C ₆₀	Blank	Na ⁺ / 4 mM	Ca ²⁺ / 1 mM	HCO ₃ ⁻ / 0.59 mM	HPO ₄ ²⁻ / 0.4 mM	HA/TOC 1.9 mg/L	SDS/ 0.5 mM
Zeta/mV	-20.07 ± 1	-14.51 ± 2.2	-3.69 ± 2	-22.81 ± 1	-24.04 ± 3	-28.98 ± 2.7	-31.32 ± 1
PS/nm	97.0 ± 2	97.9 ± 1.5	98.8 ± 2	98.1 ± 3	97.1 ± 2.5	98.4 ± 1.5	94.7 ± 1

A-: humic acid ion; SDS: Sodium dodecyl sulfate

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