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nC_{60} deposition kinetics: the complex contribution of humic acid, ion concentration, and valence

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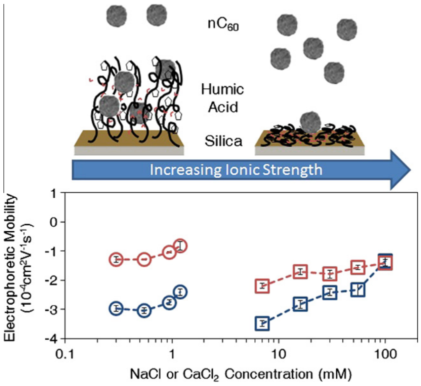
GRAPHICAL ABSTRACT



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ABSTRACT

The demonstrated toxicity coupled with inevitable environmental release of nC_{60} raise serious concerns about its environmental fate and transport, therefore it is crucial to understand how nC_{60} will interact with subsurface materials including attached phase soil and sediment organic matter (AP-SOM). This study investigated the attachment of nC_{60} onto a Harpeth humic acid (HHA) coated silica surface under various solution conditions using a quartz crystal microbalance with dissipation monitoring. The HHA coating greatly enhanced nC_{60} attachment at low ion concentrations while hindering attachment at high ion concentrations in the presence of both mono and divalent cations. At low ion concentrations, the HHA greatly reduced the surface potential of the silica, enhancing nC_{60} deposition through reduction in the electrostatic repulsion. At high ion concentrations however, the reduced surface potential became less important due to the near zero energy barrier to deposition and therefore non-DLVO forces dominated, induced by compaction of the HHA layer, and leading to hindered attachment. In this manner, observed contributions from the HHA layer were more complex than previously reported and by monitoring surface charge and calculated DLVO interaction energy alongside attachment experiments, this study advances the mechanistic understanding of the variable attachment contributions from the humic acid layer.

1. Introduction

The popularity of engineered nanomaterials (ENMs) has grown rapidly over the last decade, with the ENM market expected to

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reach a total of $64.2 billion over the next five years [27]. This increase in production will certainly lead to the eventual release of ENMs into the environment through production and manufacturing of the products or use and disposal from the consumer [13]. One particular ENM of note is buckminsterfullerene (C_{60}), which has applications throughout many fields, including biomedical technology, electronics, and optics [25,29]. Since the solubility of fullerene in water is very low [18], the nano-sized colloidal particle it forms in water (nC_{60}) is the most environmentally relevant form to study. The antimicrobial properties, aquatic toxicity, and potential human toxicity of nC_{60} [12,20,28,29] combined with the inevitable release to the environment raise serious concerns about the environmental fate and transport of nC_{60}.

As with other colloidal particles, the transport of nC_{60} throughout the environment will be determined by its aggregation and deposition processes. These processes are controlled by a complex system of variables including ionic strength, the presence of organic matter, and pH [23]. The aggregation behavior of nC_{60} in clean systems (absent of organic matter) is usually described by the classic Derjaguin-Landau-Verwey-Overbeek (DLVO) theory [9,35], which describes the stability of aqueous colloids by combining the effects of an electrical double layer repulsion (EDL) and a van der Waals (vdW) attraction. An increase in ionic strength screens the EDL repulsion and lowers the energy barrier to aggregation. Furthermore, the Schulze-Hardy rule [10] states that the valence (z) of counterions play a major role as well, predicting the critical coagulation concentration (CCC) to be proportional to z^{-6}. The aggregation behavior of nC_{60} has been shown to be in agreement with DLVO theory both in terms of sensitivity to ionic strength and proportionality to z [4,5].

The deposition of nC_{60} occurs when nC_{60} particles collide with and sorb to an immobile surface in the complex subsurface environment. Relative to the nC_{60} particles, these mineral and soil surfaces can be considered infinitely large particles and therefore deposition can be studied as a form of heteroaggregation [10]. Several studies have monitored the deposition of nC_{60} using both quartz crystal microbalance with dissipation monitoring (QCM-D) [4–6,30] and packed column experiments [3,11,22,30,37,38], however most were conducted in a simple electrolyte system with bare mineral surfaces. As ionic strength increased in the aforementioned QCM-D studies, the attachment efficiency of nC_{60} onto silica surfaces increased until reaching a maximum of 1 at the CCC, suggesting qualitative agreement with DLVO theory. Additionally, two of these studies [4,6] reported a much larger charge screening effect when a divalent cation (Ca^{2+}) was introduced, suggesting qualitative agreement with the Schulze-Hardy rule. DLVO theory describes the deposition of nC_{60} well in these clean systems, however the subsurface often contains additional variables for consideration, namely the presence of organic matter.

Soil organic matter (SOM) is ubiquitous in the subsurface environment, either dissolved or immobilized (attached) onto the surface of mineral and soil surfaces and humic substances typically represent the dominant organic components in soils and sediments [33]. Dissolved organic matter has been shown to adsorb onto the surface of nC_{60} particles and increase their stability to aggregation and deposition through steric repulsion [5,6] and, in turn, increase their mobility. The effect of attached phase soil organic matter (AP-SOM) on the deposition behavior of nC_{60}, however, appears to be much more complex. The presence of AP-SOM has been shown to enhance, hinder, or have no effect on the attachment of nC_{60}, depending on the type of AP-SOM and the ionic strength of solution [5,6,30]. One study reported that an alginate layer enhanced nC_{60} attachment in the presence of 10 mM NaCl, while hindering it in the presence of 30 mM NaCl [6]. The variable behavior was attributed to its compaction at higher NaCl concentrations, resulting in a smoother, more rigid layer, with less room for nC_{60} particle entanglement. Furthermore, in our previous work, we reported that increasing the temperature of a humic acid layer while holding all other variables constant, raised the attachment efficiency of nC_{60} from low attachment ($\alpha = 0.3$) to complete attachment ($\alpha = 1$) [26]. We attributed this to the temperature-dependent hydration of the layer, opening up previously unavailable sorption sites. Since the interaction between nC_{60} and environmentally relevant surfaces will likely play a very important role in the fate and transport of nC_{60} throughout the environment [21], it is clear that more study is needed in order to understand what role AP-SOM will play.

The purpose of this study is to further the understanding of nC_{60} deposition behavior in the presence of AP-SOM. By varying the ionic strength of the system, through both cation concentration and valence, while holding all other variables constant, the deposition rate of nC_{60} is directly monitored using a QCM-D. Deposition rate and attachment efficiency curves are then constructed over a range of ion concentrations and valences. By comparing these curves between surfaces of bare silica and humic acid coated silica, the role of ionic strength in nC_{60} deposition onto AP-SOM is elucidated, discussed, and compared to DLVO theory. Combined with our previous work regarding the role of AP-SOM physicochemical properties [26], this study illustrates the importance of AP-SOM in the transport of nC_{60} and the need for a better quantitative understanding of its role. A better understanding of these interactions would lead to more precise predictions on the potential pathways of exposure and their eventual impact on ecosystems and human health.

2. Materials and methods

2.1. Materials

Sublimed C_{60} powder (>99.9%) was purchased from MER Corporation (Tucson, AZ). Dry Harpeth humic acid (HHA) was isolated as described in our previous publication [8]. Poly-L-lysine hydrobromide (PLL, P1274) and 4-(2-Hydroxyethyl)-1-piperazineethanesul fonic acid (HEPES) were purchased from Sigma-Aldrich (St. Louis, MO). The concentration of PLL and HEPES was held constant at 0.1 g/L and 10 mM, respectively. Reagent grade NaCl (S671) and $CaCl_2$ (C79) were purchased from Fisher Scientific (Pittsburgh, PA). Silica-coated QCM-D sensors (QSX-303) were purchased from Q-Sense (Biolin Scientific, Stockholm, Sweden). 900 nm silica microspheres were purchased from Polysciences Inc (Warrington, PA) as a surrogate for estimating the electrophoretic mobility of the silica sensor surface. All solutions were prepared using ultra pure water purified by the Milli-Q Water Purification System from Millipore (Billerica, MA).

2.2. Preparation of stock suspensions and solutions

The nC_{60} stock suspension was prepared using the same method as described in our previous publication [26], similar to that described by Andrievsky et al. [1] (details of the preparation method are provided in the appendix). The resulting nC_{60} stock suspension was determined to have a total carbon content (Shimadzu TOC-V CPH/CPN, Columbia, MD) of 33.6 mg L^{-1} and a pH of 5.6. The nC_{60} stock suspension was stored in the dark at 4 °C for the entirety of the study and all experiments took place within 4 months of preparation, during which time the nC_{60} stock suspension was stable as confirmed by periodic Dynamic Light Scattering (DLS) measurements (Malvern Zetasizer Nano ZS, Worcestershire, UK).

The method for preparing the HHA stock solution is provided in the appendix. The HHA stock solution was kept in the dark for the