



Aggregation kinetics of nanosized activated carbons in aquatic environments



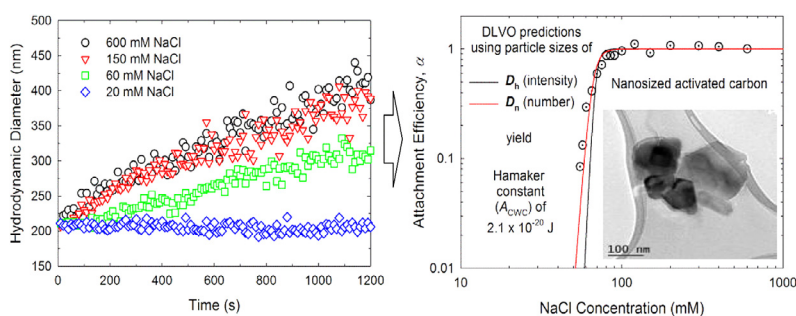
Chengyu Chen, Weilin Huang*

Department of Environmental Sciences, Rutgers, The State University of New Jersey, New Brunswick, NJ 08901, USA

HIGHLIGHTS

- Nanosized activated carbons (NACs) are manufactured particles with sizes <100 nm.
- NACs obtain negative surface charge in water by deprotonation of functional groups.
- The aggregation behavior of NACs was consistent with prediction by the DLVO theory.
- The Hamaker constants derived for AC materials are $2.1\text{--}2.7 \times 10^{-20}$ J in water.
- NACs may disperse in freshwater but can aggregate in highly saline/acidic water.

GRAPHICAL ABSTRACT



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ABSTRACT

Nanosized activated carbons (NACs) are emerging as a new class of engineered nanomaterials, but their colloidal stability governing the fate and transport in aquatic environments has not yet been evaluated. We have characterized four representative NAC materials and examined their colloidal stability and early-stage aggregation kinetics under various water chemistry conditions. The results showed that these NAC particles had intensity-weighted hydrodynamic diameters (D_h) and number-weighted averaged diameters (D_n) of approximately 200 and 100 nm, respectively, and that their aggregation kinetics exhibited both reaction- and diffusion-limited regimes in the presence of monovalent (NaCl) or divalent (CaCl_2) salt with distinct critical coagulation concentrations (CCC), indicating that their colloidal stability under the tested aqueous conditions was consistent with the classic Derjaguin-Landau-Verwey-Overbeek (DLVO) theory. The fitting of the aggregation kinetics with predictions based on DLVO theory yielded the Hamaker constant of $2.1\text{--}2.7 \times 10^{-20}$ J (A_{CWC} , aqueous medium). The study demonstrated that NACs may be relatively stable under typical freshwater chemistry conditions, suggesting their potential applications as reactive agents for remedy of contaminated water and soil systems where long-time suspension of introduced particles is desired. The observed strong colloidal stability may also indicate high possibility of NACs being nanosized pollutants in natural and engineered environmental systems.

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1. Introduction

Nanosized activated carbons (NACs) are recently developed nanomaterials with major reactivities such as adsorbability similar to traditional granular and powdered activated carbon (GAC and

* Corresponding author.

E-mail address: whuang@envsci.rutgers.edu (W. Huang).

PAC) materials [1,2]. The unique nano-size feature of NAC, along with its enormous porosity and great specific surface area (SSA), makes it potential candidates for catalyst support [3], drug carriers [4], disease tracers [5], and adsorbents for water reclamation [6]. The anticipated growth in production and use of NACs will inevitably lead to their release into natural or engineered aquatic systems [7]. Although limited studies have demonstrated insignificant cytotoxicity after short-term exposure to NACs [4,8], their potential impact on human and the environment remains unknown. Indeed, the increasing public concern over engineered nanomaterials as emerging environmental pollutants involves not only their inherent toxicity but also how they may interact with each other or with environmental solids [9]. Upon release to aquatic environments, potential risks from exposure to nanoparticles may be largely dependent on their fate and transport processes, which are strongly influenced by their aggregation tendency under different aquatic conditions [10]. It is therefore of particular interest to investigate the colloidal stability of NACs against aggregation in various aquatic systems.

Prior studies focused on the fate and transport of several important carbonaceous nanoparticles such as fullerenes [11–13], carbon nanotubes [14–16], and graphene oxide [17] in aquatic systems, but little is known for NACs. One goal of this study was to quantitatively investigate the colloidal stability of well-characterized NACs using various state-of-art instruments and the theories of particle-particle interactions. In prior studies, time-resolved dynamic light scattering (TRDLS) has been widely used to measure the aggregation kinetics of colloidal particles (fullerenes, carbon nanotubes, and graphene) under the influence of different solution chemistry [11,16,17]. The early-stage aggregation rates at different electrolyte concentrations were used to construct the attachment efficiency profiles, which often exhibited a reaction- (slow) and diffusion-limited (fast) aggregation regimes. The critical coagulation concentrations (CCC) were determined by extrapolating from both the fast and slow aggregation regimes. These studies showed that the aggregation behavior of fullerenes, carbon nanotubes, and graphene nanoparticles generally followed the predictions from the classic Derjaguin-Landau-Verwey-Overbeek (DLVO) theory with strong effects from background electrolytes [17,18].

The second goal of this study was to derive the Hamaker constant for general activated carbon (AC) materials from the colloidal stability measurements made directly for NACs. The Hamaker constant, which is highly dependent on both the external surface properties of interacting bodies and the intervening medium, provides a means for assessing the relative strength of van der Waals attractive interactions [19]. It is a key physicochemical parameter for predicting interactions of surfaces and interfaces involving particles of various sizes. For example, with the Hamaker constant, the adsorption equilibria of organic contaminants on ACs could be predicted [20] and the colloidal stability and aggregation process of nanoparticles in aquatic environments could be simulated [21,22]. The currently available Hamaker constant data for ACs, however, were either estimated from surrogate materials (e.g., carbon fibers, $5.2\text{--}6.2 \times 10^{-20}$ J [23]) [20] using the contact angle method or calculated from adsorption data ($5.0\text{--}7.8 \times 10^{-20}$ J) [24]. However, inaccuracy could be expected for these published data. For instance, AC has high surface roughness and is not suitable for the contact angle method. Surrogate materials such as carbon fibers used in contact angle measurements may have surface chemistry properties that are not well representative of AC. Meanwhile, the Hamaker constant calculated from adsorption data was presumably representative of the dispersive interactions at the external surfaces, but the measured adsorption data were indeed averaged from overall adsorption at both internal and external surfaces of AC. Hence, the Hamaker constant derived from direct

measurements is much needed for better predicting particle-particle and particle-molecule interactions for AC materials.

In this study, four NACs derived from different biogenic materials were chosen for investigating their colloidal stability under various aquatic chemistry conditions. Their aggregation kinetics and electrophoretic mobilities (EPMs) were measured over a wide range of solution chemistry conditions, and their CCC values were quantified accordingly. The measured aggregation kinetics agreed with DLVO predictions, and the Hamaker constant was derived. The study provided insight to the aggregation mechanism of NACs and suggested the potential application of NACs as reactive agents for contaminated environmental systems. The strong colloidal stability observed for NACs also draws attention to their potential adverse environmental effects as an emerging nanosized pollutant.

2. Materials and methods

2.1. Preparation of NACs

The four types of NACs (purity > 95%) with high SSA (Table S1 at the Supplementary material) were purchased from US Research Nanomaterials, Inc. (Houston, TX) and assigned as NAC1, NAC2, NAC3, and NAC4. They were analyzed for elemental compositions (Table S2) and examined with a scanning electron microscope (SEM) (Fig. S1). The aqueous NAC suspensions were prepared following a published procedure [11]. In brief, the NACs were weighed into double deionized water (DDI) (resistivity >18 M Ω ·cm) and the suspensions were mixed for 30 d then allowed to settle for 7 d. Aliquots of 20 mL were collected at 2 cm below the suspension surface and combined to form a 200-mL stock suspension for each sample. The stock suspensions after 24-h sonication were monitored to remain thermodynamically stable over the experimental time period.

2.2. Characterization of aqueous NAC Suspensions

The concentrations of NACs in stock suspension (0.1-mL samples) were measured gravimetrically using an ultramicro-balance (Sartorius M2P, Goettingen, Germany). The NACs were examined on a transmission electron microscope (TEM) (Topcon 002B, Topcon Corp., Tokyo, Japan) operating at 200 kV. Potentiometric titration was conducted to identify titratable functional groups of the NACs. Detailed procedures are summarized in the Supplementary material.

The EPMs of the NAC suspensions were measured at 25 °C using a Zetasizer Nano ZS (Malvern Instruments, Worcestershire, UK) which employs phase analysis light scattering (PALS). Electrolyte stock solutions were prepared by dissolving ACS grade NaCl or CaCl₂ in DDI and filtered through 0.1- μ m filters (Puradisc 25 TF, Whatman), with desired final solution pH adjusted with HCl and NaOH. The NAC concentration was diluted to 10 mg/L for each EPM measurement. For a given solution condition, three independent samples of the same NAC were each measured 10 times for EPM values which were converted to zeta (ζ) potentials using the Smoluchowski approximation [11].

2.3. Dynamic Light Scattering (DLS) Measurements

The effective particle sizes of NAC suspensions were measured on a Brookhaven 90Plus DLS instrument (Holtville, NY), which employed a 35-mW solid state laser operated at a wavelength of 635 nm and was calibrated with NIST-certified standards (Fisher Scientific). Prior to aggregation test, the intensity averaged hydrodynamic diameter (D_h) was determined as the initial D_{h0} ($t = 0$)

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