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Historical perspective

Heteroaggregation of nanoparticles with biocolloids and geocolloids

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ABSTRACT

The application of nanoparticles has raised concern over the safety of these materials to human health and the ecosystem. After release into an aquatic environment, nanoparticles are likely to experience heteroaggregation with biocolloids, geocolloids, natural organic matter (NOM) and other types of nanoparticles. Heteroaggregation is of vital importance for determining the fate and transport of nanoparticles in aqueous phase and sediments. In this article, we review the typical cases of heteroaggregation between nanoparticles and biocolloids and/or geocolloids, mechanisms, modeling, and important indicators used to determine heteroaggregation in aqueous phase. The major mechanisms of heteroaggregation include electric force, bridging, hydrogen bonding, and chemical bonding. The modeling of heteroaggregation typically considers DLVO, X-DLVO, and fractal dimension. The major indicators for studying heteroaggregation of nanoparticles include surface charge measurements, size measurements, observation of morphology of particles and aggregates, and heteroaggregation rate determination. In the end, we summarize the research challenges and perspective for the heteroaggregation of nanoparticles, such as the determination of α_{hetero} values and heteroaggregation rates; more accurate analytical methods instead of DLS for heteroaggregation measurements; sensitive analytical techniques to measure low concentrations of nanoparticles in heteroaggregation systems; appropriate characterization of NOM at the molecular level to understand the structures and fractionation of NOM; effects of different types, concentrations, and fractions of NOM on the heteroaggregation of nanoparticles; the quantitative adsorption and desorption of NOM onto the surface of nanoparticles and heteroaggregates; and a better understanding of the fundamental mechanisms and modeling of heteroaggregation in natural water which is a complex system containing NOM, nanoparticles, biocolloids and geocolloids.

Contents

Abbreviations: Ag, silver; Al_2O_3, aluminum oxide; Au, gold; CeO_2, cerium oxide; C60, fullerene; CCC, critical coagulation concentration; CNTs, carbon nanotubes; DLS, dynamic light scattering; DLVO, Derjaguin-Landau-Verwey-Overbeek; DOM, dissolved organic matter; EDL, electric double-layer; ENMs, engineered nanomaterials; FA, fulvic acid; GO, graphene oxide; HA, humic acid; MeO, metal oxide; MWNTs, multi-walled carbon nanotubes; NCs, natural colloids; NOM, natural organic matter; NPs, nanoparticles; nZVI, nanoscale zerovalent iron; POC, particulate organic carbon; PVP, polyvinylpyrrolidone; PZC, point of zero charge; SAXS, small-angle X-ray scattering; SEM, scanning electron microscopy; SiO_2, silicon dioxide; SLS, static light scattering; SPM, suspended particulate matter; SUVA, specific UV-absorbance; SWNTs, single-walled carbon nanotubes; TEM, transmission electron microscopy; TiO_2, titanium dioxide; TOC, total organic carbon; TR-DLS, time-resolved dynamic light scattering; X-DLVO, extended DLVO; ZnO, zinc oxide.

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1. Introduction

1.1. Nanoparticles

In recent years, nanotechnology has been developing very rapidly. Nanomaterials are commonly defined as materials with at least one dimension below 100 nm [1]. There are three types of nanomaterials [2]: (1) nanofilms and coatings, which have one dimension less than 100 nm; (2) nanotubes, nanofibers and nanowires, which have two dimensions less than 100 nm; and (3) nanoparticles (NPs), which have three dimensions less than 100 nm [2,3].

Some typical nanomaterials are: (1) metal and metal oxide (MeO): such as Ag, Cu, TiO_2, ZnO and CeO_2, which are increasingly applied in a variety of products (e.g., clothing, sunscreens, paints, coatings, catalysts) [4,5]; (2) carbon-based nanomaterials such as carbon nanotubes (CNTs) and graphene, which have wide application due to their superior electronic, mechanical, conductive and thermal properties. Typical applications include multi-walled carbon nanotubes (MWNTs) for reinforcing the strength of baseball bats [6], and single-walled carbon nanotubes (SWNTs) for biomedical applications, sensors, and electronics [7]; and (3) magnetic particles: magnetic particles have been extensively considered as adsorbents for the removal of various pollutants from water because their inherent superparamagnetic properties result in easy separation by a magnetic field [8–10]. Typical magnetic iron oxides are Fe_3O_4, and pristine and modified nanoscale zerovalent iron (nZVI) [11–13].

There are naturally occurring nanoparticles (e.g. in ashes, as soil particles or biomolecules) and unintentionally produced nanoparticles (e.g. in diesel exhaust), as well as intentionally engineered nanoparticles [2]. The physico-chemical properties of nanoparticles are different with their bulk material due to the size effect. In fact, nanoparticles are regarded as a bridge between atomic or molecular structures and bulk materials [2], and quantum physics should be applied instead of classical physics for particles in the size range of 1–100 nm [1]. Nanoparticles have some special properties, typically including: (1) size effects (reducing the particles size can lead to the change of solubility, color, absorption or emission wavelength, and conductivity); (2) composition effects (different compositions of nanoparticles result in a different physical and chemical behavior); and (3) surface effects (the surface behavior of nanoparticles are changed by their dispersibility, conductivity and other related properties) [1].

Nanoparticles are of special interest in the field of colloid science and engineering because their size range has overlap with colloidal particles. Similar to colloidal particles, the fundamental science of surfaces and interfaces is very important for nanoparticles. In the nanoscale, more atoms are found at the surfaces, which makes the nanoparticles more reactive [1]. One case in point is that nanoparticles can quickly agglomerate into larger particles due to higher surface energy [1,14–16].

Engineered nanomaterials (ENMs) are now being widely manufactured and used in medicines, personal care products [17], clothing, coatings and paints, electronics, food supplements and food packaging [2], and environmental protection [8,12,18–21]. It is very likely that the large amount of production of ENMs will lead to their release into the environment through production, application, and disposal processes [1,22,23]. For example, titanium dioxide nanoparticles (TiO_2 NPs) were modeled and predicted to be discharged to the wastewater treatment plant, landfill and other environments [4,17,24]. The application of ENMs has raised concern over the safety of these materials to human health and the ecosystem [2,14,17]. Several studies have shown that ENMs can have effects on aquatic and terrestrial organisms at certain exposure thresholds [25–30]. The release of CNT into the environment might also result in negative effects and thus causes concern [30]. Even though there is no solid evidence of acute toxicity for many nanoparticles at current predicted exposure levels, the uncertainty of their potential long-term effects still makes it necessary to understand the fate and transport of nanoparticles in the aqueous phase. The fate and transport of ENMs is influenced by a variety of factors, such as particle size and size distribution, particle number and mass concentration, particle structure and shape, elemental composition and morphology, specific surface area, surface charge, reactivity, as well as aggregation [2,14,15].

Therefore, it is vital to measure the characteristics of nanoparticles, including their aggregation, shape, solubility, surface area and surface charge [2,31]. For example, the particle structure can influence their stability or behavior, as indicated by the crystal structures of TiO_2 (e.g. rutile or anatase) [2]. Solubility also affects their fate and transport as well as their toxicity (e.g. ZnO versus TiO_2) [2]. The shape of nanoparticles (e.g. spherical, rod) can result in different aggregation, affinities or accessibilities [2,32]. The surface area can determine their reactivity and sorption, while the surface charge has an effect on particle stability and interactions with other surfaces [2]. Surface chemistry such as coatings can result in different chemical compositions and strongly influence the particle behavior or toxicity [2]. In addition, the properties of NPs can be targeted and controlled by coating or functionalization of the surface of nanoparticles [2].

Among all of the characteristics of NPs, aggregation of NPs is important because this process will increase their size and potentially decrease their uptake [2]. After release into an aquatic environment, water chemistry has significant effect on the aggregation and stability of NPs [14,33,34]. Understanding the aggregation of NPs is essential for predicting their fate and transport in aqueous systems [35].

1.2. Biocolloid, geocolloid and natural organic matter

Natural aquatic colloids are generally defined as materials with at least one dimension between 1 nm and 1 μm [36–38]. Naturally occurring colloids are ubiquitous in natural surface water and are likely to affect the aggregation and sedimentation of NPs [39]. Natural colloids include [40–43]: (1) compact inorganic colloids; (2) large and rigid biopolymers (0.1–1 μm); and (3) soil-derived fulvic compounds (few