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Authors

Wang, Hongtao
Adeleye, Adeyemi S
Huang, Yuxiong
[et al.](#)

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Historical perspective

Heteroaggregation of nanoparticles with biocolloids and geocolloids



Hongtao Wang^{a,*}, Adeyemi S. Adeleye^b, Yuxiong Huang^b, Fengting Li^a, Arturo A. Keller^{b,**}

^a State Key Laboratory of Pollution Control and Resource Reuse, Key Laboratory of Yangtze River Water Environment, Ministry of Education, College of Environmental Science and Engineering, Tongji University, Shanghai, 200092, China

^b Bren School of Environmental Science and Management, University of California, Santa Barbara, CA, 93106, USA

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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.

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Abbreviations: Ag, silver; Al₂O₃, aluminum oxide; Au, gold; CeO₂, 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; SiO₂, silicon dioxide; SLS, static light scattering; SPM, suspended particulate matter; SUVA, specific UV-absorbance; SWNTs, single-walled carbon nanotubes; TEM, transmission electron microscopy; TiO₂, titanium dioxide; TOC, total organic carbon; TR-DLS, time-resolved dynamic light scattering; X-DLVO, extended DLVO; ZnO, zinc oxide.

* Corresponding author. Tel.: +86 21 6598 0567; fax: +86 21 6598 5059.

** Corresponding author. Tel.: +1 805 893 7548; fax: +1 805 893 7612.

E-mail addresses: hongtao@tongji.edu.cn (H. Wang), keller@bren.ucsb.edu (A.A. Keller).

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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, TiO₂, ZnO and CeO₂, 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 Fe₃O₄, 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 (TiO₂ 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 TiO₂ (e.g. rutile or anatase) [2]. Solubility also affects their fate and transport as well as their toxicity (e.g. ZnO versus TiO₂) [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

nanometers) or their equivalent in pelagic waters, aquagenic refractory organic matter. In general, the concentration of NPs is expected to be much lower than naturally occurring colloids [44]. Therefore, heteroaggregation of NPs and natural colloids seems to be more important than homoaggregation of NPs. However, there are limited studies on the heteroaggregation between NPs and natural colloids in the aqueous phase. It is thus imperative to study the heteroaggregation and deposition of NPs and natural colloids.

Biocolloids include viruses, bacteria, proteins, DNA, spores, algae, protozoa and other microorganisms [45–49]. Biocolloids are of significant interest in the fate and transport of contaminants in aqueous phase, not only in groundwater, but also in surface water [45,50]. Similar with inorganic colloids (e.g., clays, aluminosilicates and iron oxyhydroxides), biocolloids can alter the aggregation and dispersion behavior of nanomaterials [46–48].

Geocolloids refer to mineral-based materials. Geocolloids widely exist not only in surface water, but also in groundwater and in soils [51,52]. Typical geocolloids include clay minerals, metal oxides, and hydroxides, all of which play an important role in the fate and transport of pollutants and nutrients in the natural environment [51–53]. Geocolloids can be either ‘particulate’ (focculated in the solid phase) or ‘colloidal’ (in suspension, or dissolved, in the solution phase) in the environment [52]. The mechanism of metal-geocolloid interaction has been widely studied, which includes chemical bonding and electrostatic force [52,54].

Natural organic matter (NOM) is widely found in surface water, groundwater, sediments and soil [55–57]. NOM is mainly the residual from plants and animals materials, as well as some of the biocolloids mentioned before [15,22,58]. NOM has been shown to interact strongly with ENMs [59], modifying their surfaces and in general making them more bioavailable [60,61]. Therefore, it is important to understand the nature of NOM. NOM is a complex heterogeneous mixture of organic compounds, covering a wide range from largely aliphatic to colored aromatic hydrocarbon structures that possess attached functional groups [55,62–64]. These functional groups include amide, carboxyl, hydroxyl, ketone, and various others [22,62]. NOM contains various complex polyelectrolytes with different molecular weights, mainly resulted from the decomposition of plant and animal residues, soluble microbial products, and extracellular polymeric substances [65–70].

Typical components of NOM include humic acid (HA), fulvic acid (FA), lignins, carbohydrates, and proteins [18,71]. Consisting of a wide variety of chemical compositions, NOM is generally negatively charged in natural waters due to the carboxylic and phenolic moieties [22,65], and the aromatic content is a major reactive component of NOM [72]. On average, about 50% of the dissolved organic matter (DOM) in rivers is humic substances [62].

The structure of NOM is still not well understood. For example, humic substances have been widely recognized as macromolecules [73], but some studies indicated that the primary molecular structures are very small (100–2000 daltons (Da)), and the macromolecular characteristics of NOM result from aggregation [62]. The aggregation mechanisms include hydrogen bonding, polyvalent cation interactions, and nonpolar interactions [62]. In general, the molecular weight of NOM in the aqueous phase ranges from a few hundreds to 100,000 Da, which is in the range of colloids [62]. HA has a molecular weight greater than 2000 Da and often colloidal in size [74,75]. HA possesses randomly condensed aromatic rings and different functional groups, as can be seen in Fig. 1 [76].

Total organic carbon (TOC) can serve to provide an overall quantification of NOM [62]. For operational purpose, TOC is usually fractionated into dissolved organic carbon (DOC) and particulate organic carbon (POC), which is separated by 0.45-micrometer (μm) membrane filtration. Typically, POC only accounts for less than 10% of the TOC, while DOC is the majority for most natural waters [62,77]. Also, DOC is more likely to strongly interact with the ENMs, so it has been suggested as a more relevant water quality parameter for understanding the effect on

ENMs. Specific UV-absorbance (SUVA, = UV absorbance/DOC) and UV-Vis (typically at 254 nm) are also used to measure the concentration of NOM in water [18,55]. The aromatic content of NOM is found to be closely correlated to the specific UV absorbance (SUVA) [72,78].

The concentration of NOM in natural waters usually ranges from ~1 to ~50 mg/L as DOC [35,77]. Singer and Bilyk analyzed the water quality of nine different water utilities across the United States, and it was found that the TOC concentrations ranged from 2.6 to 26.4 mg/L, the UV absorbance ranged from 0.030 to 1.096 cm^{-1} , while the SUVA ranged from 1.4 to 4.5 $\text{L}/(\text{mg} \cdot \text{m})$ [79]. Other studies indicated that typical NOM concentration in lake and river waters is ~0.4–4.0 mg C/L and 10–30 mg C/L for wetlands (which is equivalent to ~0.8–8.0 and 20–60 mg C/L total NOM concentration assuming 50 wt % carbon), and the NOM concentration is typically 1 mg C/L in seawater [77,80].

In summary, biocolloids are organic colloids, and geocolloids are inorganic/mineral colloids, while NOM is ubiquitous in natural water and it is closely related to biocolloids. NOM can originate either from biocolloids, or from plants and animals. A typical NOM is microbial extracellular polymeric substances (EPS), which can be produced by biocolloids [68]. In addition, NOM can be adsorbed onto the surface of geocolloids [81]. Therefore, the role of NOM should not be ignored when investigating heteroaggregation of nanoparticles with biocolloids and geocolloids.

1.3. Heteroaggregation and the role of natural organic matter

Typically, the processes of nanoparticles in the aqueous solutions include aggregation (homoaggregation and heteroaggregation), sedimentation, dissolution and chemical transformation [82]. Homoaggregation involves particles of the same type, while heteroaggregation occurs between particles of different types, size and properties [83]. Most nanoparticles tend to aggregate once they are hydrated, and this aggregation process is important for their sedimentation rates [14–16]. The properties and implication of nanoparticles will be altered once they are agglomerated into larger particles and settle out of water column [1]. In most waters, including natural waters and tap water, heteroaggregation, or aggregation between different types of particles, will take place [44]. Heteroaggregation of nanoparticle might occur with naturally occurring inorganic, organic, and biological colloids, such as hematite ($\alpha\text{-Fe}_2\text{O}_3$), colloidal organic matter, and viruses and bacteria [44].

The aggregation of nanoparticles are regulated by many factors, such as the surface charge and charge density of the nanoparticles [38,84,85], as well as adsorbed NOM or other organic molecules [14,46]. Among these factors, the role of NOM is one of the most complex [86]. The importance of NOM on the aggregation behavior of nanoparticles has led to many studies. However, due to the complex composition of NOM, most of the studies consider a specific composition of NOM, such as fulvic acid [43] or humic acid, and more recently, microbial EPS [58, 87–89]. In addition, although a number of studies have provided a

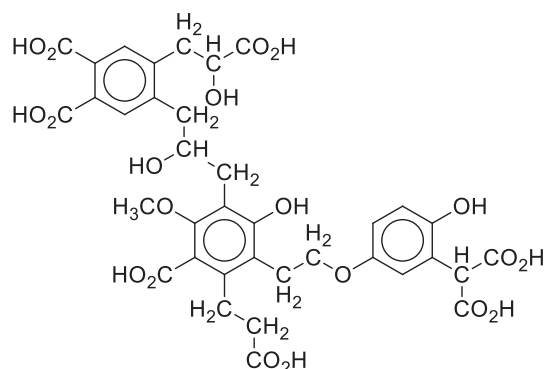


Fig. 1. Hypothetical molecular structure of humic acid.

clear understanding of the role of NOM in a homoaggregation system [14,80,90], there are very few studies that address the role of NOM in heteroaggregation [91]. Due to analytical and methodological challenges, it is still difficult to conduct systematic studies on heteroaggregation and the role of NOM. Although various studies have confirmed that NOM can adsorb onto the surface of colloids and NPs and decrease their aggregation rate via electrosteric stabilization [40, 92], it was also reported that NOM can enhance the aggregation of TiO₂ NPs due to bridging effect [81]. Therefore, it is crucial to understand the effect of NOM in the heteroaggregation of engineered nanoparticles in aqueous phase. A better investigation of the structure of NOM as well as the characteristics of ENMs is essential for understanding the mechanisms of heteroaggregation.

The purpose of this paper is to provide a critical review of the current studies, research challenges and perspectives on the heteroaggregation of nanoparticles with biocolloids and geocolloids. This review includes typical cases of heteroaggregation between nanoparticles and biocolloids and/or geocolloids, mechanisms of heteroaggregation, modeling of heteroaggregation, and important indicators used to determine heteroaggregation in aqueous phase.

2. Typical cases of heteroaggregation between nanoparticles and biocolloids and/or geocolloids

2.1. Heteroaggregation between nanoparticles and natural colloids

The heteroaggregation of NPs with natural colloids is highly likely in most natural surface waters, and can determine the fate and transport of NPs in the aqueous environment [93,94]. Quik *et al.* used water samples from two rivers in Europe (the Rhine and the Meuse) to study the aggregation of CeO₂ NPs with each other (homoaggregation) and with other particles (heteroaggregation) [91]. It was found that the main route of the removal of most nanoparticles from water is aggregation and sedimentation, while the heteroaggregation of CeO₂ NPs with or deposition onto the solid fraction of natural colloids was the main mechanism leading to sedimentation.

Since natural clay minerals are ubiquitous in aquatic environments, the heteroaggregation of nanoparticles with suspended clay minerals may be the most likely interaction once the NPs are released into natural waters [95]. It has been reported that the presence of clays can either facilitate or hinder the mobility of water contaminants under different physicochemical conditions [96]. Zhou *et al.* studied the heteroaggregation of NPs (Ag and TiO₂) and montmorillonite clay particles [95]. They found that heteroaggregation can alter the stability of nanoparticle and clay mineral mixtures. Two typical pH (pH = 4 and pH = 8) were considered in this study, one below the pH at point of zero charge (pH_{PZC}) and the other one above the pH_{PZC}. These two pH values represent two typical conditions and are useful for understanding the mechanisms of heteroaggregation. Although electrostatic interactions were shown to be the dominant force for heteroaggregation, the special structure of montmorillonite influenced the interaction. In particular, the different charges on the face and edge of the clay particles at the lower pH, and the possibility of charge screening by the electric double-layer (EDL) can result in unexpected behaviors. Even though the measured surface charge is similar at pH 4 and pH 8, montmorillonite is much less stable at pH 4 (critical coagulation concentration (CCC) around 35 mM) than it is at pH 8 (CCC around 100 mM). In a recent study [97], we investigated the effect of kaolin particles on the aggregation of TiO₂ and Ag NPs under different conditions. We found that kaolin reduces the energy barrier and the CCC at pH 4, but it promotes NPs aggregation via heteroaggregation at pH 8. Humic acid increases the energy barrier and the CCC of the binary system (kaolin + NPs). The clay particles aggregate rapidly and they destabilize the NPs by heteroaggregation. The complex interactions of clay, NPs, HA, IS and pH determine the colloidal stability of the NPs in natural aquatic

systems. The heteroaggregation between kaolin and NPs makes it a potential coagulant for removal of NPs that behave like Ag and TiO₂.

The heteroaggregation of colloidal minerals with other nanomaterials (such as graphene oxide, GO) also provides useful insights. For example, Zhao *et al.* investigated the heteroaggregation between GO and different minerals (montmorillonite, kaolinite, and goethite) in aquatic environments [98]. GO was found to significantly improve the dispersion of positively charged goethite via heteroaggregation, while the negatively charged montmorillonite or kaolinite had no interaction with GO. The major mechanism for GO–goethite heteroaggregation (pH 4.0–8.5) was electrostatic attraction. One highlight of this study was the quantitative investigation of GO adsorption in the GO–goethite heteroaggregation process. The Linear model was found to fit the adsorption isotherms of GO at different solution pH (4.0 and 6.5), and it was difficult for the adsorbed GO to desorb from goethite. It was also observed that desorption hysteresis occurred due to the formation of a multilayered GO–goethite complex with high configurational stability.

2.2. Heteroaggregation between different types of nanoparticles

By synthesizing different composite nanoparticles with specific functional groups and controlled size, one can investigate heteroaggregation between different nanoparticles. Dušak *et al.* used superparamagnetic carboxyl-functionalized silica-coated maghemite nanoparticles (cMNPs) (24 nm in diameter) and larger, amino-functionalized, silica nanoparticles (aSNPs) (92 nm in diameter) to investigate different heteroaggregation interactions between the NPs in an aqueous suspension [99]. The major methodologies used were zeta-potential for surface charge measurements, dynamic light scattering (DLS) for size monitoring and kinetics analysis, and transmission (TEM) and scanning (SEM) electron microscopy for characterizing the heteroaggregates. The smaller cMNPs in the outer layer were seen to cover the larger central aSNP homogeneously. Two major mechanisms were observed for the heteroaggregation process: one is electrostatic attractions between the NPs originating from opposite electrical surface charge, and the other one is chemical interactions (covalent bonding between the molecules at their surfaces). Covalent bonding was found to be much more effective than attractive electrostatic interactions. While most studies focus on the electrostatic attractions between the NPs in heteroaggregation [100–104], this study provides valuable information about the covalent bonding mechanism in heteroaggregation. However, investigation of heteroaggregation via covalent bonding in the presence of NOM is needed.

Carbon nanotubes (CNTs) are being considered in several consumer products, and a certain amount of release into the natural water may be inevitable. However, currently it is challenging to quantify the mass of CNTs in relevant media (polymers, tissues, soils, and sediments), and the interaction (such as heteroaggregation with NPs) of CNTs is still not clear, especially in complex and environmentally realistic systems which contain NOM [30].

Huynh *et al.* investigated the disaggregation behavior and the strength of heteroaggregates composed of multiwalled carbon nanotubes (CNTs) and hematite nanoparticles (HemNPs) in aqueous phase [105]. At pH 5.5 and 0.1 mM NaCl, heteroaggregation was observed between the negatively charged CNTs and positively charged HemNPs. Afterwards, ultrasonication bath was used to disaggregate the heteroaggregates. By using DLS to compare the sizes of heteroaggregates before and after ultrasonication, it was found that ultrasonication resulted in partial disaggregation and re-growth of heteroaggregate. At pH 11.0, however, ultrasonication was found to almost completely cause disaggregation of the heteroaggregates, and re-aggregation was not observed due to electrostatic repulsion. More importantly, a near complete disaggregation of the CNT–HemNP heteroaggregates was observed with the introduction of HA to the system. It was concluded that the increasing pH and the adsorption of humic acid on the nanoparticles enhance the disaggregation of

heteroaggregates by weakening the particle–particle bonds within the heteroaggregates [105]. It should be noted that the HA concentration used in this study was only 1 µg/L TOC. Although it was found that the presence of HA even at low concentration has a strong influence on the surface charge of the HemNPs, a thorough understanding of the role of NOM on heteroaggregation requires a study with a much wider range of TOC concentrations.

Huynh *et al.* also investigated the rates and mechanisms of heteroaggregation between multiwalled carbon nanotubes and hematite nanoparticles using time-resolved dynamic light scattering (TR-DLS) [44]. They used cryogenic transmission electron microscopy (cryo-TEM) to observe the structures of CNT-HemNP aggregates and to elucidate the mechanisms of heteroaggregation. They optimized the CNT/HemNP mass concentration ratio (CNT/HemNP ratio) to 0.0316, where the heteroaggregation rate amounts to 3.3 times the HemNP homoaggregation rate in the diffusion-limited regime. Increasing the CNT/HemNP ratio above a threshold value results in a decrease in the growth rate of heteroaggregates, probably due to a blocking mechanism. Increasing the HA concentration decreases the maximum aggregate growth rate. It is likely that HA reduces the available surface of the HemNPs, which inhibits the attachment of CNTs to the HemNP surface. One highlight of the study is the consideration of cryo-TEM to observe the morphology of heteroaggregate. However, they only used HA concentrations of up to 0.5 mg/L TOC, which is still much lower than that in most natural waters.

2.3. Heteroaggregation between nanoparticles and microorganisms

Heteroaggregation of NPs with microbial cells such as bacteria and algae is important for fate, transport, transformation, and toxicity of NPs in both aquatic and terrestrial environments [106–113]. Heteroaggregation could occur between a single particle and a cell, or via particle aggregate–cell interactions [114] – with important implications in the natural environment. For instance, NPs–microorganism heteroaggregation can lead to increased removal of NPs from wastewater during secondary treatment [106,115–118]. Interactions between cell walls of microorganisms and NPs are also thought to precede uptake and toxicity [107,108,110–112,116,119], and may be important for trophic transfer of NPs in both aquatic and terrestrial environments [108,119–121].

Using a batch sorption technique, Kiser *et al.* [117] reported adsorption of TiO₂ NPs onto wastewater biomass. In the study, up to 85% of the NPs (initial concentration = 0.8 mg/L) were removed from suspension by biomass (total suspended solids, TSS = 2.25 g/L) within 3 h. The removal data were fit by a Freundlich isotherm. Thill *et al.* [107] reported a maximum adsorption of 16 mg/m² for CeO₂ NPs (particle size = 7 nm) on the surface of *Escherichia coli* RR1. This study showed that heteroaggregation between NPs and cells can have important impacts on the two components that lead to toxicity in *E. coli* RR1, and significant reduction of CeO₂ NPs to Ce(III) [107]. Similarly, Conway *et al.* [120] reported that sorption of CeO₂ NPs to *Isochrysis galbana*, a marine phytoplankton, occurred within 1 h but toxicity was not observed until after 7 d.

Heteroaggregation between NPs and microbial biomass varied with physicochemical properties of NPs such as elemental composition ($n\text{Ag} > \text{aq-}n\text{C}_{60} > n\text{COOH-Ag} > n\text{TiO}_2$), surface modification ($\text{aq-}n\text{C}_{60} > \text{tol-}n\text{C}_{60} > n\text{C}_{60}(\text{OH})_x > n\text{C}_{60}\text{-PVP}$) [116], crystal structure (anatase $n\text{TiO}_2 > \text{rutile } n\text{TiO}_2$; $\alpha\text{-Al}_2\text{O}_3 > \beta\text{-Al}_2\text{O}_3$) [114], and morphology (microporous SiO₂ > spherical SiO₂) [114]. The surface charge of NPs is expected to affect their interactions with microorganisms although a clear trend has not yet been reported [114,116]. Using batch sorption studies, Barton and coworkers [94] reported that interaction between NPs and activated sludge mixtures (pH = 7.2, TSS ~3.81 g/L) decreased with lower (more negative) surface charge. Listed in decreasing order of interactions, with zeta potential of each NP in water (pH 5.6) added in parenthesis, they found that CeO₂ NPs (32.2 mV) ≈ TiO₂ NPs (32.7 mV) >

ZnO NPs (16.0 mV) > Ag-PVP NPs (–12.0 mV) > CeO₂-citrate NPs (–17.9 mV) > Ag-gum Arabic NPs (–27.5 mV) [94]. Heteroaggregation between CeO₂ NPs and *Isochrysis galbana* was found to increase with NPs concentration [120], and the effect of NP size on heteroaggregation with *E. coli* has also been described [122]. In the study, Morones and others observed that Ag NPs with diameter of 5±2 nm were preferentially in direct interaction with bacteria, which corresponds to the lower end of size distribution of the Ag NPs cells were exposed to (diameter = 16±8 nm).

Bondarenko *et al.* [110] showed that *Pseudomonas aeruginosa* had a higher affinity for surface interactions with Ag NPs than five other bacteria (from same or different genera), demonstrating that heteroaggregation may vary between different microbial cells. Similarly, a stronger NP–cell association was observed between $n\text{C}_{60}$ and Gram negative *E. coli* (155–342 ng-C₆₀/g-dry cell mass) than with Gram positive *Bacillus subtilis* (21–41 ng-C₆₀/g-dry cell mass) [123]. EPS, dissolved or bound to cell wall [124] have been shown to affect the physicochemical properties and stability of ENMs [15,22,58,125], and can also mediate heteroaggregation between NPs (and other nanomaterials) and cells [114,116,119]. Environmental factors such as media ionic strength, pH, and NOM or other dispersing agents can also influence heteroaggregation between NPs and microorganisms [107,114–116]. For instance, Ma *et al.* [114] showed that the anatase form of TiO₂ formed strong heteroaggregates with *Chlorella pyrenoidosa* at near neutral conditions (pH 6.8) but not at acidic or alkaline conditions. Heteroaggregation of α-Al₂O₃ with the same algae was however favored mostly in acidic conditions.

Heteroaggregation between NPs and cells occur rapidly [110,120,126], and heteroaggregates may continue to grow over time if conditions are favorable [126]. Heteroaggregation may be due to weak physical interactions via DLVO and non-DLVO forces [114] as disaggregation (desorption) has been reported in aqueous conditions that may not affect strong chemical bonds. Rhiem *et al.* [119] observed time-dependent release of CNTs from algae (80% within 72 h) after cell–CNT heteroaggregates were transferred to a CNT-free media. Release was attributed to desorption of previously adsorbed CNTs, and possibly, cytoplasmic elimination. In contrast, repeated washing did not significantly remove $n\text{C}_{60}$ associated with bacterial cells [123], which suggests that binding strength differ significantly between different nanomaterial–cell heteroaggregates.

3. Mechanisms of heteroaggregation

Heteroaggregation of NPs arises mainly from the capability of the two particles/surfaces to interact with each other, mainly via attractive and repulsive forces. These attractions may be due to physical forces or bonding resulting from chemical reactions between molecules at the nanoparticle and colloid surfaces [99]. Surface interactions between NPs (and in general, colloids) arising from electrostatic interactions has been described in detail in the literature [127]. Colloidal interactions may also arise from van der Waals attraction forces, which typically result from temporary dipoles. Bridging of two or more colloids by polymers may also lead to heteroaggregation. Hydrogen bonding is common in water and between hydrogen and several electronegative elements; and has been described in a number of NPs-based heteroaggregates. Lewis acid–base interactions are a type of chemical bonding that lead to heteroaggregation of NPs (and colloids in general) in aqueous and non-aqueous systems [47]. A heteroaggregation system can also arise from interplay of multiple mechanisms – both physical and chemical interactions [99,128,129]. The common mechanisms of heteroaggregation are shown in Fig. 2.

3.1. Electrical force

Colloids typically have electrical charges on their surfaces in aqueous media due to ionization or dissociation of surface functional groups,

binding of ions from solution, or transfer of protons or electrons between two dissimilar surfaces that are very close together [130–133]. Electrostatic interactions occur when the electrical double layers of NPs (and other colloids/surfaces) overlap [127]. Heteroaggregation may result from either weak electrostatic repulsion, attractive electrical fields from oppositely charged surfaces, and van der Waals forces, which tend to result in nonspecific spontaneous agglomeration [93,99,103,129,134–136]. Heteroaggregation resulting from electrostatic interactions has been shown in NP-NP [99,127,136], NP-clay [128], NP-natural colloid [93,128,137,138], and NP-microorganism [107,108,116,117] interactions. Hetero(aggregation) due to suppression of electrostatic forces is typically influenced by a change in solution chemistry, and can in general be predicted by Derjaguin–Landau–Verwey–Overbeek (DLVO) (or extended DLVO) theory [93,135,139]. Concentration of individual components that make up the aggregates is important since it determines the overall surface charge of the heteroaggregates [93]. Electrosteric interactions, arising when the surfaces of charged NPs are covered with polymers, have significant effects on stability of heteroaggregates with respect to changes in ionic strength [139].

3.2. Bridging

Bridging typically occurs when a high molecular weight polymer connects two or more NPs [140]. For polymer bridging to occur there should be sufficient unoccupied space on the NPs for the polymer to attach to [141], and the thickness of the polymer layer must be larger than the thickness of the electrical double layer on the NP(s) [142,143]. Polymers may bind to NPs via electrostatic interactions, covalent bonding, or via functional or ligand groups. Typically, the polymer has to be able to adsorb to the different types of NPs (or colloids/surfaces), but a phenomenon of asymmetric bridging has been described in which heteroaggregation still occurs although the polymer, in its pristine state, can only attach to one of the surfaces [142]. In asymmetric bridging the polymer first attaches to one of the surfaces, leading to a modification in polymer configuration and entropy, which enables it to attach to the other particle it may otherwise not have interacted with [142]. Although studies of asymmetric bridging in NPs-based systems are sparse, factors affecting morphology of polymers such as pH, ionic strength, and temperature [144–146] are expected to affect heteroaggregation occurring via polymer bridging. Heteroaggregation via bridging may also refer to a phenomenon where a NP connects to at least two other NPs (both similar) in a sandwich-like manner [147]. Bridging can also arise when homoaggregation occurs between similar particles that make up a heteroaggregate (e.g. due to compression

of electrical double layer) - leading to the formation of larger heteroaggregates [93,95].

3.3. Hydrogen bonding

Hydrogen bonding is common in water molecules but can also exist between electronegative atoms (e.g. oxygen) and hydrogen atoms that are covalently bound to similar atoms (in this case, oxygen) [132]. Hydrogen bonding typically occurs between nanoparticles or colloids with abundant oxygen-containing groups such as functionalized NPs, metallic oxides NPs, clays, and NOM etc. [99,128,129,148]. Sun *et al.* [129] reported that SiO₂ NPs attached to CNT surfaces via both van der Waals forces and hydrogen bonds. In fact, heteroaggregation via hydrogen bonding has been employed for separation/purification of NPs using functionalized or decorated magnetic NPs [149,150]. In aqueous media, formation of hydrogen bonds between water molecules and oxygen-containing groups on the surface of NPs may weaken heteroaggregation arising from hydrogen bonding [47]. Hydrogen bonds (5–10 *kT*) are generally stronger than common van der Waals bonds (~1 *kT*) but weaker than typical covalent bonds (~100 *kT*) [132]. Hydrogen bonding is predominantly classified as a type of electrostatic or Coulombic interaction since the hydrogen atom, in most cases, is not shared but remains covalently bound to its parent atom [132,151–153].

3.4. Chemical bonding

Heteroaggregation between different types of NPs or NPs and other colloids/surfaces arising from chemical interactions have been mostly ascribed to Lewis acid-base interactions, a type of coordinate covalent bond [47,154]. Heteroaggregation (with interaction energy in orders of tens of *kT* units) between two SiO₂ particles in a non-polar medium was ascribed to Lewis acid-base interactions between the acidic and basic monomers of the particles' surface coating polymers, which contained carboxylic and tertiary amine groups, respectively [154]. Addition of a strong acid or a strong base reversed heteroaggregation by competing for the amine or carboxylic sites, respectively. Lewis acid-base interactions also led to formation of heteroaggregates in aqueous medium between carboxyl functionalized, SiO₂-coated maghemite NPs and SiO₂ NPs functionalized with amino groups [99]. In this particular study, chemical bonding was found to be more effective than electrostatic interactions at forming heteroaggregates between the two NPs, although equilibrium was reached much slower than observed in electrostatic interactions which are more instantaneous [99,155]. Both hydrogen bonding and Lewis acid-base interactions were

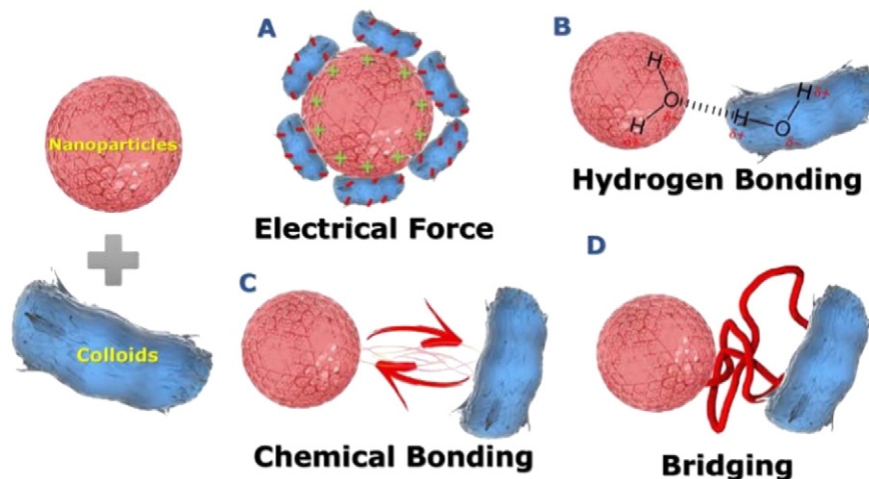


Fig. 2. Mechanisms of heteroaggregation between NPs and colloids (A – electrical forces; B – hydrogen bonding; C – chemical bonding; and D – bridging).

proposed by Yang *et al.* [128] to overcome charge repulsion between graphene oxide and clay materials, leading to heteroaggregation.

4. Modeling of heteroaggregation

4.1. DLVO

Mathematical modeling of heteroaggregation is very important to provide a more fundamental understanding, and allow prediction of the environmental behavior, fate, and transport of NPs [86]. However, there is still a gap between the experimental study and the modeling of heteroaggregation of NPs.

The classical DLVO theory has been widely employed in colloid science to explain the aggregation and deposition behavior of charged particles in the presence of simple electrolytes, and it has also been used to explain the stability of nanoparticle and micrometer-sized particles in suspension [156,157].

DLVO theory can be used to calculate the interaction energies between NPs and a collector grain (sphere-plate), as well as between NPs and NPs (sphere-sphere) [158]. For sphere-plate calculation, the interaction energies equal the sum of electrostatic double layer (Φ_{EDL}) and van der Waals (Φ_{VDW}) interactions:

$$\mathcal{O}_{DLVO}(h) = \mathcal{O}_{EDL}(h) + \mathcal{O}_{VDW}(h) \quad (1)$$

$$\mathcal{O}_{EDL}(h) = \pi\epsilon_0\epsilon r_p \left\{ 2\psi_p\psi_c \ln \left[\frac{1 + \exp(-\kappa h)}{1 - \exp(-\kappa h)} \right] + (\psi_p^2 + \psi_c^2) \ln [1 - \exp(-2\kappa h)] \right\} \quad (2)$$

$$\mathcal{O}_{VDW}(h) = -\frac{A_{123}r_p}{6h \left(1 + \frac{14h}{\lambda} \right)} \quad (3)$$

where Φ_{DLVO} , Φ_{EDL} , and Φ_{VDW} denotes the total, electrostatic, and van der Waals interaction energies, respectively; h is the separation distance between the NPs and the interface; ϵ_0 is the dielectric permittivity of vacuum (or vacuum permittivity); ϵ is the dielectric constant of the solvent/medium; κ is the inverse Debye screening length; ψ_p and ψ_c are the surface potentials of the particles and the collector; A_{123} is the Hamaker constant for the particle-water-collector; r_p is the average radius of particles (m) [158,159].

For sphere-sphere interactions (NPs-NPs), the retarded electrostatic double layer forces (Φ_{EDL}) and the van der Waals forces (Φ_{VDW}) are calculated as follows:

$$\mathcal{O}_{EDL}(h) = 2\pi\epsilon_0\epsilon r_p \psi_p^2 \ln [1 + \exp(-\kappa h)] \quad (4)$$

$$\mathcal{O}_{VDW}(h) = -\frac{A_{121}r_p}{12h \left(1 + \frac{14h}{\lambda} \right)} \quad (5)$$

where the meaning of each parameter is the same as the above defined for sphere-plate interactions; λ is the characteristic wavelength; A_{121} is the Hamaker constant for particle-water-particle [158].

DLVO theory has been employed to accurately quantify the aggregation and deposition kinetics of fullerene C_{60} NPs and to estimate their Hamaker constant [156]. The aggregation and deposition behavior of bare hematite NPs was found to be dominated by DLVO-type interactions [156]. It was also found that the aggregation process of the alginate-coated hematite nanoparticles is consistent with the classical DLVO theory [160]. Some other studies have also indicated that DLVO theory can be used to describe the platelet interactions in montmorillonite systems [161,162].

When investigating the heteroaggregation between clay particles (montmorillonite) and NPs (Ag and TiO_2) in aqueous environments, Zhou *et al.* used classical DLVO theory to calculate the heights of the

energy barriers under different pH and ionic strengths conditions using classical DLVO [95]. They emphasized the applicability of the DLVO theory was based on the following facts: (1) the particle concentrations are relatively dilute (montmorillonite as 4.8×10^{15} particles/m³, TiO_2 as 2.8×10^{15} particles/m³, and Ag as 2.3×10^{15} particles/m³); (2) montmorillonite is in its sodium form, and (3) the particle charges are relatively low.

One problem with DLVO modeling of heteroaggregation of NPs is its applicability in different systems. For example, to analyze the heteroaggregation between NPs and kaolin, one might question that using the sphere-plate equation to calculate interaction between NPs and kaolin (~500 nm) may be inappropriate, because the size of kaolin is not large enough to be considered an infinite plate for the NPs. However, in the plate-sphere model, the size of the plate doesn't need to be "infinite". In fact, kaolin and other types of clays have been considered as plates in the plate-sphere model in the field of colloid science [96,127,163].

The major issues with classical DLVO theory for predicting the stability of nanoparticles are as follows [48]: (1) DLVO only describes the short range interaction within 0.1–10 nm due to the exponential decay of the forces with distance [164,165]. Distances out of this scope will probably result in disagreement due to hydration forces [166]; (2) multivalent electrolytes with high concentration may result in the failure of DLVO. This is possibly caused by the reduction of electrostatic force and the prevalence of dispersion forces [167,168]; and (3) there are other short range non-DLVO interactions [169,170].

4.2. Extended DLVO (X-DLVO)

Although the classical DLVO theory has been found to be quantitatively in line with the behavior of NPs in aqueous phase, the major problem is that it only includes electric double layer and van der Waals interactions. Classical DLVO forces are not sufficient to accurately predict aggregation behavior, and an organic coating may result in the failure of DLVO theory. The adsorbed polymer or polyelectrolyte coatings or NOM on NPs may result in steric repulsion forces, so that they only have a net attraction in a secondary minimum. Extended DLVO is expected to address this problem and provide better simulation of aggregation in the presence of organic coatings such as NOM [46,156]. In extended DLVO (X-DLVO) theory, non-DLVO type interactions (such as short range hydration forces, structure forces, and specific chemical interaction) are incorporated into the estimation of interaction forces [171,175].

The special characteristics of NPs also challenge the limits of colloid science, causing many complexities in the applicability of DLVO theory [48]. Therefore, there is a need for expanded theoretical approaches. Some studies indicated that DLVO theory will no longer be valid when the particle sizes are smaller than 10 nm, because the particle core size, chain length of coating molecules, and electrostatic double layer thickness approach similar dimensions in this small size region [35].

In addition to steric repulsion forces due to NP coatings, there are other X-DLVO forces [171]. These additional short-range forces include bridging attraction forces [172], osmotic repulsion forces resulting from concentration of ions between two particles [173,174], hydrophobic Lewis acid-base forces originating from entropic penalty of separating hydrogen bonds in water [175,176], and magnetic attraction forces resulting from aligning electron spins [177]. These forces may interact with each other in the same aqueous phase in the case of ENMs. However, it should be noted that an accurate determination of each force is generally impossible. A case in point is the origin of hydrophobic and hydrophilic interactions, which is still not completely understood [165].

Thio *et al.* evaluated the role of organic capping agents (citrate and PVP) in the aggregation and deposition of capped Ag NPs on SiO_2 surfaces. The citrate anion has considerably less steric hindrance and some bare contact points, which is in general agreement with the X-DLVO model of colloidal interactions [178]. They also measured the

influence of solution chemistry on the adhesion of Au NPs to mica using colloid probe atomic force microscopy, and considered the X-DLVO empirical model to include the contribution of non-DLVO interactions (structural forces) between the Au NPs and mica surfaces [179]. Thus, X-DLVO modeling can reconcile the discrepancy between theory and experimental data.

Jung *et al.* investigated the enhanced transport of polymer-coated nZVI (carboxymethyl cellulose-surface modified nZVI, RNIP) in a sand column using classical and X-DLVO theory [180]. Transport of humic acid-modified RNIP (HA-RNIP) at various HA concentrations was also studied. As mentioned above, magnetic forces between particles were not included in classical DLVO calculations, requiring a non-traditional approach. In addition, the surface potential of RNIP particles was influenced by the presence of HA, which was not considered in the DLVO calculations. X-DLVO was necessary and found to be useful in this study.

Although X-DLVO equations have been employed widely in recent years to analyze measured data [181,182], there are still limitations. One major challenge is the difficulty to quantify the surface heterogeneities of collector media and NPs [181].

4.3. Application of a heteroaggregation model

Current models for the heteroaggregation of NPs are imperfect, because most of them do not include the impact of spatial and temporal factors [86]. Also, the effects of flow velocity and hydrology have not been considered in heteroaggregation. For better modeling of heteroaggregation in natural water bodies, we need more experimental datasets to provide information on these parameters that are largely unaccounted for [82].

Markus *et al.* established a mathematical model to simulate the fate and transport of NPs in the aquatic environment, where heteroaggregation is an important process [82]. The model was calibrated using published data.

Shen *et al.* modeled the heteroaggregation between NPs and micro-particles [183]. They studied the detachment of homoaggregates and heteroaggregates at primary minima during transients in aqueous phase. In their modeling, they considered two representatives for homoaggregates: (1) small colloidal clusters with well-defined structures; (2) clusters generated by randomly packing spheres using Monte Carlo method. For the modeling of heteroaggregates, the micro-particles coated with NPs were used. The DLVO interaction energies for the homoaggregates and heteroaggregates at different ionic strengths were calculated using surface element integration technique. Unlike homoaggregates, it was found that at low ionic strengths (e.g., ≤ 0.01 M) the repulsive forces dominate heteroaggregates at all separation distances. Although the classical DLVO model demonstrates that smaller particles result in lower interaction energy barriers and are favored to be irreversibly attached at primary minima, the modeling results from this study explain why viruses exhibit more conservative transport compared to microbial pathogens in the aqueous phase [183].

The Smoluchowski-Stokes model was used by Quik *et al.* to evaluate aggregation-sedimentation observations [184]. This model includes homoaggregation, heteroaggregation and sedimentation of NPs and natural colloids (NCs). It was found that the model was appropriate to predict CeO₂ NP settling, which is time- and initial concentration-dependent. An important finding of this simulation is that the heteroaggregation of NPs with NCs was identified as the dominating process for removal of NPs from water column. A calibration of the empirical apparent first order model against the mechanistic Smoluchowski-Stokes model showed excellent fit. This indicates that first order removal rates can be used as an approximation to model the fate of NPs in the aqueous phase.

One of the most important parameters for quantifying the heteroaggregation process is the attachment efficiency (α_{hetero}), which is necessary for predicting NP concentrations in the aqueous phase. By employing aggregation modeling based on the Smoluchowski

equation and laser diffraction measurements, Praetorius *et al.* developed a novel method to determine the values of α_{hetero} [93]. They studied heteroaggregation between TiO₂ NPs (15 nm) and larger SiO₂ particles (0.5 μm). It was found that the α_{hetero} values are close to 1 at pH 5, when the TiO₂ NPs and the SiO₂ particles have opposite charge. At pH 8, however, both types of particles are negatively charged and α_{hetero} varied from <0.001 at low ionic strength (1 mM NaCl) to 1 at high ionic strength (5 mM CaCl₂). It was also found that humic acid suppressed heteroaggregation in this study.

Praetorius *et al.* also developed a model to carry out detailed investigation of heteroaggregation between TiO₂ NPs and suspended particulate matter (SPM) in the Rhine River [185]. The predicted TiO₂ NP concentrations were on the order of ng/L in the water compartment and mg/kg in the sediment. It was found that the SPM properties (such as concentration, size, density) as well as the affinity of TiO₂ NPs and SPM (indicated by the attachment efficiency, $\alpha_{\text{het-agg}}$) are of vital importance for understanding the fate and transport of TiO₂ NPs in the Rhine River. The value of $\alpha_{\text{het-agg}}$ varied between 0.001 and 1 in different models.

Modeling of heteroaggregation in complex natural systems is needed to understand the heteroaggregation process in the real environment, although it is difficult due to the various biogenic and geogenic particles, NOM and other substances in the environment. A model of NPs (TiO₂) in the Lower Rhône River in France indicated that the heteroaggregation between NPs and suspended particulate matter was affected by the complexity of water chemistry. It was indicated that a reliable prediction of the fate of NPs is feasible if the water characteristic in regions near the emission sources is favorable for heteroaggregation [24]. In other words, the heteroaggregation and deposition of NPs to the sediment layer can substantially reduce the uncertainty in the prediction of the fate and transport of NPs. This indicates that heteroaggregation with natural colloids is of vital importance for the prediction of fate and transport of NPs in natural waters. Although this model was successfully used to predict the heteroaggregation in the complex rivers, it should be noted that the spatial variability in emission sources was not considered.

4.4. Fractal dimension

It has been recognized that majority of aggregates are fractal in nature. Most aggregates can be characterized by a non-integer dimensionality, i.e., the mass of a fractal aggregate, $m(R)$, is proportional to its radius, a_h , to power d_f ,

$$m(R) \propto (a_h)^{d_f}$$

where d_f is termed fractal dimension. Experimental d_f values are found in the range of 1.7–2.5 [186]. d_f is related to the aggregation rate: the slower the aggregation, the more particles have time to configure themselves into a more compact structure, and the higher the fractal dimension. Typical diffusion-limited aggregates have d_f of 1.7–1.8, while reaction-limited aggregates are often found with d_f values around 2.1 [186]. Two common techniques are used to determine the fractal dimension, DLS and static light scattering (SLS).

The theoretical basis of the DLS technique is that a relationship between hydrodynamic size a_h and time t exists as follows,

$$a_h(t) \propto (1 + t/t_a)^{1-d_f}$$

where t_a is the characteristic Brownian aggregation time for doublet formation, given by $t_a = 1/(k_1 N_0)$. The determination of d_f can be accomplished with a log-log plot of the hydrodynamic size as a function of time.

The basis of the SLS technique is that the structure factor, $S(q)$, is given by

$$S(q) \propto q^{-d_f}$$

where the scattering vector, q , is given by $q = (4\pi/\lambda) \sin(\theta/2)$, λ is the wavelength of the laser, and θ is the scattering angle. $S(q)$ is proportional to the average scattered intensity, $I(q)$, which is the data collected by SLS. Therefore, the slope of the linear region of a $\log I(q) - \log q$ gives the fractal dimension.

The fractal dimension can be used to determine nanoparticle affinity for heteroaggregation in environmental matrices [94], to calculate the aggregate size in modeling, to understand the effect of heteroaggregation on the fate of NPs in water, and to analyze the heteroaggregate structure [184].

5. Important indicators for heteroaggregation process

5.1. Zeta potential

Zeta potential is a physical property of colloids which represents the electric potential between the slipping plane of particles' double layer and the bulk fluid. It is a measure of surface charge on NPs and colloids in general [130]. The zeta potential is a key indicator in the interaction among colloids, NOM and NPs, which suggests the degree of electrostatic repulsion between adjacent particles. The value of zeta potential is usually associated with solution chemistry (e.g. pH and ionic strength) [14,22,125]. Recent studies have also shown that media temperature can influence zeta potential [15,187]. Zeta potential is commonly determined by measuring electrophoretic mobility, the velocity of a particle in a unit electric field, using instruments such as Malvern Zetasizer Nano [91,146,188–191] and Brookhaven Zetaplus [192]. Zeta potential is related to the electrophoretic mobility via the Henry equation:

$$U_E = \frac{2\varepsilon\zeta f(\kappa a)}{3\eta}$$

where U_E is electrophoretic mobility, ζ is zeta potential, ε is dielectric constant, η is viscosity and $f(\kappa a)$ is Henry's function.

5.2. Size

Studies have been conducted to investigate the effect of particle size on aggregation (homoaggregation and heteroaggregation) properties [140]. Up till now, the most popular techniques used to determine the size of NPs include electron microscopy - TEM and SEM [193,194], and DLS for particles in suspension [195], and small-angle X-ray

scattering (SAXS) [196]. TEM is the most direct method since size measurements can be obtained from particle images. However, the size distribution is limited to the sample number, and lack of contrast or overlap of particles frequently complicates the analysis [197]. DLS is useful for determining the size of aggregates in real time, although it has a weakness of being biased towards larger particles/aggregates [196].

5.3. Heteroaggregation rate

TR-DLS is usually used to determine evolution of the hydrodynamic radius with time and aggregation rates [198]. In addition, multiangle light-scattering techniques are capable of distinguishing homoaggregates from heteroaggregates [199]. Thus, multiangle static and dynamic light scattering have emerged as powerful tools to probe the particle aggregation processes *in-situ* [200,201]. In most studies of the kinetics of heteroaggregation at an early stage, an averaged stability ratio was calculated using the DLS data.

Some techniques for characterizing heteroaggregation are listed in Table 1.

6. Research challenges and perspectives

Based on the above analysis, we propose the following research challenges to be addressed in the future:

- The determination of α_{hetero} values and heteroaggregation rates;
- Combined application of DLS with other instruments such as electron microscopy for a wider range of measurements of heteroaggregation;
- 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 NPs;
- The quantitative adsorption and desorption of NOM onto the surface of NPs and heteroaggregates;
- Better understanding of the fundamental mechanisms and modeling of heteroaggregation in natural water which is a complex system containing NOM, NPs, and NCs.

Addressing the above mentioned challenges will lead to a better understanding of the heteroaggregation of NPs with biocolloids and geocolloids. This is not only important for the fundamental science of fate and transport of nanoparticles, but also significant for the applied science and engineering of control and removal of nanoparticles in aqueous environments.

Table 1
Techniques for characterizing heteroaggregation.

Technique	Features	Strengths	Limitations	Ref.
DLS	Size distribution of nanoparticles and colloids;	Fast and simple operation; used to determine aggregation rates;	Low resolution; low accuracy for large particles	[44,93,95,99,105,198,200,201]
Electron microscope	TEM	Size, shape, and physical morphology of individual nanomaterials; can be coupled with an energy-dispersive X-ray spectroscopy (EDXS) to provide information of chemical and electronic structure.	Require dry sample; limited field of view or analysis of samples; lack of contrast	[98,99,107,114]
	Cryo-TEM		Low image contrast; Low signal to noise ratio	[44,105,202,203]
	SEM		Dry sample needed; limited field of view or analysis of samples; coating may be required to increase conductivity	[99]

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