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Review

Behavior of engineered nanoparticles in aquatic environmental samples: Current status and challenges

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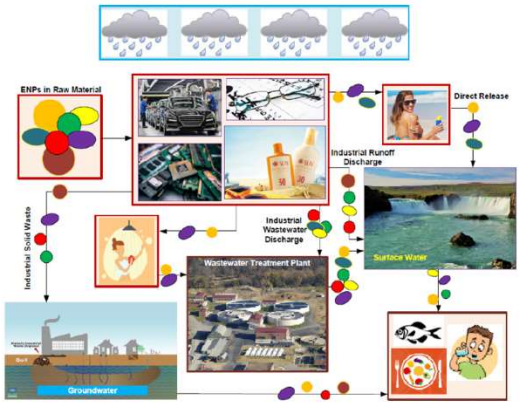
HIGHLIGHTS

- Regulatory overview of discharge of engineered nanoparticles (ENPs) in environment
- Overview of the capabilities of predictive tools
- Influence of environment and physiochemical properties of ENP on fate and toxicity
- Behavioral case studies of ENPs behavior in realistic environmental conditions

GRAPHICAL ABSTRACT



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ABSTRACT

The increasing use of engineered nanoparticles (ENPs) in consumer products has led to their increased presence in natural water systems. Here, we present a critical overview of the studies that analyzed the fate and transport behavior of ENPs using real environmental samples. We focused on cerium dioxide, titanium dioxide, silver, carbon nanotubes, and zinc oxide, the widely used ENPs in consumer products. Under field scale settings, the transformation rates of ENPs and subsequently their physicochemical properties (e.g., toxicity and bioavailability) are primarily influenced by the modes of interactions among ENPs and natural organic matter. Other typical parameters include factors related to water chemistry, hydrodynamics, and surface and electronic properties of ENPs. Overall, future nanomanufacturing processes should fully consider the health, safety, and environmental impacts without compromising the functionality of consumer products.

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Contents

1. Introduction

Engineered nanomaterials, manufactured nanomaterials, or engineered nanoparticles (ENPs) are incidental or manufactured materials containing "nanometer" sized particles in an unbound or agglomerated state. ENPs are classified based on their size and constitution. As per the European Union (EU), more than 50% of the particles in ENPs have one or more external dimensions in the size range of 1–100 nm (European Commission, 2020). Per the British Standards Institution and American Society for Testing Materials, at least one dimension of ENPs is between 0 and 100 nm (P. A. Specification, 2007; Delay and Frimmel, 2012). The International Organization for Standardization/Technical Specifications (ISO/TS) 80004-2:2015 requires all the dimensions to be between 0 and 100 nm (Benko, 2017).

The rapid discoveries of various ENPs in the last two decades highlight a need for standardized methods that focus on their accurate characterization. There is a need to develop centralized databases for referencing ENPs' environmental fate, transport, and toxicology parameters. There is a paucity of detailed information on the exposure matrix of ENPs in the environment. Furthermore, ENPs exhibit unique fate and behavior characteristics compared with conventional inorganic and organic contaminants, including their colloidal and soluble forms. Thus, regulating the discharge of ENPs into the environment has been a challenging task (Schwirn et al., 2020)

Regulating discharge of ENPs is significantly hampered by the lack of established and documented standards. For example, different characterization methods have reported varied results for the same ENP (standard deviation = 1–100 nm) (Clausen and Hansen, 2018; *Nat. Nanotechnol.*, 2019). European Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) has recently updated the regulations for an environmental chemical hazard assessment and exposure assessment for risk characterization of registered nanoforms and sets of nanoforms. These updated regulations are set to standardize safety testing methods and provide a common basis for the mutual acceptance of test data across the EU (European Union Observatory for Nanomaterial, 2020). These REACH guidelines developed a number-based particle size distribution approach for quantifying the fraction of the constituent particles in the size range of 1–100 nm (European Commission, 2020). However, the US Environmental Protection Agency (USEPA) suggests a weight-based threshold for the ENPs' size distribution (*Nat. Nanotechnol.*, 2019). Although the weight-based approaches can accurately measure the particle sizes at the nanoscale, they do not consider the toxic impacts associated with their nanometer scale. There is a need to develop new approaches for standardizing the characterization and toxicity analysis of ENPs across communities. It is also critical to incorporate classifications of nanoparticles based on their structure, properties, composition, along with their toxicity parameters into the regulatory standards.

Consumer products are modified with ENPs to mirror their outstanding chemical, photoactive, optical, and thermal functions. The use of silver (Ag) nanoparticles in medical applications alone has grown annually by 5% since 2000 (Clausen and Hansen, 2018). Current methods of designing and manufacturing ENPs focus solely on enhancing the performance of consumer products without considering their life cycle environmental impacts. For example, titanium dioxide (TiO_2) nanoparticles doped with metal ions offer superior performance related to their electronic excitation states, photocatalytic activity, durability, and energy efficiency, particularly in energy devices. However, these doped ENPs significantly reduce their photobleaching effect, making them more resistant to photodegradation (Jahana et al., 2017) and increasing their retention times and cell toxicity in aqueous environments. The energy efficiency of doped TiO_2 nanoparticles increases in the order of Ni- < Cu- < Mn- < Fe-TiO_2, whereas the acute toxicity to zebrafish embryos decreases in the order of Fe ≥ Ni > Cu > Mn-TiO_2 (Park et al., 2014). This research shows the need to use Mn dopants for improving energy efficiency without increasing toxicity (Park et al., 2014).

Environmental behavioral studies involve collecting and analyzing environmental samples to determine the fate and transport behavior of ENPs. Such information, along with the production volumes and preferred pathways of ENPs, can be used to predict the environmental abundance of ENPs (Clausen and Hansen, 2018; European Union Observatory for Nanomaterial, 2020). The current study focuses on the behavioral case studies (versus bench-scale studies) of five major ENPs, namely TiO_2 (n-TiO_2), silver (n-Ag), carbon nanotubes (CNTs), zinc oxide (n-ZnO), and cerium dioxide (n-CeO_2). The production volumes of these five ENPs have already reached the commercial levels, and their presence in the natural environment is also imminent. Systematical evaluation of these ENPs was possible via extramural funding from several federal agencies, including USEPA (N. N. Initiative, 2020), U.S. Environmental Implications of Nanotechnology (CEINT), Nanomaterial FAte and Speciation in the Environment (NanoFase), and Safer and Ecodesign Research and Education applied to nanomaterial DEvelopment, the new generation of materials safer by design (SERENADE) project. While silicon dioxide (n-SiO_2) is another ENP that is widely used, there are a limited number of reports on their environmental behavioral studies (Sengul and Asmatulu, 2020; *Addit.*

Polym., 2017; Inshakova and Inshakov, 2017; Goswami et al., 2017; De Matteis, 2017).

First, we discuss the classes of ENPs based on the structure, properties, chemical composition, mechanisms of the ENPs' entry into surface water at various stages of their life cycle, and environmental conditions that determine the ENPs' fate and transport under field conditions. Then, we introduce the environmental behavioral studies, focusing on the interactions among ENPs and environmental surfaces (soil, sediment, and natural organic matter), specifically under the influences of typical physical, chemical, and photochemical processes.

2. Classes of ENPs and their toxicity

Nanoparticles can belong to the classes of incidental, intentional, or natural nanoparticles. Although ENPs are not as prominent as natural nanoparticles, they exert negative water resource impacts due to their potential toxicity (De Matteis, 2017). Based on their structure, properties, and chemical composition, ENPs can be arranged into four categories: (i) engineered inorganic nanoparticles (EINPs), (ii) engineered organic nanoparticles (EONPs), (iii) engineered polymeric nanoparticles (EPNPs), and (iv) miscellaneous nanoparticles (Misc). Table 1 lists, by category, examples and the target properties of the ENPs to use them in the products.

2.1. Ecotoxicity of ENPs

ENPs remain reactive and stable and exert potential toxic effects in the natural water systems (Sweet and Singleton, 2011). They damage the cell structure of the exposed cells and potentially cause cell death (Sweet and Singleton, 2011). There exists significant evidence about their potential ecotoxicity impacts (De Matteis, 2017; Dimapilis et al., 2018; Lv et al., 2016; Correia et al., 2019; Leareng et al., 2020; Yang et al., 2012). The properties of aqueous media and ENPs themselves influence their toxicity (Khan et al., 2019). A greater production of consumer products containing ENPs increases the likelihood of ENPs reaching surface waters. Here we summarize the toxic effects of n-TiO_2, n-Ag, CNTs, n-ZnO and n-CeO_2 on a diverse range of indigenous microorganisms.

The n-ZnO particles' antimicrobial activity renders them toxic to selected organisms. Three known mechanisms of their antimicrobial properties include the release of reactive oxygen species (ROS), release of Zn^{2+}, and direct contact of n-ZnO with the bacterial cell wall (Dimapilis et al., 2018). The release of ROS damages DNA, cellular membranes, or cellular proteins, ultimately causing the death of the exposed cells (Dimapilis et al., 2018). The n-ZnO particles do not have to enter the cell themselves to damage the cells (Mishra et al., 2017) as close presence to the cell membrane can cause changes in the cell's microenvironment, which in turn increases the permeability of the cell membrane and prompts the cell to intake the nanoparticle (Mishra et al., 2017). Rainbow trout (*Oncorhynchus mykiss*) exposed to n-CeO_2, resulted in an increase of glutathione S-transferases enzyme activity in the gills of the fish (Correia et al., 2019). A potential antioxidant response was also reported, with a significant increase of catalase activity observed in the livers of the fish (Correia et al., 2019). Irrespective of the size ranges (2–15 nm), both pristine and functionalized forms of n-Ag can interfere with the results obtained from spectroscopy-based assays (e.g., cytotoxicity assays, such as 3-(4, 5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT), neutral red (NR), Hoechst, and Resazurin). Therefore, the cytotoxic effects of n-Ag particles determined by spectroscopy-based assays may be unreliable (Mello et al., 2020).

Physical properties (e.g., length, aspect ratio, surface area, degree of aggregation, purity, concentration) have been reported to impact the toxic effects of CNTs (Khan et al., 2019; Jebel and Almasi, 2016). The extent of such impact by individual physical properties may be different. For example, SWCNTs modified with metals can be more toxic than their pristine forms (Gorelik O and Arepalli, 2000). This dependency dictates the need for controlling the CNTs structure during manufacturing to mitigate their potential environmental toxicity effects. Graphene oxide (GO) particles at levels of 50 mg/L, considered high concentration for environmental conditions, have been reported to be toxic in water systems (Ye et al., 2018). Their electronic charge further influences their oxidative stress and toxicity impacts (Ye et al., 2018).

Polymer coated ENPs also exhibit toxicity. For example, the exposure of zebrafish embryos to PVP/polyethyleneimine (PEI) coated n-Ag (10 μg Ag L^{-1}–10 mg Ag L^{-1}) resulted in high toxicity at LC_{50} at 120 h = 50 μg Ag L^{-1}, but causing 100% mortality during the first 24 h of exposure at 0.1 mg Ag L^{-1}. While Nguyen et al. reported that uncoated n-Ag particles are less toxic than coated n-Ag particles and the toxicity depends on the size of the coated n-Ag, Yang et al. reported no correlation between size and toxicity of coated n-Ag (Yang et al., 2012; Nguyen et al., 2013).

3. Environmental release

Water bodies in the vicinity of the point sources experience high ENP loading than those away from point sources (Gottschalk and Nowack, 2011). The extent of such loading can be better understood by tracking the ENPs released throughout their life cycle. Here, we present an overview of the ENPs' release patterns under different stages, including production (Stage 1), incorporation of ENPs in consumer products (Stage 2), the usage of the consumer products (Stage 3), and their disposal (Stage 4) (Fig. 1.) (Caballero-Guzman and Nowack, 2016).

ENPs are inadvertently released during Stages 1 and 2, before a consumer product leaves the manufacturing facility. This is particularly true for powder products that exist in the air. At the end of the production stage, cleaning equipment with water or solvents results in ENPs contaminated wastewater. The concentration of ENPs in such wastewaters is reduced by wastewater treatment operations before discharge to surface waters (Gottschalk and Nowack, 2011). The ENPs discharged on the surface interact with the media constituents (e.g., water, sediments, and natural organic material (NOM)) and depending on the interactions, they can travel in water, be retained in sediments, or undergo irreversible transformation. The residence time of ENPs in water ("aging") influences the ultimate fate of ENPs in the water (Gottschalk and Nowack, 2011).

A snapshot of the release case scenarios for four classes of ENP-based consumer products (coatings, textiles, cosmetics, and automotive) is presented in Table 2. Stages 3 and 4 contribute to the most discharge

Table 1
Classes of engineered nanoparticles (Inshakova and Inshakov, 2017; Goswami et al., 2017; De Matteis, 2017; Chen and Schluesener, 2008; Hoecke et al., 2009; Farré et al., 2011; Pop et al., 2006; Bandaru, 2007; Bosi et al., 2003; Khan et al., 2019; Dimapilis et al., 2018; Mishra et al., 2017; Jebel and Almasi, 2016; Sirelkhatim et al., 2015; Caballero-Guzman and Nowack, 2016; Lv et al., 2016; Klaine et al., 2008).

Category	Target properties	Example applications	Examples
EINPs	Photocatalytic, antimicrobial, antifungal, and optoelectrical	Sunscreens, cosmetics, paints, varnishes, textiles, paper, plastics, dyes, and drug carriers	Fe, Ag, and Au (Zero-valent metals), TiO_2, ZnO and CeO_2.
EONPs	Electrical conductivity, chemical, optical and high strength material	Electronics, optics, and aerospace	Fullerenes, Graphene and CNTs
EPNPs	Magnetic and biocompatibility	Drug carriers, DNA-transfecting agents, and chemical sensors.	Dendrimers
Misc	Optical and electrical; chelating effects	Medical imaging and solar cells	Nanofoils and Quantum Dots

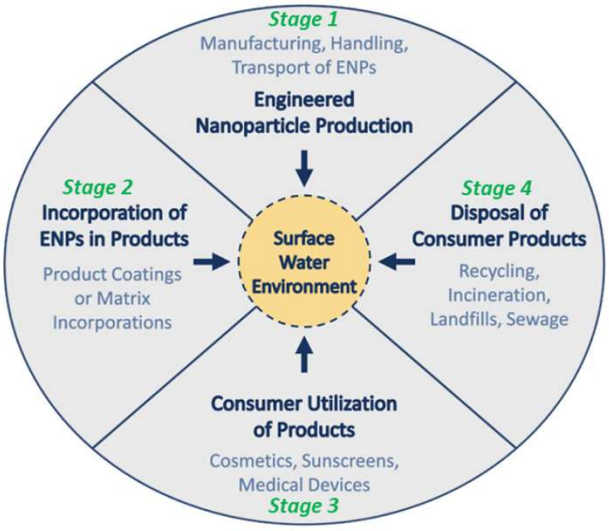

Fig. 1. Four life cycle stages of ENPs with respect to their release into the environment.

of ENPs into water and wastewater systems (Boxall et al., 2007). Nearly 1% of the ENPs' mass from these products reaches the environment. In the case of products based on aerosols and liquid suspensions (e.g., body sprays), 1–5% of the ENPs' mass is released into the environment (Giese et al., 2018). Furthermore, they are released into the environment as soon as they are used. For example, n-TiO_2 from sunscreen and cosmetic products are released into the water resources within few hours after their application.

3.1. Prediction of ENPs released into the environment

Release mechanisms can affect the abundance, bioavailability, and toxicity of ENPs and influence public health risks. The first approach is to track their mass flows on a life cycle basis. Such information can be obtained from gray literature, patents, peer-reviewed publications, and LCA reports (Caballero-Guzman and Nowack, 2016; Boxall et al., 2007; Hendren et al., 2011; Hendren et al., 2013; Wigger et al., 2015). However, such an approach is limited because it often relies upon the worst-case scenario, which assumes all ENPs produced will end up in the environment (Caballero-Guzman and Nowack, 2016).

Another approach is to extract information directly from the use-case scenarios. Wigger et al. reported a case study of n-Ag particles from cotton and polyester textiles released during use, recycling, incineration, and disposal stages were considered (Wigger et al., 2015). A drawback of this method is the lack of quantitative data on ENPs released during each of these four stages. For reliable prediction of the ENPs' production volumes and their releases, accurate information on consumption rates of ENPs at each stage is needed. For example, low production volumes but extensive use of n-Ag products results in a slower release of n-Ag during the production stage but at a higher rate during their application stage than n-SiO_2 and n-CeO_2 (Giese et al., 2018). n-Ag particles are heavily used in cosmetic and skincare products, which are released each time people wash their skin. In contrast, n-SiO_2 particles are used exclusively in textiles and n-CeO_2 particles in glass products, which have a low wear-out rate and hence slower rates of release in the environment than n-Ag. Another approach is to group the consumer products under respective categories (e.g., electronics, medical devices, cosmetics, and textiles), based on physical or functional traits. Then, their aggregate release volumes can be predicted (Caballero-Guzman and Nowack, 2016). Although it is not fair to assume that all the products within a group display the same release behavior, such methods are handy when there is a lack of data about ENPs in an application. Hendren et al. developed a new mechanistic approach using principles of diffusion, sorption, and kinetics. This approach uses the assessment of the degree of transformation of n-Ag particles and then profiles their release and persistence in the water on a temporal basis (Hendren et al., 2013). This approach is effective only when the parameters that control the ENPs release are known. It suffers from a drawback that the ENPs are assumed to remain in the same chemical and physical form once released into the environment (Adam et al., 2018).

Adam et al. have reported a probabilistic material flow analysis approach for predicting the ENPs released into water. This approach considers the relative proportions of ENPs in product-embedded, matrix-embedded, pristine, transformed, and dissolved forms (Adam et al., 2018). As per their predictions, n-Ag particles released into the water environment are primarily in transformed forms (82%) and n-TiO_2 particles in a pristine form (97%). Based on a modeling study by Giese et al., the concentration of n-CeO_2 in freshwater was predicted to be 1 pg/L in 2017 and ~ 100 ng/L by 2050 (Giese et al., 2018).

The prior studies have focused on tracking ENPs in wastewater flows (Shi et al., 2016; Markus et al., 2018; Choi et al., 2018a; Johnson et al., 2011) to assess their amenability in wastewater treatment plants. Choi et al. have measured the levels of n-TiO_2 and n-ZnO particles in the inflow of a wastewater treatment plant at Maryland, USA, using inductively coupled plasma - optical emission spectrometry (ICP-OES) and scanning electron microscopy (SEM) in tandem. Their study reported 21.6 to 391.0 μg/L TiO_2 and 20.0 to 212.0 μg/L ZnO in the wastewater influent (Choi et al., 2018a). Other recent studies have analyzed ENPs in surface waters. n-Ag and n-CeO_2 particles have been reported to be in a range of 0.3 to 2.5 ng/L and 0.4 to 5.2 ng/L, respectively, in water samples collected along the rivers Meuse and IJssel in the Netherlands using single-particle inductively coupled plasma-mass spectroscopy (SP-ICP-MS) (Peters et al., 2018).

Sanchis et al. assessed Sava River (Southeastern Europe) water samples using high performance liquid chromatography (HPLC) coupled to high-resolution mass spectrometry (HRMS) and noted C_{60} fullerene concentrations of 8 pg/L to 59 ng/L in water (Sanchís et al., 2018). Wen et al. found concentrations of Ag in <0.45 μm fractions in Texas rivers in the range between <0.01 to 62 ng/L, but between 0.4 and 6.4 ng/L in the Trinity River estuary (Galveston Bay) (Wen et al., 1997). In contrast to US and European rivers, much higher n-Ag concentrations (0.13–10.16 mg/L) were noted by Syaffiuddin et al. in Malaysian rivers (Syafiuddin et al., 2018). In addition, Syafiuddin et al. attributed the

Table 2
Four classes of consumer products and ENPs release case scenario.

Category	Consumer products	ENPs	Release case scenarios
Coatings (Hsu and Chein, 2007; Künniger et al., 2014; Shandilya et al., 2015; Zanna et al., 2010)	Metal, glass, plastic, wood, textile coatings	Ag, CeO_2, CNT, TiO_2, ZnO, $BaSO_4$, $CaCO_3$	Wearing by mechanical action or by exposure to aggressive environments
Textiles (Lombi et al., 2014; Mitrano et al., 2014; Stefaniak et al., 2014; Windler et al., 2012)	Gloves, jackets, pants, towels, socks, jackets	Ag, Au, CNT, TiO_2, ZnO, Silica, $CaCO_3$	Wear, wash, recycle, and disposal
Cosmetics (Botta et al., 2011; Holbrook et al., 2014)	Eyeliner, lip gloss, sunscreens, skin creams	Ag, Al_2O_3, Au, Carbon Black, TiO_2, ZnO	Application on skin and wash
Automotive (Le Bihan et al., 2013)	Bumpers, car dashboards, car wax	Al_2O_3, CeO_2, CNT, Ti, Fullerenes, $CaCO_3$	Mechanical stresses and weathering

noted temporal variability in n-Ag concentration to the dilution of n-Ag load by wastewater discharges and seasonal variation in the river flows (Syafiuddin et al., 2018). They observed the highest n-Ag concentration during July, which is considered a dry summer month. Similar temporal variation is also noted by Dumont et al. for n-Ag and n-Zn in their simulation study for European waters (Dumont et al., 2015).

Some researchers report elemental particle concentration by size rather than elemental mass concentration of the particles. This makes comparison across some reports difficult because the calibration curves are prepared as intensity versus particle diameter rather than particle mass concentration. Wu et al. used SP-ICP-MS in tandem with transmission electron microscopy coupled with an energy dispersive X-ray spectrometer (TEM-EDS) and quantified the titanium-ENPs particle concentration in Lake Taihu, China as 2.28×10^8 particles per liter with a mean size of 65 nm (Wu et al., 2020). Using SP-ICP-MS in the Barcelona catchment area, Spain Sanchis et al. detected n-Ti concentration ranging 23.2×10^6 and 298×10^6 particles per liter, n-Ag in the range 17.9×10^6 to 45.1×10^6 particles per liter while the concentrations of n-Ce in the watershed ranged from 18.1×10^6 to 278×10^6 particles per liter (Sanchís et al., 2020).

Although the analytical techniques used for ENPs analysis employ advanced detection instrumentation and are varied among studies, they demonstrate the capability to detect ENPs in the environmental samples. To establish a basis and transferability of the results across research studies, regulators, and other practicing professionals, there is an urgent need to establish a standard analytical protocol for ENPs analysis.

4. Fate and transport mechanisms of ENPs

It is important to consider dynamic models for predicting the fate and transport behavior of ENPs under the influence of the bio-physiochemical processes in the water media and properties of ENPs themselves (Klaine et al., 2008). Prior studies have quantified the release of various ENPs (Hendren et al., 2013; Dumont et al., 2015; Praetorius et al., 2012a; Sun et al., 2014; Mackay et al., 2006; Nowack, 2017; Liu and Cohen, 2014). For example, the nanoFate model takes into effect the dynamics of a suite of processes, including homoaggregation, heteroaggregation, dissolution, oxidation, and sulfidation (Garner et al., 2017). In addition, the nanoFate model can be used to predict soluble ENPs that can accumulate at levels equivalent to the minimum toxic threshold values in freshwater and soils (Yao et al., 1971). This model was used to study the releases of n-CeO2, nano copper oxide (n-CuO), n-TiO_2, and n-ZnO in the San Francisco Bay over ten years. However, the accuracy of such predictions is limited due to the lack of ENPs' environmental release data and insufficient understanding of the key mechanisms that influence their ability to reach surface waters during the consumer-use stage (Inshakova and Inshakov, 2017). For example, the interactions between the metal ENPs with ligands (carboxyl groups in NOMs) and anions (Cl^-, PO_3^{3-}, SO_4^{2-}, OH^-) are governed by kinetics of relevant complexation reactions. The resulting complexes could strongly bind ENPs together and influence their solubility and amenability to the coagulation and filtration processes (Stumm and Morgan, 2012). Also, the nature of these complexes influences the amenability of ENPs to the natural attenuation processes and, subsequently, their toxicity levels (US-EPA, 2012). The ENPs and their transformed products could inhibit the growth of microorganisms through the disruption of cell membranes, oxidation of proteins, genotoxicity, interruption of energy transduction, formation of reactive oxygen species (Klaine et al., 2008).

Colloidal stability influences the behavior of ENPs in water (Chen et al., 2010; Elimelech et al., 2013; Hunter, 2003; Yao et al., 1971) because stable ENPs resist aggregation for an extended period. Similar particles interact to undergo homoaggregation Higher levels of the NOM promote the heteroaggregation of ENPs (Chen et al., 2010). Although heteroaggregation is often the predominant form, its relative domination depends on the chemical makeup of the water and the concentration and properties of ENPs (Chen et al., 2010). The aggregation occurs during the transport and attachment processes (Chen et al., 2010; Hunter, 2003). The transportation processes induce collision among the particle, a step necessary for embarking on the aggregation. Brownian motion, fluid motion, and differential sedimentation can influence the transportation of ENPs (Hunter, 2003). The attachment of two ENPs in proximity is again dependent on the properties of both the environment and ENPs.

Deposition is an extreme form of heteroaggregation (Elimelech et al., 2013), which occurs during transport and attachment stages. As ENPs travel in surface waters via Brownian motion, solid surfaces intercept ENPs and disrupt their natural movements (Chen et al., 2010; Elimelech et al., 2013; Hunter, 2003; Yao et al., 1971). As ENPs collide and stick to the solid surfaces, their transportation will slow down and settling will begin, which is a part of their sedimentation (Chen et al., 2010; Elimelech et al., 2013; Hunter, 2003; Yao et al., 1971). In summary, both hydrodynamics and particle–particle interaction parameters influence the attachment mechanisms (Hunter, 2003).

The surfaces of charged particles interact with counterions in surface waters to cause a screening effect. Owing to specific adsorption, these surface charges can result in charge neutralization or charge reversal (Elimelech et al., 2013; Hunter, 2003; Israelachvili, 2015). The surface site density of the solution influences the charges induced by the functional groups. Also, the electrolyte concentration and valence of counter ions control the intensity of the screening effects (Chen et al., 2010).

Capping agents or surface functional groups can be adsorbed onto the surface of an ENP to enhance its colloidal stability. Hydrophilic polymers attached to the ENP surfaces result in their decreased aggregation (Hunter, 2003). As part of steric stabilization, the hydrophilic polymer chains extend into the water, thereby increasing the free energy and enhance the stability of ENPs (Hunter, 2003). Sterically stable ENPs remain dispersed even at high salt or electrolyte concentrations (Chen et al., 2010). Electrosteric stabilization occurs when polyelectrolytes bind to the surface of an ENP, and both steric and electrostatic repulsions arise simultaneously. Unlike steric stabilization, electrosteric stabilization is heavily dependent on solution chemistry (Chen et al., 2010). Changes in the solution chemistry such as pH, ionic strength, and ion concentrations can shift the properties and structure of the polyelectrolytes and the overall surface charge of the ENP (Chen et al., 2010). NOMs in surface waters can affect the surface charge of an ENP. Particle interactions with NOMs induce steric or electrosteric stabilization (Chen et al., 2010). Key transformation processes that influence fate and behavior of ENPs in aquatic environments are summarized in Table 3. The principal mechanisms controlling ENPs behavior can be easily understood by assuming that only one of the discussed processes occurs at a given time. The situation is more complicated due to the abundance of natural constituents and ions present in surface waters. As the ENPs interact with other substances in the environment, the properties of the ENPs continue to change.

The key physicochemical properties of ENPs that impact their behavior in surface waters include chemical composition, mass, particle number and concentration, surface area concentration, size distribution, specific surface area, zeta potential, surface contamination, solubility, surface functional group, and surface capping agent chemistry (Klaine et al., 2008). A higher zeta potential, i.e., high surface change ($>+30$ mV or <-30 mV) indicates that ENPs are electrically stable and that they resist homoaggregation. A lower zeta potential ($<+25$ mV or >-25 mV) indicates that ENPs will undergo heteroaggregation. As summarized in Table 4, n-Ag, n-TiO_2 and n-ZnO show greater aggregation potential than CeO_2.

The environmental conditions of surface waters also influence the behavior of ENPs in surface waters. The ionic strength, pH, the concentration of electrolytes and NOMs present in surface waters, temperature, flow velocity, and other water chemistry parameters are all vital properties that determine the fate and transport of ENPs in surface waters (Fig. 2) (Chen et al., 2010). Although various physiochemical

Table 3
Key transformation processes that influence fate and behavior of ENPs in aquatic environments (Klaine et al., 2008; Nowack et al., 2012; Quik et al., 2010; Stone et al., 2010).

Environmental transformation process		Expected outcomes of the transformation
Chemical and photochemical processes	Photochemical reactions	Chemical changes to ENPs, surface coatings, and surface properties occur due to the presence of light. The photochemical reactions influence the aggregation, agglomeration and adsorption behavior of ENPs.
	Redox reactions	ENPs undergo oxidation or reduction, causing a loss or gain of an electron to another chemical species, respectively. Environmental parameters play a role in determining if this process will occur.
	Dissolution/speciation	ENPs dissolve or release ions or molecules into surface waters. The dissolution process depends on the materials' properties as well as the water properties.
Physical processes	Aggregation/agglomeration	Aggregation occurs when strong chemical bonds or electrostatic interactions cause particles to irreversibly cluster together. Agglomeration occurs when weak van der Waals forces cause particles to cluster together. This process is reversible and dependent on surface water properties.
	Sedimentation/deposition	When ENPs agglomerate and fall out of suspension due to gravitational settling. This process is affected by fluid viscosity and particle density and limited by the rate of agglomeration.
Interactions with surfaces/substances	NOM adsorption	When natural organic matter (e.g., humic acid, fulvic acid, and humin) binds to the surface of an ENP, altering the surface properties and behavior of the ENP in surface waters.
	Sorption to other surfaces	When ENPs attach to other substances and surfaces/objects in surface waters. This process can be thought of as an extreme form of heteroaggregation.

properties impact the fate and behavior of ENPs in surface waters, ENPs are primarily affected by their particle size (Goswami et al., 2017). As a result of their small particle size, the surface areas of ENPs are significantly more extensive and reactive. This allows ENPs to interact more efficiently with microorganisms than larger particles (Chen and Schluesener, 2008; Auffan et al., 2009).

The behavior of ENPs in aqueous systems depends upon their physicochemical properties, such as mobility, size, polydispersity and bioavailability. For instance, ENPs that prefer solid phases are less mobile in water and thus less amenable to bioprocesses. Such ENPs could be removed from water systems by adsorption treatment (Bezbaruah et al., 2009; Gimbert et al., 2007). For ENPs that prefer an aquatic environment, the water quality parameters (e.g., pH, ionic strength, and dissolved organic matter) play a critical role (Boxall et al., 2007). Therefore, both the surface properties of ENPs and water quality parameters will determine their abundance in water systems. However, owing to their small size and unique properties, it is extremely challenging to detect and quantify ENPs under field conditions. Therefore, future research priorities should include developing methods that are transferable to detect and characterize a wide variety of ENPs, including complex or carbon-based materials in real-world complex matrices and the determination of their transformations in such environments (Johnston et al., 2020).

5. Environmental behavioral case studies

ENPs entering a WWTP eventually reach surface water environments in unaltered or altered forms. The type and degree of alterations depend on the properties of the ENPs and carrying media and the characteristics of WWTP processes and the surface water environment (Fig. 3, changes coded by different colors and shapes). However, there is a lack of understanding of how the condition of the media and the ENPs themselves affect their transformations in real situations. These challenges render it difficult to predict the transport and behavior changes of ENPs, and finally regulate ENPs release volumes. An overview of recent studies on the fate and transport of real environmental samples of five prominent ENPs (n-TiO_2, n-Ag, CNTs, n-ZnO, and n-CeO_2) in surface waters is summarized in Table 5.

5.1. n-TiO_2

n-TiO_2 can occur in three different crystal structures – rutile (tetragonal), anatase (tetragonal), and brookite (orthorhombic) (Gottschalk and Nowack, 2011; Carp et al., 2004), allowing them to exist in various shapes and sizes which behave differently in aquatic environments. Zhu et al. studied the aggregation of a rutile form of n-TiO_2 coated with 5 wt % silicon dioxide under different molar concentrations of humic acid

Table 4
Physiochemical properties of interest for engineered nanoparticles in various engineered nanoparticle categories.

ENP	Precursor/surface capping agent	Zeta potential [mV]	Particle size [nm]
Engineered inorganic nanoparticles			
Ag (Chen and Schluesener, 2008; Wang et al., 2017)	$AgNo_3$, Au, Citrate, Tannic Acid, EDTA, Graphene	−28.3	10–34
Au (Ghosh et al., 2011; Mittal et al., 2013)	$HAuCl_4$, Ag, Pd, Citrate, Biotin	–	1–50
CeO_2 (Hoecke et al., 2009; Quik et al., 2010; Futaba et al., 2006; Kim et al., 2012)	$Ce(NO_3)_3 \cdot 6H_2O$, Citrate, and Oleic Acid	51.3 ± 1.3	5–40
TiO_2 (Bianco et al., 2005; Trojanowicz, 2006)	Oleic Acid, Oleyl Amine, Triethanolamine, Pt, Ag	22.5 ± 1.9	10–20
ZnO (Ahamed et al., 2010; Dwivedi et al., 2015; Tejamaya et al., 2012)	3-Aminopropyl triethoxysilane	23	20–100
Engineered organic nanoparticles (EONPs)			
SWCNTs (Trojanowicz, 2006; Hardman, 2005)	Graphite Si, TiO_2, Methane	–	0.4–30
MWCNTs (Trojanowicz, 2006; Abbasi et al., 2014)	Graphite, Hydrocarbons	–	1.4–100
Fullerenes (Hu et al., 2015)	Graphite, CTAB Chloride, Triton X − 100, BSA	–	0.5
Graphene nano-foil (Stone et al., 2010; Zhu et al., 2015)	Graphite, Si or SiO_2, Cu, and Al	–	100–300
Engineered polymeric nanoparticles (EPNPs)			
Ag-PEG (Hu et al., 2015; Zhu et al., 2015; Rao et al., 2015)	Polyethylene Glycol, $AgNO_3$	–	10–80
Ag-PVP (Li et al., 2016; Park et al., 2008)	Polyvinyl pyrrolidone, $AgNO_3$	-10	50
CeO_2 (Choi et al., 2018b)	Polyvinyl pyrrolidone, Cerium (III) Acetate Hydrate	–	8–40
TiO_2 (Choi et al., 2018b)	Poly (Acrylic Acid), *N,N*-Dimethyl Acetamide	–	20–60
Dendrimers (Abbasi et al., 2014; Majedi et al., 2014)	Ammonia, Methanol Methyl Acrylate	–	1–10
Miscellaneous nanoparticles			
Quantum Dots (Peng et al., 2017; Peng et al., 2015)	$CdCl_2$, H_2Te, Citrate, Glutathione	–	10–20

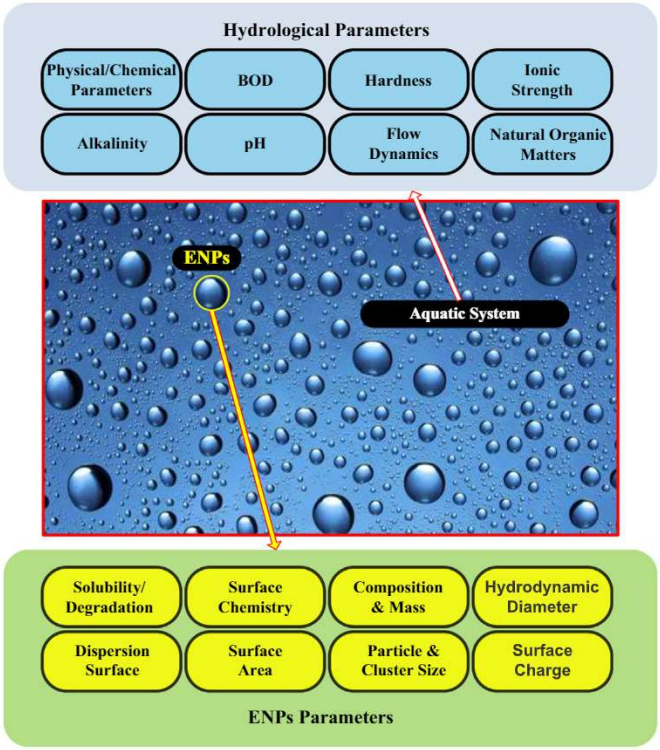

Fig. 2. An overview of the physiochemical properties and hydrological parameters that impact the fate and properties of ENPs in surface water.

([HA]) and different pH conditions (Zhu et al., 2014). The coated n-TiO_2 displayed a point of zero charge (pHpzc) at pH = 6. The observations of the study are presented in Table 6. At pH = 4, the negatively charged HA neutralized charges on n-TiO_2, which resulted in a decrease in TiO_2 zeta potential (ζ) and hence an increase in the particle aggregation. However, at [HA] > 94 μg/L, a charge reversal led to a lowering aggregation rate and increasing stability of n-TiO_2. At pH = pHpzc (= 5.8), and [HA] = 32 μg/L, a decrease in ζ indicates that n-TiO_2 is stabilized. At pH = 8, the n-TiO_2 particles were stable both in the presence and absence of humic acid (HA) (Tan et al., 2009).

Li et al. studied the influence of ionic strength, solution chemistries, and HA on the fate of n-TiO_2 (81% anatase and 19% rutile) in 34 water samples from 24 different lakes and 5 brackish water samples (Li et al., 2016). The zeta potential and initial hydrodynamic diameter have not been found to affect the aggregation and deposition rates. However, the ζ of the n-TiO_2 experienced a charge reversal (from positive to negative) upon contact with water in the pH range of 5.8–8.7. This behavior was due to the opposite charges of the TiO_2 nanoparticles and the NOM and polyvalent anions in the water samples. Increased ionic strength resulted in increased electrical conductivity and decreased repulsive forces. The high alkalinity (Ca^{2+} and Mg^{2+}) of the real samples further promoted the aggregation effect (Li et al., 2016; Lee et al., 2016). Due to the higher ion concentration, the brackish water displayed the highest sedimentation rate, followed by the nutrient-rich lake (highest value of electric conductivity, alkalinity, pH and turbidity), humus-poor lake (lowest concentration of Fe, Mn, and lowest value of color, chemical oxygen demand and turbidity) and then the humic lake (highest value of color and COD, but the lowest value of electric conductivity, alkalinity and pH) samples. Among the different water properties studied, pH, electrical conductivity, and turbidity reported to be significantly influenced the stability of n-TiO_2 particles.

Lv et al. reported that both lake and seawater samples promote aggregation and subsequent sedimentation of n-TiO_2. The initial n-TiO_2 concentration (10–100 mg/L) and flow velocity can significantly influence the size and stability of n-TiO_2 under ambient conditions (Lv et al., 2016). The turbulence and temperature of the water (10–60 °C) also impact the fate of n-TiO_2 particles in aquatic water systems. Warmer temperatures can be expected to lower the ζ and hydrodynamic diameter and slower the sedimentation rate (Lv et al., 2016). The influence of turbulence on the size and shape of n-TiO_2 aggregates is variable. For example, higher velocity improves the collision frequency of the n-TiO_2 particles, especially at a lower environmental concentration of ENPs. However, higher turbulence can result in the

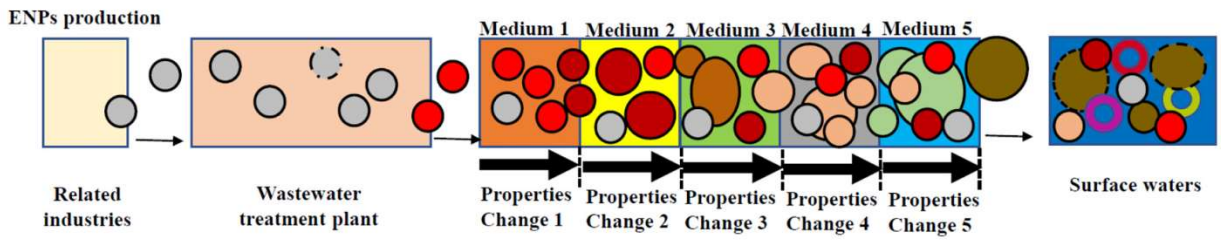

Fig. 3. Fate and transport of ENPs from production site to surface waters.
• ***Notes:*** *Varying color refers to changes in particle's chemistry; changing shapes and sizes indicate aggregation and disaggregation. Transformed chemistry of discharged ENPs can be observed by changed, sizes, and shapes.*

Table 5
Summary of fate and transport of ENPs in an aqueous environment.

ENP	Nanoparticle dependent behavior	Fluid dependent behavior
n-TiO_2	• Bioavailability is higher due to its large surface area and adsorption capacity • Strong oxidation of n-TiO_2 alters DLVO interactions with other chemicals/SPM in water, thereby influencing bioavailability.	• Nutrient-rich and ion rich brackish waters favor rapid deposition
n-Ag	• Fate is ultimately controlled by dissolution- aggregation behavior. Long-term fate is influenced by the aggregation of particles, thereby causing their deposition in the sediment zone. • The presence of functional groups (e.g., capping agents such as citrate) on n-Ag show poor aggregation behavior even in aquatic environments with high ionic strength. • Diffusion becomes the dominant transport mechanism with functionalized n-Ag, i.e., capped with citrate or PVP	• Exhibit persistency in NOM-rich waters because the presence of NOM facilitates increased adsorption of n-Ag to the particles of microcosm in water.
CNTs	• Oxygen-rich functional groups and the diameter of CNTs determine their fate in water systems. • Hydrophobicity nature favors aggregation and sedimentation of CNTs in water media. • Functionalized CNTs with increased surface oxygen content exhibit greater dispersibility in aquatic media (e.g., MWCNT-COOH are more dispersible than MWCNT-OH) (Schwyzer et al., 2012; Smith et al., 2012) • MWCNTs with a larger diameter, as compared with SWCNTs, were found to have looser entanglements, greater adsorption of NOMs, and thus greater steric and/or electrostatic stabilization (Lin and Xing, 2008).	• NOM increases the stability of the CNTs in aquatic environments through electrostatic repulsion and steric effects (Chowdhury et al., 2012; Hyung et al., 2007). • Ionic strength can have the opposite effect on CNTs. Divalent cations accelerate the aggregation by forming connections between negatively charged particles (Chen and Elimelech, 2007). Increased ionic strength results in a compressed electric double layer of particles, further promoting aggregation (Chen and Elimelech, 2007).
n-ZnO	• Physicochemical properties of n-ZnO and the concentration of Zn^{2+} ions influence the toxicity of the ZnO nanoparticles towards other organisms (Ahamed et al., 2010; Omar et al., 2014; Zhang et al., 2009).	• Aggregation and sedimentation behaviors are affected by the pH, presence of electrolytes and NOM concentrations of aquatic media. • n-ZnO aggregate owing to weak electrostatic repulsions between the particles when pH of water approaches the pHpzc value (Ahamed et al., 2010). • The rate of aggregation of n-ZnO is high at higher electrolyte and NOM concentrations. However, an increase in NOM concentration (i.e., humic acid >10 ppm) beyond a threshold limit decreases the surface charge of n-ZnO and thereby increasing their stability
n-CeO	• The ecotoxicity of is fundamentally governed by their charge. They carry a net positive charge in the absence of NOM	• Charge reversal takes place due to the presence of NOM in water, i.e., the n-CeO become negatively charged due to the sorption of humic acid on their surface. Compression of the electrical double layer and binding of cations to the adsorbed HA functional groups caused the shift in the EPMs of the nanoparticles (Chen and Elimelech, 2007; Li and Elimelech, 2004). Divalent ions are more efficient in screening surface charges on nanoparticles than monovalent ions

disaggregation of colloidal particles, which is what Lv et al. observed: when the flow velocity increased from 0 m/s to 0.32 m/s, the hydrodynamic diameters of the colloidal particles decreased for the initial n-TiO_2 concentration (10–100 mg/L) (Lv et al., 2016).

5.2. n-Ag

Typical to natural aquatic environments, charge-stabilized n-Ag particles remain stable even under low ionic strength and high concentration of NOMs (Chinnapongse et al., 2011). Sterically stabilized n-Ag particles are also less likely to aggregate under high ionic strength (Baalousha et al., 2015) and less prone to dissolution (Ellis et al., 2016). However, the type of surface coating is a primary factor that influences the fate and transport behavior of the n-Ag particles. This can be understood by reviewing the findings from a recent study that analyzed the diffusion mechanisms of n-Ag coated with polyvinylpyrrolidone (PVP) (PVP-nAg) in three different water sources, namely ultrapure water (UPW), moderately hard water (MHW), and MHW spiked with Suwannee River fulvic acid (MHW-SRFA) (Ellis et al., 2016). The stability of the PVP in MHW was attributed to the coating on n-Ag (Zhu et al., 2015; Badawy et al., 2010), whereas the stability in the MHW-SRFA was due to the absorption of NOM to the PVP-nAg surfaces (Zhu et al., 2015). However, n-Ag particles coated with citrate (cit-nAg) remained stable in UPW compared with MHW due to the migration and dilution effects in the MHW media (Ellis et al., 2016; Badawy et al., 2010). This finding has been corroborated with other recent studies that reported the aggregation of the cit-nAg particles in simple electrolytes (Tejamaya et al., 2012; Zhang et al., 2012). The cit-nAg particles displayed the precipitation and dissolution behavior in the MHW media but not in UPW media. Such behavior was not apparent for PVP-nAg, even in the MHW media. These findings indicate that the dispersion behaviors of the n-Ag particles are influenced by the media- and surface-coating-dependent parameters (Ellis et al., 2016; Hinderliter et al., 2010). The aggregation behavior in the MHW media was due to the cations that interact with the charged cit-nAg (Ellis et al., 2016). Na^+ and Cl^- in the MHW media can also neutralize the citrate stabilizer (Akaighe et al., 2012). Moreover, co-precipitation behavior with Cl^- could enhance aggregation (Levard et al., 2013). Cit-nAg particles that have been exposed to MHW-SRFA media experienced combined sedimentation- and diffusion-dominant behaviors (Ellis et al., 2016). Overall, deposition and adsorption processes are influential in the transport behavior of n-Ag and also suggest that the SRFA in the media could displace the citrate capping agent by recoating the particle with NOMs, resulting in steric stabilization (Baalousha et al., 2008; Bae et al., 2013).

Badawy et al. studied stabilization mechanisms of four different types of n-Ag particles including hydrogen reduced n-Ag (H_2-Ag), cit-nAg, PVP-nAg, and branched-polyethyleneimine-coated n-Ag (BPEI-Ag) in three different electrolytes (NaCl, $NaNO_3$, and $Ca(NO_3)_2$). All four n-Ag particles have followed the DLVO theory and displayed reaction-limited or diffusion-limited regimes (Badawy et al., 2010). Net forces between electrostatic barriers stabilized the nanoparticles in the reaction-limited regime, in which the surface charges of the n-

Table 6
Rutile n-TiO_2 behavior in variable pH humic acid waters (Tan et al., 2009).

pH	Noticed behavior
4 (i.e., pH < pHpzc)	ζ of n-TiO_2 decreased and the hydrodynamic diameter of the resulting aggregate increased with increasing concentration of HA with maximum aggregation at [HA] = 94 μg/L with corresponding ζ = 0 mV
5.8 (i.e., pH = pHpzc)	Rapid aggregation in the absence of HA with the rate of aggregation decreased with an increase in HA level.
8 (i.e., pH > pHpzc)	-No aggregation and no change in the ζ.

Ag particles were screened by the higher ionic strength of the electrolytes in the diffusion-limited regime (Badawy et al., 2010). H_2-Ag showed the least resistance to aggregation than cit-nAg and had a higher hydrodynamic diameter (HDD) due to the source of its stability (absorbed OH^- ions onto the surface of the nanoparticles) (El Badawy et al., 2010). This behavior confirmed that nanoparticles could be stabilized through the same mechanism, but they behave differently. Thus, the behavior of the nanoparticles is predominantly dependent on the surface chemistry of the nanoparticles (Badawy et al., 2010). The sterically stabilized n-Ag and PVP-nAg were stabilized through steric repulsion caused by the PVP polymer itself (Badawy et al., 2010). The electrosterically stabilized BPEI-nAg particles were stabilized by the presence of the amine groups in BPEI that ionize as a function of pH, resulting in increased colloidal stability (Badawy et al., 2010). The reaction-limited and diffusion-limited regimes were not observed in BPEI-nAg until the nanoparticles were exposed to extremely high ionic strengths. Also, BPEI-nAg did not display aggregation behavior. Overall, capping agents are the factors that control the fate, transport, and toxicity of silver nanoparticles (Badawy et al., 2010). Furthermore, the research revealed that sterically and electrosterically-stabilized nanoparticles exhibit more stability than electrostatically stabilized nanoparticles (Li et al., 2016). Therefore, DLVO theory can predict the behavior of electrostatically stabilized n-Ag regardless of capping agents (Badawy et al., 2010).

5.3. CNTs

The pristine forms of CNTs are hydrophobic and can be expected to aggregate in water. However, NOMs that are ubiquitously present in natural waters can increase their stability through electrostatic repulsion and steric effects (Chowdhury et al., 2012; Hyung et al., 2007). Their stability is further influenced by the aggregation and sedimentation processes (Lin and Xing, 2008). The ionic strength can exert a counterintuitive impact on the fate of CNTs. Divalent cations can promote the aggregation of CNTs by connecting them with negatively charged particles (Chen and Elimelech, 2007). When introduced into electrolytes (NaCl and $CaCl_2$), untreated MWCNTs aggregate immediately, whereas HA-treated MWCNTs remain dispersed due to electrostatic repulsion and steric effects (Chen and Elimelech, 2007). In deionized water, adsorbed HA did not affect the morphology of MWCNTs, whereas cation bridges and irregular patches were observed on HA-MWCNTs in $CaCl_2$ solution, leading to aggregation of MWCNTs. Such aggregation behavior is consistent with DLVO theory as reaction-limited and diffusion-limited regimes were observed in both electrolyte solutions. The critical coagulation concentration (CCC) for CNTs have been reported to be close to the critical deposition concentration (CDC), indicating that the aggregation state was related to the deposition behavior (Chen and Elimelech, 2007). The aggregation state of CNTs is also affected by the ionic strength of the solution (Lin et al., 2012).

Seasonal changes can also affect the behavior of CNTs in water environments. Higher temperatures promote Brownian motion of CNTs and subsequently improve the frequency of their collision. This explains the decreased mobility of MWCNTs in warmer climates (Stürzenbaum et al., 2013). In certain situations, the dispersion of CNTs is jointly influenced by their own properties as well as those of the media (Glomstad et al., 2018). Glomstad et al. studied five different CNTs (SWCNT, MWCNT-15, MWCNT-30, MWCNT-OH, MWCNT-COOH) in four types of media (TG201-NOM, MHRW-NOM, M7-NOM, natural water). MWCNT-COOH showed the highest dispersibility compared with MWCNTs and MWCNT-OH (except in M7-NOM). These differences were attributed to the increased levels of surface oxygen content and carboxyl groups in MWCNT-COOH compared with MWCNT-OH (Glomstad et al., 2018) (Schwyzer et al., 2012; Smith et al., 2012). The higher dispersibility of CNTs in the MHRW-NOM media can be attributed to the lower ionic strength (Lin et al., 2012). The non-functionalized MWCNTs were not affected by media properties.

The dispersibility of SWCNTs (0.5–0.9 mg/L) and functionalized MWCNTs (example, MWCNT-COOH = 3.0–6.6 mg/L) in natural water were lower compared with synthetic-NOMs media, whereas the non-functionalized MWCNTs (1.5–2.8 mg/L) had similar dispersibility in all four media types, further proving their insensitivity to media properties (Glomstad et al., 2018). The non-functionalized and functionalized MWCNTs shared similar dispersibility behavior in natural waters, showing that the surface oxygen content does not play a critical role in natural waters (Glomstad et al., 2018).

5.4. n-ZnO

Toxic effects stem not only from the presence of Zn ions but also from their interactions with the surfaces of target organisms, including algae (Mello et al., 2020). n-ZnO toxic effects towards *Bacillus subtilis* have been reported to be influenced by the physicochemical properties of the water (Leareng et al., 2020). For example, a greater reduction in the viability of *Bacillus subtilis* cells was observed when n-ZnO (100–1000 μg L^{-1}) was mixed with the samples from the Elands River compared with Bloubank River (BR). Leareng, et al attributed such variability to differences in the water samples' chemistry (Leareng et al., 2020).

Peng et al. reported that aggregation and sedimentation behaviors of n-ZnO particles (coated with 2% of 3-aminopropyl triethoxysilane) are significantly affected by pH, and the presence of electrolytes and NOM. The n-ZnO particles have been reported to remain stable at pH < 10.3 (the pHpzc of ZnO) (Peng et al., 2015). Upon the addition of NaCl and Na_2SO_4, their aggregation and sedimentation increased owing to the increased levels of Cl^- and SO_4^{2-} that neutralize the surface charges. The nanoparticles were stable at both lower levels (<1 meq/L) and relatively higher levels of Na_2SO_4 (>20 meq/L). The inverted stability can be attributed to a drop in ζ as the surface charge turns from positive to negative (Peng et al., 2015). Compared with NaCl, a lower concentration of Na_2SO_4 was needed to promote aggregation and sedimentation behavior. Unlike wastewater samples with low TOC concentration, n-ZnO particles in wastewater samples with high ionic strength displayed a reduction in dissolution leading to reduced stability, likely owing to the formation of Zn complexes (Omar et al., 2014; Zhang et al., 2009).

Majedi et al. reported most aggregation and sedimentation behavior of n-ZnO in high ionic strength water samples compared with that of lower ionic strength samples (Majedi et al., 2014). The increased temperature can increase the Brownian motion that can lead to increased collisions resulting in particle aggregation or lead to disaggregation of n-ZnO colloids. Water chemistry can be the dominant driving force behind aggregation behavior of n-ZnO in water. For example, samples with high ionic strength and the presence of divalent ions may have higher influence on the aggregation of n-ZnO compared to change in temperature. The dissolution of n-ZnO is pH-dependent; it is the highest in low pH (6.4–6.8) and lowest in high pH water samples (8.0–8.4) (Majedi et al., 2014). Because the solubility of n-ZnO is an exothermic process, Majedi et al. studied dissolution kinetics of n-ZnO by assessing the concentration of dissolved zinc versus temperature and found that the solubility decreased with increasing temperature. In addition, the temperature and surface charge influence the adsorption capabilities of n-ZnO and hence their stability. The adsorption of NOMs and Zn^{2+} increases with increasing surface area of n-ZnO and temperature of the water samples, proving adsorption mechanisms are thermodynamically driven. Overall, the aggregation is not directly or significantly affected by temperature changes (Majedi et al., 2014). However, adsorption capabilities and surface charges are influenced by media temperatures. Therefore, temperature variations can impact the behavior, surface interactions, and ultimately the toxicity of n-ZnO once they reach surface waters.

5.5. n-CeO_2

Li et al. studied the effect of Suwanee River Humic Acid (SRHA) on the aggregation of n-CeO_2 in KCl and $CaCl_2$ solutions (Li and Chen,

2012). With the addition of SRHA, the surface charge of n-CeO_2 changed from positive to negative in both the KCl and $CaCl_2$ solutions. As the concentration of the KCl and $CaCl_2$ solutions increased, the EPMs of the n-CeO_2 became less negative and less positive (no SRHA) in the absence and presence of SRHA (1 and 10 ppm HA), respectively. Compression of the electrical double layer and the binding of cations to the adsorbed HA functional groups caused the shift in the EPMs of n-CeO_2 (Chen and Elimelech, 2007; Li and Elimelech, 2004). This shift was more predominant in the $CaCl_2$ solution than in the KCl solution due to divalent ions (i.e., Ca^{2+}) (Li and Chen, 2012). Divalent ions are more efficient in screening surface charges on nanoparticles than monovalent ions such as the K^+ ions in the KCl solution (Li and Chen, 2012).

At all concentrations (0.005–0.5 M) of the KCl solution, the SRHA in the solution stabilized n-CeO_2 (Saleh et al., 2010). However, SRHA had a disparate effect on the nanoparticles in the $CaCl_2$ solution. At lower concentrations (~≤0.004 M) of $CaCl_2$, the SRHA adsorbed onto the surface of the n-CeO_2, causing steric repulsion that stabilized the particles and hence inhibited aggregation (Saleh et al., 2010). At higher concentrations (~≥0.008 M) of $CaCl_2$, the adsorbed SRHA on the particle surfaces aggregated together through intermolecular bridging via a Ca^{2+} complexation, thus, enhancing aggregation behavior (Saleh et al., 2010). The presence of SRHA also affected the CCC values (Saleh et al., 2010). In absence of SRHA, in KCl, CCC was approximately 36.5 mM while in the solution with SRHA at 1 ppm and 10 ppm, the CCC was greater than 500 mM. Similarly, The CCCs under conditions of no HA, 1 ppm HA and 10 ppm HA in $CaCl_2$ solutions are approximately 9.5, 8.0 and 12.0 mM, respectively.

Oriekhova and Stoll studied the effects of pH and fulvic acid (FA) on the stability of CeO_2 nanoparticle - fulvic acid complexes (Oriekhova and Stoll, 2016) in three electrostatic scenarios: pH = 3.0 ± 0.1 < pHpzc, pH = 7.0 ± 0.1 = pHpzc, and pH = 10.0 ± 0.1 > pHpzc. Additionally, the researchers explored the stability of CeO_2 nanoparticle - fulvic acid complexes in varying pH conditions and over time. The baseline zeta potential and average z-average diameter were + 51.3 ± 1.3 mV and 185 ± 75 nm, respectively (Cerrillo et al., 2016). After submerging the nanoparticles in ultrapure water (at 3.0 pH), aggregates formed in irregular shapes. SEM images displayed formations of dimers, trimers, and larger aggregates ranging in size from 30 nm (for individual nanoparticles) to 300 nm (for larger aggregates). As the pH increased, the surface charge decreased, promoting aggregation. At pH = 3.0 ± 0.1 < pHpzc, the n-CeO_2 were positively charged, whereas fulvic acid was negatively charged at all pH ranges. The difference in surface charges resulted in an energetically favorable situation for fulvic acid, allowing the fulvic acid to adsorb to the surface of the n-CeO_2 and forming an electrostatic complex and stabilizing the nanoparticles (Glomstad et al., 2018). At the isoelectric point, 0.25 mg/L of FA, the nanoparticles reached a neutral surface charge, promoting aggregation behavior. As the FA concentration further increased, partial disaggregation was initiated, and the nanoparticles returned to a stable condition. At pH = 7.0 ± 0.1 = pHpzc, the charge of the n-CeO_2 nanoparticles was close to zero, causing the aggregation of particles. As the concentration of FA increased, the stability of the nanoparticles increased and induced partial disaggregation. At pH = 10.0 ± 0.1 > pHpzc, the charge on the CeO_2 nanoparticles was negative owing to the hydrophobic interactions on the FA-adsorbed particle surface.

Oriekhova and Stoll also explored the effect of time and pH on the stability of the FA-CeO_2 complexes. The maximum FA concentration was added at once, introducing immediate adsorption on the nanoparticle surface and a significant charge inversion (Oriekhova and Stoll, 2016). The positively charged surface of the n-CeO_2 was neutralized by hydroxyl ions at a pH close to the pHpzc (Oriekhova and Stoll, 2016). There was no change in the z-average diameter because of the high cohesive energy between the FA and the nanoparticles (Oriekhova and Stoll, 2016). At this point, desorption of the FA from the n-CeO_2, an unenergetically favorable condition, was required to destabilize the nanoparticles (Oriekhova and Stoll, 2016). The particles remained stable over seven weeks.

5.6. Summary

As n-TiO_2, n-Ag, n-CeO_2, CNTs, and n-ZnO are currently the most prevalent ENPs in consumer products, their presence in surface waters is imminent. Thus, it is crucial to investigate the environmental fate behavior of these ENPs and associated ecological health risks in surface waters (Li et al., 2016; Keller and Lazareva, 2013). Recent studies demonstrated that natural organic matter interacts with ENPs and significantly influences their fate and behavior. Such interactions can trigger a chain of events that can result in nanoparticles transformation, changing their physicochemical properties, reaction rates, and ultimately their solubility (Glomstad et al., 2018; Li and Chen, 2012; Lowry et al., 2012). These transformations alter the original properties of ENPs, increasing their stability, mobility, residence time, toxicity, and bioavailability in surface waters (Glomstad et al., 2018; Li and Chen, 2012). Particle size also influences their behavior. Smaller ENPs will be more reactive towards other nanoparticles, natural colloids, and indigenous microorganisms in surface waters. Nanoparticles aggregation and transformations affect nanoparticles' susceptibility to ingestion and transport via organisms residing in surface waters and hence influence their toxicity (Li and Chen, 2012). For example, the unique properties of n-CeO_2 and their stability in varying pH conditions over long periods can transform the nanoparticles into a new class of nonbiodegradable pollutants, hence persistence in the environment is extended compared with the original n-CeO_2 (Li and Chen, 2012).

Environmental field conditions are often much more complex and dynamic than synthetic lab samples commonly used in fate, transport, and toxicity studies (Glomstad et al., 2018). For example, Li et al. uncovered that n-TiO_2 nanoparticles experience different deposition in the environment than one could predict in commonly used distilled media (Li et al., 2016). Elevated water temperatures result in more dissolved oxygen, causing desorption of toxic Zn^{2+} and NOMs from the surface of the nanoparticles (Ma et al., 2013; Praetorius et al., 2012b). Hence, organisms in the water could suffer from the formation of reactive oxygen species and experience exposure to toxins (Ma et al., 2013; Praetorius et al., 2012b). These phenomena can significantly affect organism growth rates and other physiochemical phenomena (Dwivedi et al., 2015). Therefore, there is an urgent need for more studies that cover a wider range of media properties that closely represent field environmental conditions.

6. Outlook

Due to the potential health impacts of ENPs, it is important to regulate their discharge into the environment. To achieve such a regulatory framework, a baseline record of current releases and occurrences of ENPs in the environment and standard methods of detecting their signatures are needed. Such methods will improve much-needed reliability, reproducibility, and comparability of data acquired from diverse studies but focusing on the same ENPs (European Union Observatory for Nanomaterial, 2020; Gupta and Xie, 2018). These methods could explain the differences in the fate, transport, and toxicity behavior of ENPs, in correlation to differences in their intrinsic properties of ENPs (charges, size and structure, and surface functional groups). Future nanomanufacturing methods should also consider the environmental and sustainability performance of ENPs. For example, the current literature suggests that the toxicity impacts of CNTs' are primarily influenced by their purity and surface parameters (length, aspect ratio, surface area, degree of aggregation), which in turn are impacted by the manufacturing methods (Yuan et al., 2019). However, the extent of influence of individual surface properties is yet to be concreted. Future manufacturing techniques should consider the electronic properties and subsequent cytotoxicity impacts of CNT, along with the typical performance parameters.

ENPs in the environmental sample may not be amenable to typical methods of detection and quantification. Therefore, advanced methods of detection and quantification of ENPs are needed to understand their environmental fate, toxicity, and to establish a baseline water quality profile needed for their environmental management. Limitations of the current state-of-the-art instrumentation to track and quantify ENP properties in real environmental conditions is evidence by the fact that most of the current research is based on synthetic media and controlled laboratory conditions. Many research studies assume that ENPs retain their pristine nature, which is not necessarily true as they are subjected to complex transformations upon their release.

Many reports on ENPs' environmental behavior are based on simplified laboratory conditions. Although they provide a good starting point, field studies are required to corroborate these findings. To establish such field monitoring, future research should standardize procedures that target surface water sampling (e.g., grab sampling versus continuous sampling, material of sampling equipment to avoid contamination), sample processing (e.g., sonication versus centrifugation, filtration), and ENPs detection at expected environmental levels (pg/L to ng/L).

A measurement-driven approach should be used to establish baseline conditions of ENPs in surface waters and to gauge whether the ENPs are a concern in surface waters, and, if applicable, controlling their release through enforceable regulations. In the interim, model predictions will provide the basis for expected levels of ENPs in the environment. Such models are often based on a life cycle analysis approach. For improved accuracy of the model prediction, the reporting of production volumes, consumer use, and release rates of ENP-embedded products into the environment are urgently needed. Although progress has been made in modeling the release of ENPs to the environment, calibration of the model predictions with monitored data has not been performed.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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