Nanoparticles: structure, properties, preparation and behaviour in environmental media

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Abstract There is increasing interest and need to develop a deeper understanding of the nature, fate and behaviour of nanoparticles in the environment. This is driven by the increased use of engineered nanoparticles and the increased pressure to commercialise this growing technology. In this review we discuss the key properties of nanoparticles and their preparation and then discuss how these factors can play a role in determining their fate and behaviour in the natural environment. Key focus of the discussion will relate to the surface chemistry of the nanoparticle, which may interact with a range of molecules naturally present in surface waters and sediments. Understanding these factors is a core goal required for understanding the final fate of nanomaterials and predicting which organisms are likely to be exposed to these materials.

Keywords Nanoparticle · Synthesis · Fate · Behaviour · Surface

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Introduction

There has been a rapid increase in interest in nanotechnology and the use of nanoparticles in commercial applications. However, there is little known of the fate and behaviour of engineered nanoparticles in the environment. The properties of nanoparticles differ remarkably from small molecules and their chemistry and synthesis necessitates that they be considered more like complex mixtures than small molecules. The ability of the molecules to attach to the surface of nanoparticles and exchange with other molecules already placed there indicates that careful consideration of the chemistry of nanoparticles and how it relates to their fate in surface waters and sediments is key to predicting their final fate. We have set out to briefly introduce at a basic level the properties and synthesis of nanoparticles and then review the state of current understanding relating to the fate and behaviour of nanoparticles in the environments with particular focus on engineered nanoparticles.

Discussion

Nanoparticles and their origins

Nanoparticles are generally defined as particulate matter with at least one dimension that is less than 100 nm. This definition puts them in a similar size domain as that of ultrafine particles (air borne particulates) and places them as a sub-set of colloidal particles (SCENIHR 2005).

A considerable fraction of the solid matter on earth can be found in the size range of colloids and nanoparticles. In the last 2 decades scientists have shown that colloids and nanoparticles are present everywhere in the environment

(McCarthy and Zachara 1989; Wiggington et al. 2007). By definition nanoparticles constitute a sub-fraction of what is defined as "colloids" by the IUPAC (IUPAC 1997) (Fig. 1). Since the definition of colloids and nanoparticles is based on a simple spatial dimension of an object, the variety of colloids and nanoparticles found in the environment is large, and the composition of environmental colloidal systems is complex and heterogeneous.

A colloidal system is in general a two-phase system made up from a dispersing medium and a dispersed medium, and both may be gas, liquid or solid. Widely known are dispersions (solid in liquid), emulsions (liquid in liquid) and aerosols (solid in gas). In nature the dispersing medium is mainly water and air, while the dispersed media are mainly solids of inorganic, organic or biological origin or mixtures of these (Buffle et al. 1998; McCarthy and McKay 2004). Aqueous dispersions and aerosols are hence the dominating colloidal systems in the environment. This, however, neglects the huge pool of colloidal particles that are bound in soils and sediments as aggregated structures and from where aggregates and single colloids can be released (Ryan and Gschwend 1994). Colloids in the environment can be of natural origin, formed by processes taking place for millions of years, or of anthropogenic origin. Atmospheric colloids may be produced by combustion processes, emitted as by-products in technological processes, by accidental and intended release, but will once settle and become a part of the terrestrial and aquatic environment. Nevertheless, colloids may be transported over large distances in the atmosphere and even naturally produced structures similar to carbon nanotubes have been found in thousands of years old samples from ice-cores of the arctic (Esquivel and Murr 2004).

Depending on their origin environmental aquatic colloids can be divided into four groups (Fig. 2). Additionally to the categorisation developed by others (e.g., Nowak and Bucheli 2007) we distinguish anthropogenic from engineered nanoparticles according to their nature as an unintended by-product from technological processes and on the other side resulting from target-oriented manufacture.

Subgroups are examples of environmentally relevant types: inorganic nanoparticles and organic nanoparticles. There has therefore been a recent drive to define more closely nanoparticles, especially engineered nanoparticles (ENPs). There have been several reports on nanoparticles and nanotechnology (The Royal Society and The Royal Academy of Engineering 2004; NIOSH 2004). It is generally accepted that whilst the definition of other small particles often uses a simple scale to define size, in the case of nanoparticles, such a simplistic definition overlooks their unusual and diverse properties. This has led in some cases to the use of the properties of the materials as a key defining factor regarding the material, which is now being suggested (SCENIHR 2007).

Nanoparticle structure

Although it is often tempting to consider nanoparticles as simple molecules, they are in fact complex mixtures. Even in the simplest cases one must consider the interactions of at least two different aspects of the material. Whilst they may absorb light like a dye and appear to dissolve like any

Fig. 1 Size domains and typical representatives of natural colloids and nanoparticles. Operationally defined cut-off is given for filtration at 0.45 μm
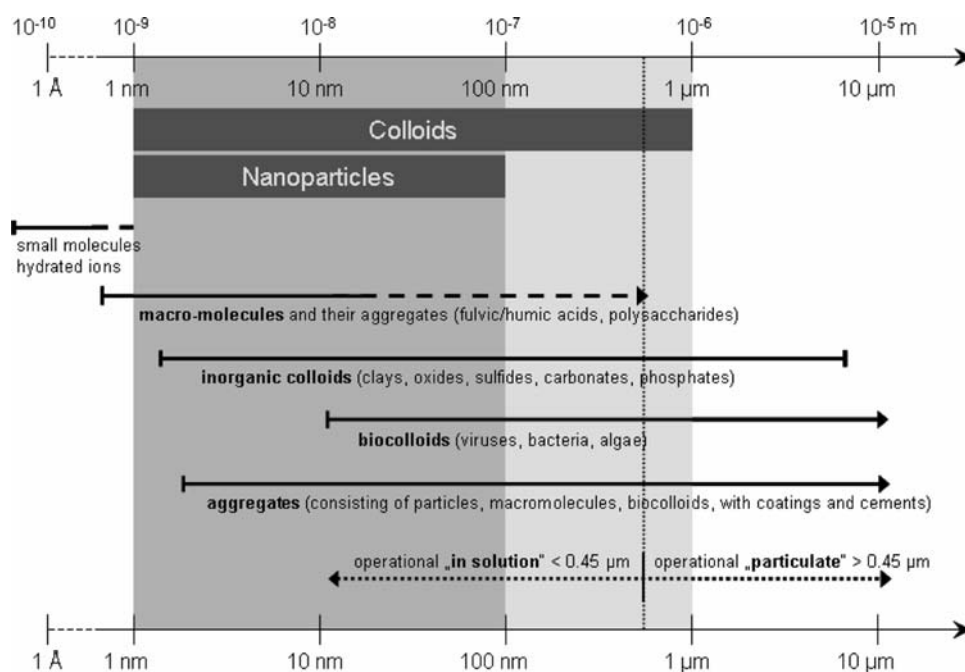
Fig. 2 Categorisation of environmental colloids according to origin and composition

environmental aquatic colloids				origin
natural colloids		anthropogenic colloids	engineered nanoparticles	
inorganic colloids	organic colloids	wear & corrosion products	standard industrial products	composition
- silicates (e.g. clays)	- macromolecules	- from tire & brakes	- polymers	
smectites	humic acids	- from catalysts (e.g. Pt, Pd)	- surfactants	
montmorillonite	fulvic acids	- metals (wear in bearings)	- dyes & pigments	
nontronite	polysaccharides	- metal oxides (roof run-off)	- metal oxides	
hectorite	proteins	- additives to lubricants	NP metals & metal oxides	
chlorites	peptides		- metals (Au, Ag, Fe)	
mica	exo-polymers, EPS	waste & combustion products	- metal oxides (of Ti, Zn, Zr, Ce...)	
kaolinite	- bio-colloids	- soot	- metal tubes and wires	
- oxides / hydroxides	bacteria	- "anthropogenic" humic acids	carbon based	
Fe-oxohydroxides	viruses	from e.g. waste dumps	- fullerenes	
Mn-oxides	fungi	- tar leachates in plumes	- single & multi walled nanotubes	
- carbonates	- coal/soot/black carbon	- fly ash	hybride structures	
- phospates	- cellular debris	- fine dust (inorganic & organic)	- quantum dots	
- metal sulfides			- functionalized materials	
- polym. silicic acid			- core-shell structures	

other small molecule, their actual behaviour is often subtly different and is usually the result of the different components of the material. Any nanoparticle will have an exceptionally high surface area to volume ratio; this is one of the reasons for some of their unusual properties. However, this high surface area also means that the surface of any given nanoparticle is an important component of the material. So even the simplest nanoparticle will have a surface chemistry, which is distinctly different from that of the core material. In the case of silica the material will have a core structure of SiO_2, but the surface would have a chemistry more comparable to a formula $Si(O)_{(2-x)}(OH)_{(2x)}$ (Paparazzo 1992). The result of this is that the outer layer of atoms in the particle has a different composition from the rest of the particles. One layer of atoms is approximately 0.4 nm thick; there is a significant number of atoms with a different chemistry from the rest of the atoms on the particle. This means that for a 6-nm silica nanoparticle, approximately 7% of the Si atoms will be on the surface, and therefore the surface chemistry of the particle will have a significant contribution. Furthermore, the surface of the nanoparticle will be the first aspect experienced either by the environment or by an organism.

In many cases the exact composition of the surface of the nanoparticle is intimately related to their final application. For example, a nanoparticle designed to interact with biological systems will have suitable functional groups attached to its surface, such as short chain peptides. In fact, in many cases the surface functionalisation is critical to producing nanoparticles that exhibit the correct properties. This is often due to the fact that many nanoparticles lose their unique properties once they have aggregated and precipitated from suspension. Great effort is therefore expended in preparing nanoparticles that suspend in the media of choice. This usually involves preparing nanoparticles that have some coating that facilitates dispersion of the particles. In some cases these coatings are in the form of surfactants that form transient Van-der-Walls interactions with the surface and exist in equilibrium with the free surfactant molecule. In other cases a molecule or ion is bound to the surface of the particle so imparting stabilisation of the particle suspension. The modes of stabilisation of colloids of this type will be discussed later.

A nanoparticle can therefore be split into two or three layers; a surface that may often be functionalised, a shell material that may be intentionally added and the core material. Often nanoparticles are only referred to by their core material because this is the part of the nanoparticle that results in key properties for most applications.

The surface

The surface of a nanoparticle may be functionalised with a range of metal ions, small molecules, surfactants or polymers. It is well known that the base catalysed hydrolysis of tetraethyl orthosilicate results in particles of 10–350 nm that have a charged surface (Park et al. 2002). This has been shown to be the result of deprotonation of the SiOH groups at the surface of the particle resulting in the formation of a $SiO^- M^+$ where M^+ is a suitable monovalent cation such as sodium. Preparing a nanoparticle with a charged surface is a convenient way to prepare nanoparticles that disperse in aqueous media. However, many materials do not have convenient surfaces for stabilisation of localised charges. In many of these cases, it is common to use a small molecule that will bind to the surface of the particle by a covalent-like bond and also contain groups capable of carrying a charge. Citrate stabilised gold and silver sols come under this category (Henglein and Giersig 1999). Similarly thiopropanoic acid has also been used (Yonezawa and Kunitake 1999). Another method for preparing a stable dispersion of

nanoparticles is to use a surfactant such as sodium dodecylsulfate (SDS) (Qiu et al. 1999). In this case the nanoparticle forms in the core of a micelle with the hydrophobic interactions of the surfactant tail and the particle surface drives the binding of the surfactant to the surface of the particle. It is important to remember these systems are different from those where a molecule is covalently bound to the surface of the nanoparticle in that the surfactant is in equilibrium with free surfactant molecules in the media (Shaw 1992). If the system is diluted, then this equilibrium will shift so that the concentration of the free surfactant is maintained at the critical micelle concentration. This equilibrium will shift as the expense of colloid stability and therefore excessive dilution will result in colloid instability and precipitation. A final type of surface-active molecule includes those based on monofunctional long-chain molecules such as amines, phosphines, carboxylates and thiols. These molecules bind to specific sites on the surface of the nanoparticle and have long chains that extend into the dispersion medium, thereby imparting stability. Generally these are applied to the surface of the particle during preparation and can be later modified. Often stability is limited to organic solvents although new materials based on polyethylene glycol (PEG) are now being prepared in our group. It is not unusual to prepare such materials for dispersion in hydrophobic solvents and then modify their surface with PEG in order to impart water dispersability.

The shell

This is a layer of chemically different material from the core material. In a sense the outer layer of any inorganic nanomaterial may be considered to be different from that of the core and therefore be considered to be a shell. However, the term shell is usually applied to a second layer that has a completely different structure from that of the core material as opposed to a serendipitous variation in chemistry due to being at the top layer of the particle. Some excellent examples of these materials are the core/shell quantum dots, which contain a core of one material, such as cadmium selenide, and a shell of another, such as zinc sulfide (Malik et al. 2002). Other examples may be drawn from polymer nanoparticles such as polystyrene-polyanaline (Luo et al. 2007). Whilst these types of material may be prepared intentionally, it does not imply that they can also occur through other processes. For example, it is well known that iron nanoparticles rapidly form layers of iron oxide at their surface after preparation. These layers do not necessarily penetrate the whole particle, and therefore the nanoparticle itself may be a core shell structure as opposed to a pure iron nanoparticle (Sun et al. 2007). These materials are usually prepared intentionally and are unlikely to occur serendipitously.

The core

This is essentially the centre of the nanoparticle and usually used to refer to the nanoparticle itself. This trend is common in the physical sciences where the particular properties of a nanoparticle under study are generally related to the composition of the core, or in some cases the core and shell. However, there are examples where it has been shown that the exact composition of the whole nanoparticle is implicit in accurately determining its overall properties (Wuister et al. 2004). It should be noted however that in general the properties of interest to the physics and chemistry communities are generally dominated by the properties of the core. However, the same rules do not necessarily apply to ecotoxicology. It is highly likely that the core of the nanomaterial will play a key role in the nanoparticle toxicity; however, this does not mean that the fate and environmental behaviour of a nanoparticle will be dominated by core composition.

A second important consideration when discussing the core of a nanoparticle is the immense variation that may be found there. This is particularly the case when considering inorganic nanoparticles. It is well known that most inorganic materials may exist in more than one phase and that the phase of the material may have a dramatic effect on its physical properties. Whilst nanoparticle may be prepared in a pure single phase, it is sometimes the case that two phases are present. It is tempting to assume that the fate and behaviour of the nanoparticle are independent of the phase; however this is also unlikely to be the case (Rempel et al. 2006).

Furthermore, even careful descriptions of nanoparticle can lead to misleading assumptions. For example, consider a collection of particles where the core material is TiO_2 with particle diameters of 30 nm ($\pm$10 nm) comprising 75% anatase and 25% rutile. These data could be considered to give a full description of the material. However, there are many ways to understand this description: a mixture of rutile and anatase particles with the same size distribution, a mixture of small anatase particles and large rutile particles (or vice-versa), a mixture of nanoparticulate anatase contaminated with a small amount of bulk (>100 nm) rutile, a collection of nanoparticles, each of which have a mixed phase composition of 75% anatase and 25% rutile in each particle, etc. It is tempting to interpret these data to mean the first case, however, given the difference in the chemistries of rutile and anatase this is probably the lease likely scenario. It is well known that, in nanoparticles, many crystal defects and other twinning and packing phenomena may result in very complex core compositions (Christian and O'Brien 2005). Whilst it is impractical to analyse all materials for ecotox testing to these levels, it is important that these possible variations

are born in mind so that they can be considered if some unusual results become apparent at a later date.

A final and more general consideration regarding nanoparticles should be their morphology. Whilst many nanoparticles which are already generally used are nominally isotropic, there are many other morphologies which can be attained. Perhaps the most common is a simple rod or wire, such as a carbon nanotube (CNT). However, tetrapod, tear drop, dumbbell and dendrite structures have also been prepared for a range of materials (Mana et al. 2000; Ung et al. 2007). Often control of these shapes is related to the phase of the components of the system, but also may be related to changes in composition of the materials themselves. Whilst very few of these materials have yet to find commercial applications, there is the obvious possibility that one day they will, and therefore the exact morphology of the nanomaterial will also become a much more complex issue.

Intrinsic properties of nanoparticles

The fate, behaviour and therefore the ecotoxicology of nanoparticles will be closely related to their intrinsic properties. There are several aspects to nanoparticles which can easily be dismissed in error due to their apparent ability to behave more like molecules than larger colloidal suspensions. We will discuss here a simple description of particles in suspension; a more detailed discussion may be found else where (Shaw 1992).

Particle mobility

The process of diffusion is controlled by several factors: gravitational forces, buoyancy and Brownian motion. These factors can all be taken into account using Einstein's law of diffusion:

$$Df = kT \tag{I}$$

where D = diffusion coefficient, f = the frictional coefficient for the particle, k = Boltzmann constant and T = temperature.

The frictional coefficient of a nanoparticle may be derived from Stokes law:

$$f = 6\pi\eta a \tag{II}$$

where η = the viscosity of the medium and a = particle radius.

This means that the diffusion coefficient is inversely proportional to the radius of the particle and the average displacement of a single particle in time t will be proportional to the inverse square root of the particle radius. Figure 3 shows a plot of the average distances moved after 20 time units for particles of different sizes. This shows
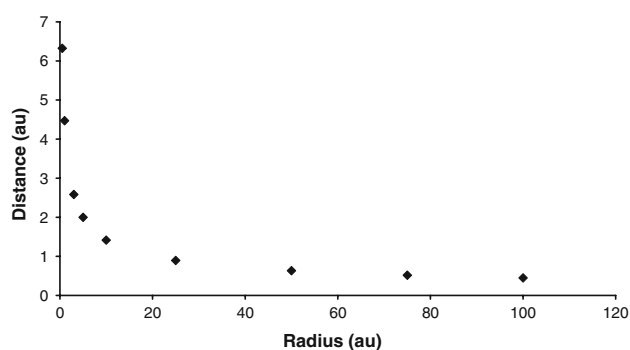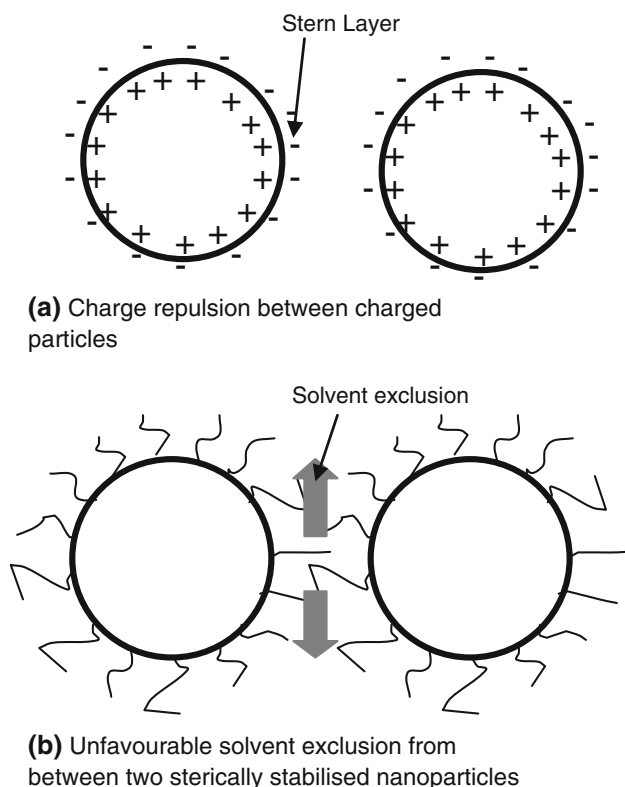

Fig. 3 A graph showing the dependence of diffusion rate on the radius of particles after 20 s

that the distance moved by a particle of 50 nm will be an order of magnitude less than that of a particle, or molecule, 0.5 nm is diameter.

Surface energy and colloid stabilisation

The small size of nanoparticles would imply from simplistic calculations that they should form stable dispersions because they are subject to Brownian motion to a significant degree. However, this would be neglecting the high surface energy of the nanoparticles. Any collision event between two particles will result in agglomeration and precipitation of the nanoparticles from solution. It is therefore necessary to stabilise the dispersion of the nanoparticles by providing a barrier to close approach of two particles. Typical barriers are either based on charge or steric stabilisation of the colloid. In the first case a charged surface is present which has associated counter ions and some solvent molecules which are tightly bound to the surface of the particle; this is called the Stern layer. The associated charge at the surface causes repulsion of like charges according to coulombs law so providing a barrier to aggregation (Fig. 4a). In steric stabilisation a relatively long molecule is tethered to the surface of the particle. The long chain of the molecule will have a high affinity for the solvent. The barrier to aggregation is therefore related to the relative interactions of the polymer chain with itself and with the solvent. In order for the particles to aggregate solvent must be eliminated from between the two particles and from around the chains; this is energetically unfavourable and therefore presents a barrier to aggregation (Fig. 4b). These two types of stabilisation may act very differently. For example, changes in ionic concentration have a dramatic effect on the stability of charge stabilised colloids at much lower concentrations than sterically stabilised colloids. This is because the increase in ionic strength shields the charge of two approaching particles and reduces the effectiveness of the Coulomb repulsion. Furthermore, polyvalent ions may exchange for the

(a) Charge repulsion between charged particles

(b) Unfavourable solvent exclusion from between two sterically stabilised nanoparticles

Fig. 4 A diagrammatic representation of (**a**) a charged stabilised nanoparticle and (**b**) a sterically stabilised nanoparticle

monovalent ions on the surface of charge stabilised colloids. This often results in rapid precipitation and aggregation of particles, whereas sterically stabilised systems are much less susceptible.

Optical properties of nanoparticles

One particular subset of nanoparticles is the quantum dot. These are generally particles with diameters of less than 10 nm, although in some cases the particle size may be as large as 50 nm. They have perhaps the most distinctive size-related properties of all nanoparticles. Quantum dots are semiconducting nanoparticles where their dimensions are so small the size of the particle affects the intrinsic band gap of the semiconductor. A simple way to understand this is to consider a semiconductor as consisting of a valence and conduction band which are the result of the bonding and antibonding configuration of the crystal lattice. A simple diatomic system will have a single bonding and a single antibonding orbital. As more atoms are added to the lattice the new bonds will have slightly different bonding and antibonding energies. For a large lattice these orbitals will begin to form a continuum which is considered as the band in the final bulk material. It is therefore clear that at some point the number of bonds in the semiconductor particle will not be a good approximation to an

infinite lattice and the band structure will begin to change. This results in a widening of the bandgap of the semiconductor. Most quantum dots exhibit photoluminescent properties. A photon of incident light can excite an electron from the valence band of the semiconductor to the conduction band leaving a hole in the valence band. This photon then has various possible fates: recombination of the electron and hole with the emission of light, trapping of the electron/hole in a defect in the crystal, reaction with the capping agent resulting in the formation of a radical, reaction with the solvent to form a radical. Many of these processes will also occur in particles which do not exhibit quantum confinement; however the minimum energy required to form the excited state will increase as the particle size decreases in a quantum-confined system. This minimum energy is the bandgap of the particle. This is a small but important area of nanotechnology, and the authors would direct the reader to some excellent reviews on the preparation and properties of quantum dots if more detail is required (Trindade et al. 2001).

Catalysis

Any nanoparticle will have a very high surface area to volume ratio. The surface area to volume ratio scales with the inverse of the radius. This means that the percentage of atoms available at the surface of a particle for catalysing a reaction will also scale with the inverse of the radius of the particle. For example, a nanoparticle of gold with a diameter of 5 nm will have 31% of its atoms at the surface, whereas at 50 nm this drops to 3.4% and at 1 micron this falls to 0.2%. In addition to the number of surface atoms available for reaction, the chemistry of these sites may also vary from the bulk material because of variations in the lattice structure at the surface of the particle. The result of this is that materials prepared in a nanoparticle form can have much higher activity in catalytic processes than the bulk material (Yoo 1998) and in some cases materials which may be thought of as poor catalysts, such as gold, can be found to have excellent catalytic properties when prepared in a nanoparticle form (Sau et al. 2001).

Preparation of nanoparticles

There are two main methods for the preparation of nanoparticles: top down and bottom up. The former related to the preparation of nanoparticles by "cutting" larger pieces of a material until only a nanoparticle remains. This is commonly achieved using lithographic techniques or etching; however grinding in a ball mill can also be used in some cases. The more convenient method for producing nanoparticles on a commercial scale is to use a bottom-up approach where a nanoparticle is "grown" from simple
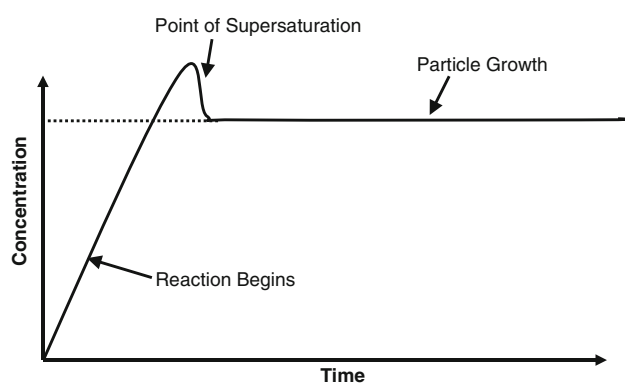
Fig. 5 A diagram showing a simplified summary of nanoparticle particle formation

molecules. The size of the nanoparticle may be controlled in a number of ways such as limiting the concentration, functionalising the surface of the particle or using a micelle to template the growth. The bottom-up approach relies on the principle of supersaturation to control particle size (Fig. 5).

In the early stages of the reaction the concentration of the final material rises rapidly, but no precipitation occurs until the saturation limit is reached (shown by the dotted line). If the reaction is proceeding fast enough the saturation limit may be exceeded before material begins to precipitate from solution. These initial particles will then act as seeds for the final particles and, in an ideal system, any further production of the final material will occur at the particle surface resulting in particle growth. This explanation is very simple and the reality may be much more complex (Christian and O'Brien 2005), but this principle is a defining factor in all bottom-up approaches. The general differences come from the medium in which the reaction is conducted, and this can play a key role in defining the final properties and surface chemistry of the particle. There is insufficient space here to consider all the permutations; however we will discuss some of the common methods employed in preparing the major classes of nanomaterials.

Metal oxides

Two methods are commonly used to prepare oxide-based nanomaterials: stabilised precipitation and flame pyrolysis. We will discuss the case for titania (TiO_2). TiO_2 pigments are commonly prepared by the hydrolysis of titanium sulfate via the sulfate process or by the aerial oxidation of titanium tetrachloride. Similar methods have been used to prepare titania nanoparticles including the hydrolysis of compounds such as titanium alkoxides in the presence of a capping agent (Hague and Mayo 1994; Dhage et al. 2003). These methods have the added benefit of further size control and surface functionalisation. TiO_2 nanoparticles can also be prepared by oxidising a solution of titanium

tetrachloride ($TiCl_4$) in a flame (Tsantilis et al. 2002). Essentially a solution of the metal-oxide precursor is sprayed into a flame, and the oxide particles are formed during the burning process. This method does not allow for any in situ tailored surface functionalisation, and any charge stabilisation of the final particles will be a result of further reactions upon suspension of the material in a solvent (i.e., water).

Polymers

Polymer nanoparticles are generally prepared by emulsion polymerisation. In this method an emulsion of monomer (e.g., styrene) is prepared using a non-solvent (i.e., water) and a surfactant (i.e., sodium dodecylsulfate SDS) (Shim et al. 2004; Pons et al. 1991). The free-radical polymerisation is initiated by a water-soluble initiator such as ammonium persulfate, and the size of the final particles is limited by the dimensions of the micelles. The kinetics of the reaction are so rapid that there are often radicals trapped in the nanoparticles at the end of polymer chains. The particles formed by this method generally have the surfactant trapped in the polymer particles as their long aliphatic chains either become entangled in the polymer network or as they become grafted onto the polymer by side reactions with the radicals. These particles are therefore usually charge stabilised.

Other particles

There is a wide range of different nanoparticles which have been reported in the literature which are neither polymer nor oxide based. Many of these have been prepared by either stabilised precipitation or by micelle templating. A good example of these is the formation of cadmium sulfide nanoparticles. These particles have been prepared by both methods (Christian and O'Brien 2005; Trindade et al. 2001; Dios et al. 2005), which generally rely on the reaction of two precursors such as cadmium chloride and sodium sulfide or the decomposition of a metal organic precursor (Trindade et al. 2001). Often the surface coating of these particles is hydrophobic, and they do not disperse well in aqueous media; however hydrophilic particles have been prepared (Winter et al. 2005). If a micelle method is used to prepare this type of particles, there is no incorporation of the surfactant into the crystal lattice of the final material and therefore it is possible for the surfactant to be removed either by sequential washing or by extreme dilution.

Nanowires and nanotubes

There are several methods for preparing nanowires and tubes (Dupuis 2005, Wang and Li 2006), many of which

are related to those described above. Currently perhaps the most investigated nanotube is that of carbon (CNT). These nanotubes have not been prepared by simple application of the above methods and require a more complex approach. Usually these materials are prepared by "growing" the tube out of a droplet or nanoparticle of a metal. In this case a precursor gas such as ethylene is decomposed anaerobically in the presence of a metallic particle. The carbon is rapidly absorbed into the metal droplet and, as the graphitic material begins to form, it migrates to the surface. This eventually results in the extrusion of a wire structure from the surface of the particle. This method is called the vapour-liquid-solid (VLS) method (Kukovitsky et al. 2000).

Clearly the methods used to prepare nanoparticles will have a massive impact on their purity and surface chemistry and therefore also on their final properties. Variations in particle phase, shape, size and surface chemistry can have a massive impact on properties. Similarly the method of preparation will have an impact on purity, size distribution, surface chemistry and the types of by-products likely to be present in the final material. Understanding these factors is key to understanding the materials we are working with and therefore interpreting the results obtained.

Behaviour of nanoparticles in the aquatic environment

Attention has been devoted to the toxicology (Lam et al. 2006; Nel et al. 2006; Oberdörster et al. 2005) and health (Helland et al. 2007; Kreyling et al. 2006) implications of NPs, while the environmental behaviour of engineered nanoparticles has been less studied (Biswas and Wu 2005; Helland et al. 2007; Wiesner et al. 2006). To better understand the likely fate and behaviour of NPs in aquatic systems, it is essential to understand their interaction with natural water components such as environmental colloids and natural organic matter under a variety of physicochemical conditions such as pH, ionic strength (I) and type and concentration of cations. Little information about these interactions is yet available specifically for the engineered nanoparticles. Thus, the understanding of environmental impact of NPs will significantly benefit from the previous knowledge about environmental colloids (Lead and Wilkinson 2006). This section therefore gives an overview on the state of the art in the interaction of NPs with natural water components (colloids, natural organic matter (NOM), contaminants and cations). It is believed that these interactions will be controlled by processes such as the formation of NOM surface coatings on NPs, aggregation, disaggregation, aggregate structure and interaction with micropollutants, which are summarized in Fig. 6 and discussed below.

Interaction with pollutants

In natural aquatic systems, sparingly soluble contaminants are predominantly bound to particle surfaces or complexed by, i.e., humic substances. Due to their high surface to mass ratio, natural NPs play an important role in the solid/water partitioning of contaminants. Contaminants can be adsorbed to the surfaces of NPs, absorbed into the NPs, coprecipitated during formation of a natural NP or trapped by aggregation of NPs which had contaminants adsorbed to their surfaces (Lead et al. 1999; Lyven et al. 2003). In general it is difficult or even impossible to differentiate between these states or processes, and they may be described as sorption processes (not distinguishing between ad- or absorption). CNTs have been used for the sorption of a variety of organic compounds from water such as dioxins (Long and Yang 2001), polyaromatic hydrocarbons (PAH) (Gotovac et al. 2006), polybrominated diphenyl ether (PBDEs) (Wang et al. 2006) chlorobenzenes and chlorophenols (Cai et al. 2005; Peng et al. 2003) and pesticides thiamethoxam (Zhou et al. 2006). Oxidized and hydroxylated CNTs have also been used for the sorption of metals such as copper (Liang et al. 2006), nickel (Chen and Wang 2006), cadmium (Liang et al. 2004), lead (Li et al. 2002), silver (Ding et al. 2006), zinc (Lu and Chiu 2006), americium(III) (Wang et al. 2005) and rare earth metals (Liang et al. 2005). Fullerenes have been used for the sorption of organic compounds (naphthalene) (Cheng et al. 2004) and for the removal of organometallic compounds (Ballesteros et al. 2000). Zero valent iron-oxide NPs have been applied for the remediation of organic contaminants (Obare and Meyer 2005; Zhang 2003). Nanoporous ceramic sorbents have been used for the immobilization of cationic metals (Mattigod et al. 2006).

Sorption of contaminants onto NPs depends on their properties such as composition, size, purity, structure and solution conditions such as pH and ionic strength. Pure anatase TiO_2 NPs exhibited stronger affinity and higher sorption capacity than materials that were predominantly composed of anatase with additional amounts of rutile (Giammar et al. 2007). Acid treatment greatly modified the properties of CNTs such as material purity, structure and nature of the surface which made CNTs become more hydrophilic and suitable for sorption of low molecular weight trihalomethane (THM) molecules (Lu et al. 2005). Sorption is size dependent; the affinity of Cu^{2+} for hematite follows the order 7 nm > 25 nm = 88 nm and sorption on 7 nm particles occurs at lower pH values in comparison to particles with 25 or 88 nm diameter. This indicates the uniqueness of the surface reactivity of iron-oxide NPs with decreasing diameter (Madden et al. 2006). The sorption capacity of lead to TiO_2 NPs (20–33 nm) was always higher, on mass basis, than to the bulk material (520 nm).

Fig. 6 Schematic representation of the interaction of engineered NPs with natural water components
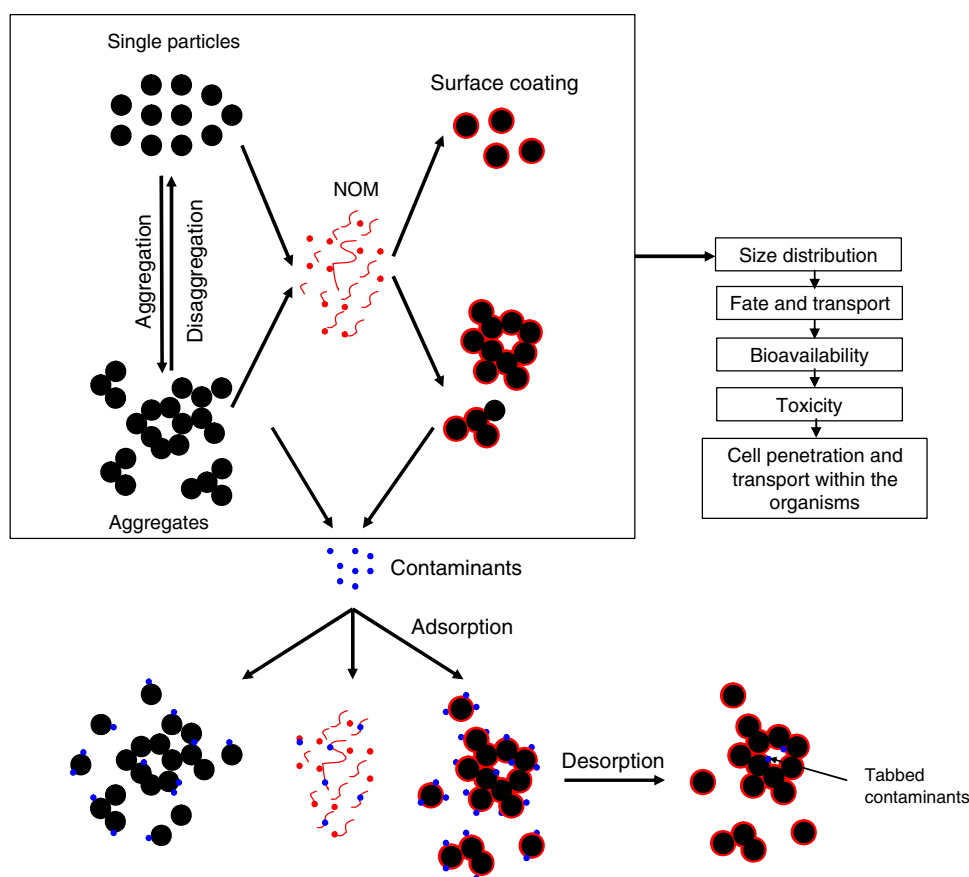
However, the bulk material had a higher sorption capacity when it was normalized to surface area and exhibited stronger affinity (Giammar et al. 2007). The sorption of contaminants onto nC_{60} fullerenes depends also on aggregate structure (fractal dimension or aggregates porosity, discussed later) and increases by several orders of magnitude with the higher dispersal (Cheng et al. 2004) and porosity (Yang and Xing 2007) of nC_{60}. Adsorption/desorption hystereses were observed and related to structural rearrangement of aggregates and the formation of closed interstitial spaces in NP aggregates which prohibit desorption (Cheng et al. 2004; Yang and Xing 2007). Porosity increases the time required to reach sorption equilibrium of Zn^{2+} to powdered activated carbon (average pore size of 2.46 nm) in comparison with CNT (no pores), as Zn^{2+} has to move from the exterior surface to the inner surface of the pores (Lu and Chiu 2006).

Metals sorption into MWCNTs is pH dependent and shows increasing affinity and capacity with increasing pH as expected from the sorption behaviour of metals onto natural colloids carrying a variable surface charge (Liang et al. 2006). At pH above the point of zero charge (PZC), surfaces are negatively charged due to the dissociation of surface functional groups providing electrostatic attractions that are favourable for the sorption of cations. The decrease

of pH leads to the neutralization or charge reversal of surface charge and so the decrease of cation sorption (Liang et al. 2005). The sorption capacity of Zn^{2+} onto CNT increased with the increase of pH in the pH range 1–8 and reaches a maximum in the range 8–11 (Lu and Chiu 2006). The adsorption of trihalomethanes (THM) onto CNTs fluctuates very little in the pH range 3–7, but decreases with pH value as pH exceeds 7 (Lu et al. 2005).

Clearly the interaction of contaminants with NPs is dependant on NPs characteristics such as size, composition, morphology, structure, porosity, aggregation/disaggregation and aggregate structure. However more research is required to determine and quantify this dependency.

Surface coating by NOM

Previous research on natural colloids has shown that humic substances (HS) form surface films of several nanometres on macroscopic surfaces (Lead et al. 2005) and on colloidal particles (Baalousha and Lead 2007; Hunter and Liss 1982). More recently, it has been shown that HS sorbs to zero-valent iron NPs (Giasuddin et al. 2007), iron-oxide NPs (Baalousha et al. 2008a), CNT (Baalousha et al. 2008b; Hyung et al. 2007) and fullerene NPs (Chen et al. 2007), resulting in the formation of nanoscale surface

coating. The thickness of this surface coating was found to be of the order of 0.8 nm on iron-oxide NPs in the presence of 25 mg l^{-1} humic acid (Baalousha et al. 2008a) and of about 1.0 nm on CNT in the presence of 10 mg l^{-1} humic acid (Baalousha et al. 2008b). The average size of only 0.8–1.0 nm, compared with a known hydrodynamic size of HA of 1–2 nm (Lead et al. 2005), indicates the formation of patchy films or the flattening of the HA molecules on sorption. Such surface coating can modify the nature of NPs. Surface coating has been shown to influence the surface charge of NPs (Baalousha et al. 2008a), i.e., suppressing the positive charge and enhancing the negative charge depending on the NP PZC and solution pH. Sorption of HA molecules to iron-oxide NPs (Baalousha et al. 2008a), fullerene NPs (Chen et al. 2007) and CNT (Baalousha et al. 2008b; Hyung et al. 2007) was suggested as a stabilization mechanism (enhanced the stability by steric stabilization mechanism) and explained by the increase in electrophoretic mobility. Surface coating of NPs by NOM is likely to affect aggregation behaviour (discussed later), resulting in reduced aggregation through charge stabilization (Jekel 1986) and steric stabilization mechanisms (Tipping and Higgins 1982) or enhanced aggregation through charge neutralization and bridging mechanisms caused by fibrillar attachment (Buffle et al. 1998).

Aggregation of nanoparticles: effect of HA and cations

As with natural colloidal particles (Buffle et al. 1998), NPs are expected to be dominated by aggregation. However, studies on the aqueous stability and aggregation of NPs at environmentally relevant conditions are scant. Brant et al. (2005) studied the aggregation and deposition of fullerene NPs in aqueous media at variable ionic strength. While in the absence of electrolytes nC$_{60}$ stayed stable over time, 0.001 M solution ionic strength (NaCl) was enough to destabilise the nC$_{60}$ by screening their electrostatic charge and produce large aggregates that settle over time (Brant et al. 2005). The addition of humic acid has been shown to enhance the stability of fullerene NP suspension in the presence of NaCl and MgCl$_2$ and low concentrations of CaCl$_2$ (Chen and Elimelech 2006). However, at high concentrations (above 10 mM) of CaCl$_2$, enhanced aggregation of fullerene NPs was observed due to a bridging mechanism by humic acid aggregates (Chen et al. 2007). HA molecules were found to form aggregates, through intermolecular bridging via calcium complexation, which bridge the fullerene primary particles and enhance their aggregation. This aggregation mechanism has also been observed in the case of alginate-coated NPs undergoing enhanced aggregation through alginate gel formation (Chen et al. 2006) and in the case of naturally occurring sub-micrometer iron-oxide particles in the presence of

NOM and CaCl$_2$ concentrations higher than 10 mM due to a bridging mechanism (Tipping and Ohnstad 1984).

Extracted Suwannee River humic acid (SRHA) and natural surface water (actual Suwannee river water with unaltered NOM background) have been shown to stabilize multi-wall carbon nanotubes (MWCNT) (Hyung et al. 2007). The enhancement of the single-walled carbon nanotube (SWCNT) stability in the presence of SRHA, due to nanoscale surface coating and thus increased electrostatic repulsion, was confirmed by (Baalousha et al. 2008b). However, extensive flocculation of CNT (i.e., formation of floating aggregates and partial sedimentation of other aggregates of CNT) was observed when mixed with natural waters from a lake, presumably due to the high ionic strength and the presence of divalent cations such as Ca. Apparently, sorption of humic substances enhances the stability and inhibits the aggregation of CNT to a certain extent (Hyung et al. 2007), However, cations, particularly divalent cations such as Ca^{2+} and Mg^{2+}, reduce the stability of CNT in the absence or presence of NOM surface coating (Baalousha et al. 2008b).

Electrolytes such as NaCl, MgCl$_2$ and CaCl$_2$ induce the aggregation of alginate coated hematite NPs. In the presence of NaCl and MgCl$_2$, alginate-coated hematite nanoparticles aggregate through electrostatic destabilization. In the presence of CaCl$_2$, the aggregation rate was much higher than that which conventional diffusive aggregation predicts. This was explained by the formation of an alginate-coated hematite gel network and the cross-linking between unadsorbed alginate that might form bridges between hematite-alginate gel structures (Chen et al. 2006). The increase of solution pH was found to induce the aggregation of iron-oxide NPs with maximum aggregation close to the point of zero charge (PZC) of about 8.0. The addition of SRHA was found to shift the PZC and the aggregation of iron-oxide NPs to lower pH values, neutralize the positive surface charge at pH values below the PZC and to enhance the negative charge at pH values above the PZC. Thus, in this case SRHA had a dual role as a coagulant or a stabilizer below and above the PZC, respectively (Baalousha et al. 2008a).

Other than pH, ionic strength and NOM, the concentration of NPs can influence their aggregation behaviour. Concentration-dependent aggregation of iron-oxide NPs (Baalousha 2008) and zero-valent iron oxide (Phenrat et al. 2007) has been observed. The rate of aggregation and size of individual aggregates formed increased with increasing particle concentration (Phenrat et al. 2007).

Obviously, natural waters will have complex effects on NP stability, aggregation and sedimentation through different mechanisms of nanoscale surface film formation, charge enhancement and steric stabilization by NOM, charge neutralisation by ionic strength or specifically by

binding cations such as Ca, bridging by fibrils and bridging by aggregated NOM. These interactions need further investigation in order to predict the fate and behaviour of engineered NPs in natural aquatic systems.

Variation in aggregates structure in function of HA concentration: fractal dimension

The conformation and porosity of NP aggregates vary significantly with the medium physicochemical conditions such as pH, ionic strength, concentration of NPs and concentration of NOM. The structure of NP aggregates can be described by fractal dimension (Rizzi et al. 2004). Fractal dimension provides information about the morphology of the aggregate related to the irregularity, the mass distribution within the aggregate, aggregate porosity and compactness. Fractal dimension has a value in the range 1–3: 1 for a linear aggregate and 3 for a compact sphere. Aggregates of NPs such as fullerenes (Chen et al. 2007; Rudalevige et al. 1998), CNT (Sun et al. 2004), iron oxide (Baalousha et al. 2008a; Chen et al. 2006; Phenrat et al. 2007), and natural colloidal particles have been observed to form fractal structures. The fractal dimension of kaolin aggregates decreased with the addition of HA to a minimum value and stayed constant with the further increase of HA (Sokolowska and Sokolowski 1999). The fractal dimension of iron-oxide NPs was found to vary in the presence of HA molecules. For instance, Fig. 7, a typical TEM micrograph, shows the variation of aggregate structure due to the addition of SRHA molecules at pH 6. In the absence of HA, iron-oxide NPs form open porous aggregates with a fractal dimension (D_1 1.16 ± 0.06, D_2 1.78 ± 0.06 and D_3 1.87 ± 0.06), whereas in the presence of HA, they form compact aggregates with a fractal dimension (D_1 1.74 ± 0.10, D_2 1.95 ± 0.01 and D_3 2.06 ± 0.02) (Baalousha et al. 2008a).

Aggregate structure is an important factor, controlling their fate and behaviour and their interaction with contaminants. The more porous the aggregate, the lower the fractal dimension, resulting in faster sedimentation in comparison to higher fractal aggregates or impermeable spheres (Johnson et al. 1996; Li and Logan 2001). Adsorption/desorption hysteresis of naphthalene to fullerenes NPs was explained by the blockage of the pores with the aggregates after sorption takes place, i.e., variation in their fractal dimension (Cheng et al. 2004). Aggregate structure also influences their disaggregation as will be discussed later.

Disaggregation of NPs by HA molecules

Disaggregation is as important as aggregation processes in determining NPs fate and behaviour and interaction with trace contaminants. However, no studies are available on the disaggregation of NPs except one study performed on iron-oxide NPs (Baalousha 2008). NOM has been shown to induce the disaggregation of iron-oxide NP aggregates (5–10 µm), likely due to formation of surface coating of NOM on the surface and pore surface of the aggregates and thus the enhancement of surface charge as confirmed by electrophoretic mobility measurements. This induces an increase of the degree of repulsion within the aggregate matrix and results in aggregate rupture. A previous study has shown that polymers are able to separate two stuck colloids, even when the separation distance was on the order of few nanometers (primary minimum) (Ouali and Pefferkorn 1994).

There are two possible mechanisms of aggregate breakup based on aggregates structure, i.e., the location of the weakest cross section where the aggregates might break and given the different rates of disaggregation: surface erosion (slow rate) and large-scale fragmentation. In surface erosion, small particles are separated from the surface

Fig. 7 Variation in the structure of iron-oxide nanoparticles due to the interaction with SRHA molecules at pH 6 as observed by transmission electron microscope (**a**) FeO (100 mg l^{-1} Fe) and (**b**) FeO (100 mg l^{-1} Fe) + HA (5 mg l^{-1}), scale bar = 100 nm
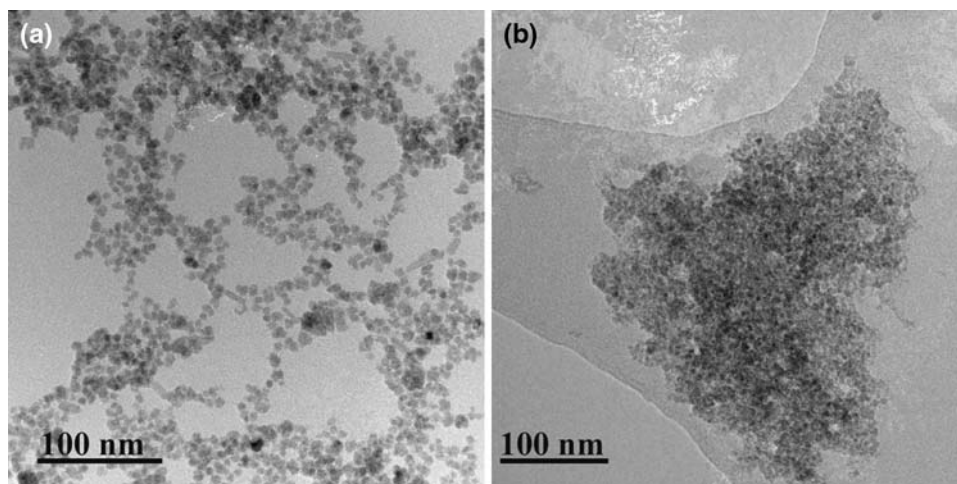
of the aggregate while in large-scale fragmentation (fast rate) the aggregates split into pieces of comparable sizes (Jarvis et al. 2005). Highly branched aggregates with small fractal dimension breakup by fragmentation mechanisms, while compact aggregates with high fractal dimension favour breakup by surface erosion mechanisms (Yeung and Pelton 1996). Disaggregation depends also on the way NP aggregates interact with HA. HA adsorption on NP aggregate surfaces may develop in two steps. The first, fast step corresponds to purely covering the aggregate apparent surface by HA and a second slower step corresponds to the diffusion of HA through the already adsorbed layer and the reptation of HA into the restricted zones near to neighbouring interfaces, i.e., aggregate pores. It has been shown that the adsorption of polyelectrolyte to colloidal particles surfaces induced aggregate fragmentation after an initial lag time, which is the time required for polymer reptation within the porous matrix of aggregates and sorption to the surface of the particles (Ouali and Pefferkorn 1994; Pefferkorn 1995). Clearly the disaggregation depends on the structure of the aggregates, i.e., their fractal dimension, and more research is needed to investigate the possible disaggregation of NPs in the environment and the role of natural organic matter on this process.

Environmental significance

NPs may impact the environment in three possible ways: (1) direct effect on biota, i.e., toxicity, (2) changes in the bioavailability of toxins or nutrients, (3) indirect effects on ecosystem, i.e., break-up of refractory natural organic substances and (4) changes of the environmental microstructures. Understanding the interactions between NPs and natural colloids is crucial to estimate the potential impact

of NP and ensure environmentally sustainable production and use of NPs. This review shows that the exact behaviour will depend in a complex manner on NP properties, organic matter type and concentration and on solution conditions such as pH and ionic strength.

Surface coating, aggregation and disaggregation will largely determine the bioavailability and the fate and behaviour of NPs through (1) controls on transport in surface and ground waters and (2) sedimentation in surface waters or deposition and filtration in soils and groundwaters. Stabilization of NPs by surface coating may maintain them within the water column and increase their transportation distances and rates. Aggregation will likely lead to settling of NPs to the sediments and consequently to reduced transportation in the water column, which potentially makes benthic organisms a key receptor for NPs. Disaggregation will result in the formation of small aggregates that can be resuspended and become mobile in the water column and which may carry pollutants as well as nutrients, and thus results in their transport (Fig. 8).

Aggregation and sedimentation of NPs can be responsible for the scavenging of colloids from the water column to the sediment (Baalousha et al. 2008b) and will lead to the formation of porous microstructures of both natural colloids and NPs that can change their structure (fractal dimension) depending on the medium physicochemical conditions, i.e., pH, ionic strength, concentration of NPs and concentration of NOM. The porosity of these microstructures/aggregates controls the circulation of water, nutrients and soluble compounds within the aggregates, sorption of chemicals and sedimentation rate. Each of the components of microstructures (i.e., NPs, colloids and NOM) can adsorb significant amounts of nutrients and thus serve as nutrient reservoirs for the microorganisms

**Fig. 8** Schematic plot of pathways and important transformation reactions in the aquatic environment
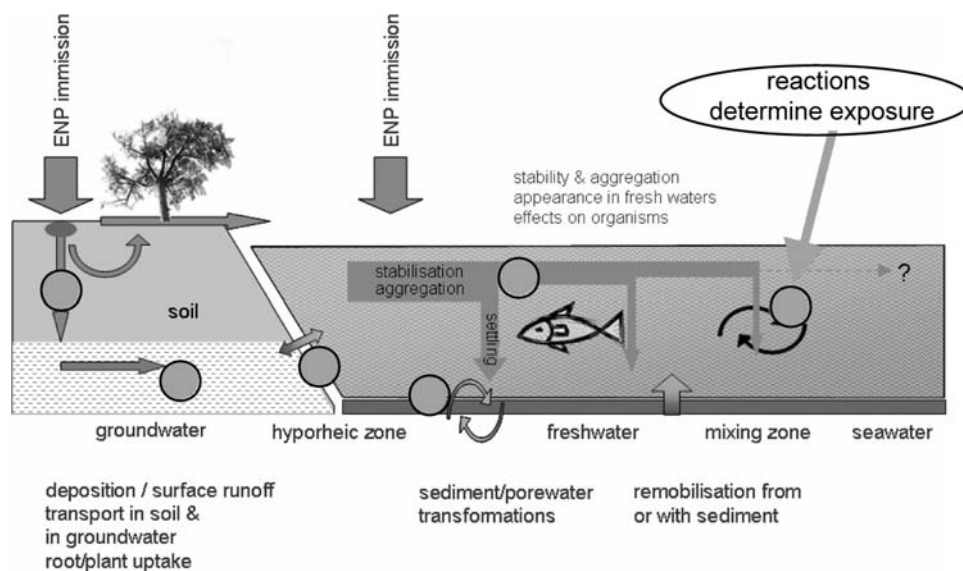
that are included within the microstructure. Therefore, the introduction of NPs into aquatic medium will influence its microstructure, metals and nutrient bioavailability and ultimately the sustainability of life (Buffle 2006; Huang et al. 2005).

Behaviour in porous media

General mechanism

The transport of NPs in porous media is, among others, dominated by their size, shape and charge distribution. Transport or filtration of NPs in porous media like soils or aquifers is divided into two steps (McDowell-Boyer et al. 1986): (1) collision and (2) attachment to the soil or sediment grains themselves (the collector). While the attachment is a function of the electrostatic interactions between the NPs and the soil, the mechanisms leading to a collision can be further divided into surface, straining and physical–chemical filtration. If NPs are prevented from penetrating into the media due to their size, a filter cake or a surface mat will form above the media (surface filtration). NPs which are capable of entering the media can be mechanically removed by sieving or straining in smaller pore spaces (straining filtration/sieving). In addition, for unsaturated systems, filtration at a gas-water interface has to be taken into account.

For small NPs physical and chemical forces are decisive. The collisions of small NPs with a collector occur as a result of three processes: diffusion, interception and sedimentation (Fig. 9).
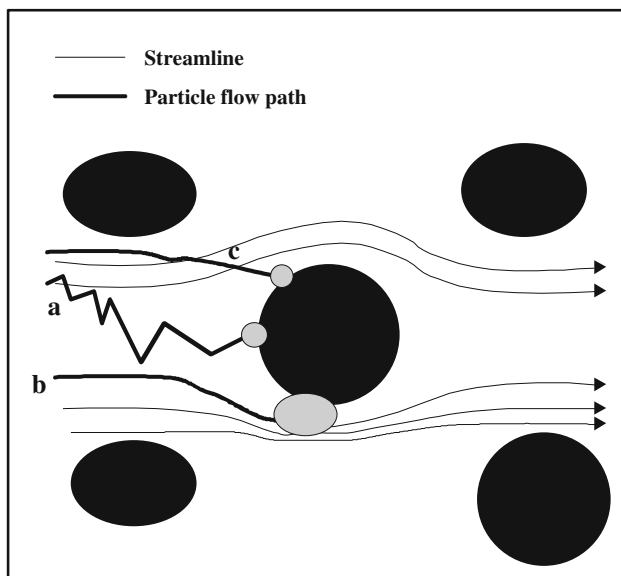
Small NPs and aggregates (<1 μm) are mainly transported by Brownian diffusion. NPs which move on their flow path close to the soil material can make contact by interception. This is attributed to a difference of NP velocity and collector. A further agglomeration mechanism takes place due to differences in density. For NPs with a higher density than the transport medium the sedimentation process has to be considered. Finally (not displayed in Fig. 5), NPs can be retained in the soil by pore size exclusion or sieving (McDowell-Boyer et al. 1986; O'Melia and Tiller 1993). While the maximum size of mobile NPs is limited by straining filtration and pore velocity, concentration and size distribution of NPs in the nanometer size range are controlled by physico-chemical filtration. A minimum filtration rate can be observed at a size range close to 1 μm for a density close to 1 g/cm^3 and around 0.2 μm for NPs with a density around 3 g/cm^3, where straining filtration is less effective in most systems and physico-chemical filtration does not yet reach its maximum.
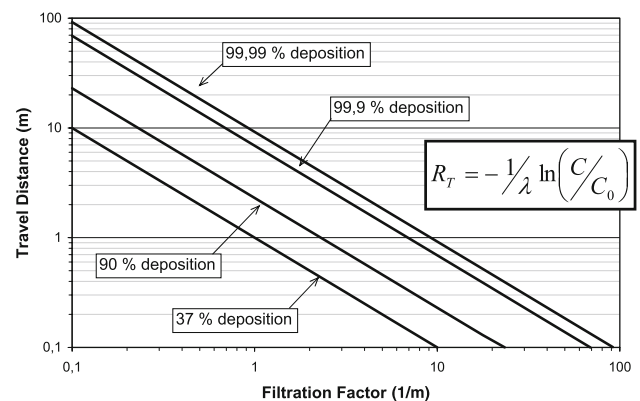
Filtration models for NPs/porous media collision

Iwasaki (1937) described filtration as a first order kinetic,

$$C_P = C_{0P} e^{(-\lambda \cdot \Delta x)} \tag{1}$$

and

$$R_T = -\frac{1}{\lambda} \ln\left(\frac{C_P}{C_{0P}}\right) \tag{2}$$

where C_P is the NP concentration at the travel distance x, C_{0P} is the original NP concentration, λ is the filtration factor in m^{-1} and R_T is the colloid travel distance in m at a given retention rate. The correlation between the filtration factor and travel distance is given in Fig. 10.

Developed by Yao (1968), Yao et al. (1971) and extended by Rajagopalan and Tien (1976), the so-called filtration theory enabled the calculation of the filtration

Fig. 9 Particle filtration by (a) diffusion, (b) interception and (c) sedimentation (modified after Yao (1968))

Fig. 10 Correlation between filtration factor and travel distance for a given deposition rate

factor and thus colloid transport in saturated media. The four different mechanisms of colloid filtration, i.e., sieving/straining, sedimentation, diffusion and interception, have been described by the following equations (Yao 1968):

$$\lambda = \frac{3(1-n)\gamma}{2d_k}\alpha = \frac{\gamma}{d_k}\alpha \tag{3}$$

and

$$\gamma = \gamma_D + \gamma_I + \gamma_G + \gamma_S \tag{4}$$

$$\gamma_D = 0,9\left(\frac{k_B T}{\mu v_f d_p d_K}\right)^{\frac{2}{3}} \tag{5}$$

$$\gamma_I = \frac{3}{2}\left(\frac{d_p}{d_k}\right)^2 \tag{6}$$

$$\gamma_G = \frac{gd_p^2(\rho_p - \rho_W)}{18\mu v_f} \tag{7}$$

$$\gamma_S = 2,7\left(\frac{d_p}{d_k}\right)^{\frac{3}{2}} \tag{8}$$

This model is somehow simplified and neglects the influence of adjacent collector grains and the hydrodynamic retardation (Tien and Pajatakes 1979). In order to account for these processes, Rajagopalan and Tien (1976) introduced the Happel parameter A_S and modified the equations to account for the hydrodynamic retardation:

$$\gamma_D = 0,9A_S\left(\frac{k_B T}{\mu d_p d_k v_f}\right)^{\frac{2}{3}} \tag{9}$$

$$\gamma_I = A_S\left(\frac{4A_H}{9\pi\mu d_p^2 v_f}\right)^{\frac{1}{8}}\left(\frac{d_p}{d_k}\right)^{\frac{15}{8}} \tag{10}$$

$$\gamma_G = 0,00338A_S\left(\frac{(\rho_P - \rho_W)gd_p^2}{18\mu v_f}\right)^{1,2}\left(\frac{d_k}{d_p}\right)^{0,4} \tag{11}$$

$$A_S = \frac{(1-y^5)}{(1-\frac{3}{2}y+\frac{3}{2}y^5-y^6)} \quad \text{and} \quad y = (1-n)^{\frac{1}{3}} \tag{12}$$

where d_k = effective grain size in m, n = porosity, γ = elementary filtration rate, α = collision efficiency, γ_D = diffusion, γ_I = interception, γ_G = gravitation, γ_S = sieving, k_B = Boltzmann constant in J K^{-1}, T = absolute temperature in K, v_f = apparent flow velocity in m s^{-1}, d_p = colloid size in m, g = gravitational acceleration in m^2 s^{-1}, μ = dynamic viscosity in kg m^{-1} s^{-1}, ρ_p = colloid density in kg m^{-3}, ρ_W = fluid density in kg m^{-3}, A_S = Happel parameter and A_H = Hamaker constant in J.

Figure 11 shows the sum of the four different forces and the total filtration curve. A typical minimum in NP filtration in porous media can be observed at 1 μm for NPs with a density of 1 g/cm^3.
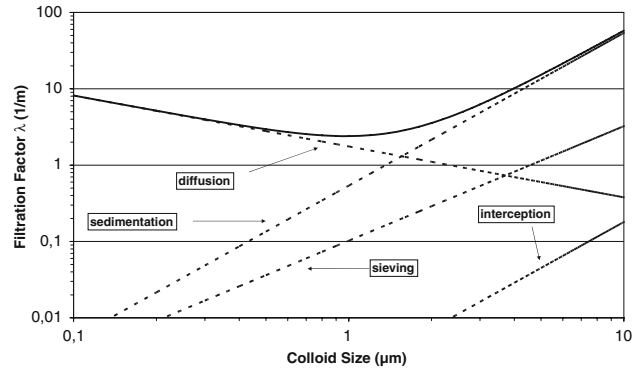

Fig. 11 Filtration theory modelling for diffusion, sedimentation, sieving and interception

However, no gas phase is included in all models mentioned above; consequently calculations using these equations for an unsaturated soil system should be regarded with care and only as a first estimation. In unsaturated soils preferential flow, like fingering, macro porous flow and retention or transport at the gas/water interface have to be included in transport predictions. Even though for laboratory experiments several model approaches were successfully applied including theses mechanisms, up to now there is no reliable estimation of NPs filtration in unsaturated field scale soil systems.

Models for NPs/porous media attachment

Equations 1–12 are only valid if the collision between two NPs or a NP and a soil grain leads to attachment. This means that the collision efficiency α is 1 (Eq. 3). Obviously, the charge of a NP is a major parameter in NPs filtration, as well as all factors influencing the electrostatic forces between two charged NPs.

Almost all minerals in natural soils or sediments carry a negative surface charge due to their crystallographic properties or the sorption of anionic polyelectrolytes like HA. Also many NPs possess a negative surface potential that is influenced by surface groups and the pore water chemistry. This leads to repulsive forces and decreased attachment factor α. An opposite charge of NPs and collector material leads to an enhanced attachment. Colloidal stability, which means the tendency not to change their state of dispersion, is a fundamental element for NP transport (Stumm 1992). The stability of NPs is dependent on the interaction of a number of factors like density, surface charge, surface chemistry, size distribution, water chemistry and water flow velocity. Alike for NPs, the soil/sediment surface charge arises from three possible mechanisms: (1) chemical reactions at different pH values influence functional groups (e.g., –OH, –COOH) and effect variable charges. At the zero point of charge, NPs tend to
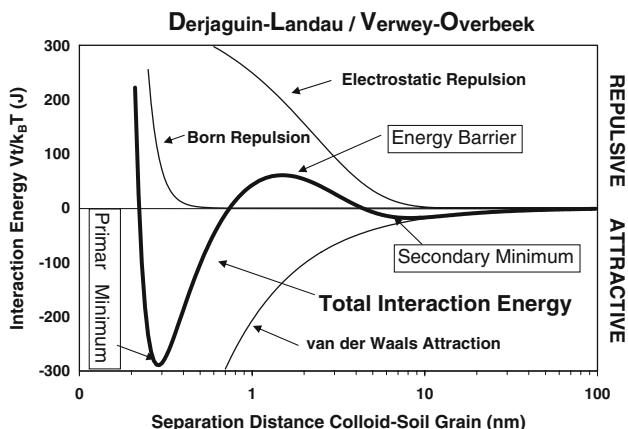
Fig. 12 DLVO model for total interaction energies between a spherical NP and a flat collector

Fig. 13 Correlation between collision efficiency and energy barrier (DLVO model)

destabilize and coagulate; (2) substitution of ionic of different charges (e.g. Si/Al) cause permanent charges; (3) adsorption of hydrophobe substances (Stumm and Morgan 1996).

Based on the DLVO theory, the stability of NPs is influenced by the attraction of van der Waals forces and the repulsive electrostatic forces.

In Fig. 12 the total interaction energy between two NPs or a NP and a collector can be calculated by the sum of the repulsive forces, i.e., the double layer force V_{DDL} (Eq. 13) and the Born force V_B (Eq. 14), and the attractive (Eq. 15) van der Waals force V_A (Ruckenstein and Prieve 1973; Spielmann and Cukor 1973).

$$V_{DDL} = \frac{\varepsilon \varepsilon_0 d_p}{2} \Psi_P \Psi_K \ln \left(1 + e^{-\kappa h} \right) \tag{13}$$
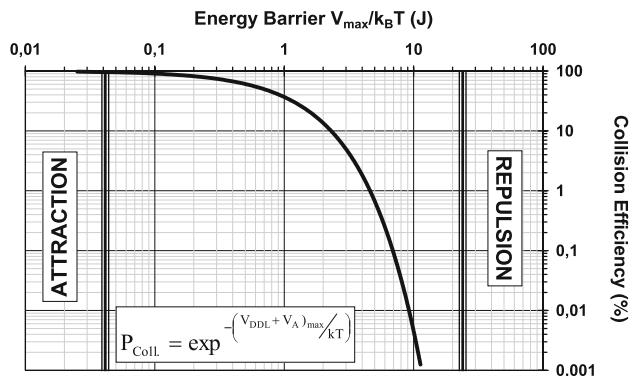
and

$$V_B = \frac{AH^6}{7560} \left(\frac{4d_p + h}{d_p + h^7} + \frac{3d_p - h}{h^7} \right) \tag{14}$$

$$V_A = \frac{A}{6} \left[\ln \left(\frac{h + d_p}{h} \right) - \frac{d_p}{h} \frac{h + \frac{d_p}{2}}{h + d_p} \right] \tag{15}$$

where V_{DDL} = diffuse double layer repulsion in J, V_B = Born repulsion in J, A = Hamaker constant in J, h = NP-collector distance in m, H = Born parameter in m, κ = Debye-Hückel parameter in m^{-1}, Ψ_P = surface potential NP in V, Ψ_K = surface potential collector in V, d_p = NP diameter in m, ε = relative dielectric constant, ε_0 = absolute dielectric constant in A s V^{-1} m^{-1}

If the electrostatic repulsive forces are dominant, the approximation (=attachment) of a NP to the collector is hindered by an energy barrier and depends on the expansion of the diffuse double layer. The dimension of this layer can be influenced by the ionic strength of the water and the NP/collector surface charge. A high surface charge

and a low ionic strength favour the stability and transport of NPs. The filtration efficiency α in Eq. 3 will be less then 1 if an energy barrier prevails, thus filtration theory will fail if the reduced collision rate is not taken into account. The theoretical efficiency of a collision (=attachment) P_{coll} is given by Eq. 16 (Ruckenstein and Prieve 1973).

$$P_{coll} = \exp - (V_{DDL} + V_A)_{\frac{max}{k_B T}} \tag{16}$$

Figure 13 shows the decrease of the collision efficiency with an increasing energy barrier. We can deduce from Fig. 13 that, theoretically, an energy barrier of more than 10 k_{BT} will impede NP attachment to a collector. This would favour transport in the porous media and lower the filtration capacity of a soil or sediment.

Conclusions

It is clear that the rapid growth of interest in engineered nanoparticles has presented many challenges for ecotoxicology, not least being the effort required to analyse and understand the nanoparticles themselves. A considerable amount of progress has been made in understanding the fate of nanoparticles in porous media and a limited understanding of the fate of nanoparticles in surface waters is being developed. It seems likely that, although the nanoparticles themselves are complex systems, a reasonable understanding of their fate and behaviour in the natural environment may be developed.

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