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Nanoparticles in wastewaters: Hazards, fate and remediation

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ABSTRACT

The increasing use of nanoparticles will inevitably result in their release into the aquatic environment and thereby cause the exposure of living organisms. Due to their larger surface area, high ratio of particle number to mass, enhanced chemical reactivity, and potential for easier penetration of cells, nanoparticles may be more toxic than larger particles of the same substance. Some researchers have been showing some relations between nanoparticles and certain diseases. However, the doses, surface shapes, material toxicity and persistence of nanoparticles may all be factors in determining harmful biological effects. In order to better evaluate their risks, potential exposure route of nanoparticles has to be taken into consideration as well. Finally, a brief summary of techniques for nanoparticle removal in waters and wastewaters is presented, but it seems that no treatment can absolutely protect the public from exposure to a large-scale dissemination of nanomaterials.

1. Introduction

Particles in the nano-sized range, for example soot and organic colloids, have been present on earth for millions of years. Recently, however, nanoparticles have attracted a lot of attention because of our increasing ability to synthesize and manipulate such materials [1]. The Woodrow Wilson Database listed an inventory of 1317 consumer products containing engineered nanoparticles (March 2011) currently on the market, which has grown by nearly 521% since March 2006. The largest product category is health and fitness (including cosmetics and sunscreens), with a total of 738 products, followed by home and garden (209), automotive (126), food and beverage (105).

Commercially important nanoparticles include metal oxide nanopowders, such as silica (SiO₂), titania (TiO₂), alumina (Al₂O₃) or iron oxides (Fe₃O₄, Fe₂O₃), and other nanoparticle materials like semiconductors metals or alloys. Besides these, molecules of special interest that fall within the range of nanotechnology are fullerenes and dendrimers (tree-like molecules with defined cavities), which may find application for example as drug carriers in medicine [2].

Nanowires, nanotubes or nanorods as linear nanostructures can be generated from different material classes. As one of the most promising

linear nanostructures, carbon nanotubes can be expected to find a broad field of application in nanoelectronics, catalysis, design of novel gas sensors, enzymatic biosensors, immunosensors and DNA probes, and also as fillers for nanocomposite materials with special properties [3–5].

Nanolayers are another important topic within the range of nanotechnology. Through nanoscale engineering of surfaces and layers, a vast range of functionalities and new physical effects (e.g. magnetoelectronic or optical) can be achieved. Moreover, the surfaces and layers of nanoscale are often needed to optimize the interfaces between different material classes (e.g. semiconductors on silicon wafers), and to have the desired special properties [3]. In addition, nanolayers can also be coated to fight erosion, corrosion in metals.

Nanoporous (usually called mesoporous) materials with the pore-size in the nanometer range have a broad range of industrial applications due to their outstanding properties [2]. Their large surface area which generally certifies large quantities of active centers, as well as their narrow pore size distribution makes mesoporous materials widely used in shape-selective catalysis, membrane filtration and energy storage [6–9].

The reasons that make these nanomaterials so different and so intriguing may be as follows. The extremely small feature size at the nanoscale is of the same scale as the critical size for physical phenomena. Fundamental electronic, magnetic, optical, chemical, and biological processes are different at this level. Surfaces and interfaces are also important in explaining nanomaterial behavior. In bulk materials, only a relatively small percentage of atoms will be at or near a surface or interface (like a crystal grain boundary). In nanomaterials,

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the small feature size ensures that many atoms, sometimes half or more in some cases (size < 5 nm), will be near interfaces. Surface properties such as energy levels, electronic structure, and reactivity can be quite different from bulk ones, and then give rise to quite different material properties [10].

Such exceptional properties of nanomaterials might not only favor their applications, but also cause their novel toxicity. In fact, the reactive surface of ultra-small particles can result in the direct generation of harmful oxyradicals (ROS): these can cause cell injury by attacking DNA, proteins and membranes [11–13]. Furthermore, the ability of these particles to penetrate the body and cells (e.g., via fluid-phase endocytosis and caveolae) provides potential routes for the delivery of nanoparticle-associated toxic pollutants to sites where they would not normally go [13]. Nanoparticles can then behave like a vector on which hazardous compounds are concentrated. It is worth knowing that medicinal applications of nanoparticles benefit the same property to deliver drugs to diseased cells in order to improve the bioavailability of a drug; but biodistribution of some nanoparticles may not be known exactly, so they may accumulate in the body over time, leading to potential dangers.

Summarily, as the nanotechnology industries start to come on line with larger scale production, it is inevitable that nanoscale products and by-products will enter the aquatic environment [13,14], since industrial products and wastes tend to end up in waterways (e.g., drainage ditches, rivers, lakes, estuaries and coastal waters) despite safeguards. Accidental spillages or permitted release of industrial effluents in aquatic systems could lead to direct exposure to nanoparticles for humans via inhalation of water aerosols, skin contact and direct ingestion of contaminated drinking water or particles adsorbed on vegetables or other foodstuffs [14]. More indirect exposure could arise from ingestion of organisms such as fish and shellfish (i.e. mollusks and crustaceans) as a part of the human diet.

2. The potential hazards of nanoparticles

Although the risks of nano- or ultrafine particles seem to be plausible, hazards relevant to humans and other mammals have been studied. Much of this research has been done with experimental mammals, but animal experiments cannot be the only basis for precise quantitative estimates regarding actual risk for humans because of the differences between experimental animals and humans that make extrapolations uncertain [15,16].

2.1. Risks of inhaled nanoparticles

The high deposition efficiency of inhaled nanoparticles in the pulmonary region increases in people with asthma or chronic obstructive lung disease [17]. Inflammation of the lung is often seen as a response to the inhalation of nanoparticles as well. In addition, exposure to carbon nanotubes can give rise to the formation of interstitial granulomas in animal experiments [15].

2.1.1. Metal oxide nanoparticles (TiO_2 and SiO_2)

In vivo pulmonary toxicity studies in rats, Warheit et al. [18] demonstrated that ultrafine TiO_2 had low inflammatory potential and lung tissue toxicity. Studying the effect of ultrafine carbon and TiO_2 particles ranging from 12 to 220 nm, Möller et al. [19] saw evidence for impaired defense ability in the rat lung. Renwick et al. [20] showed that ultra fine TiO_2 and carbon black particles impaired phagocytosis by alveolar macrophages more strongly than fine particles of the same materials. There was also evidence that nanoparticles might act as an adjuvant for allergic sensitization [15].

Moreover, submicron and nanoscale amorphous silica spheres and rods as model materials were synthesized by Brown et al. [21] for shape-driven toxicological experimentation. Their results showed that

shape-driven agglomeration may be a factor in the pathogenesis of particle-induced lung disease.

2.1.2. Carbon nanotubes and carbon nanoparticles

In the studies of Möller et al. [19] and Renwick et al. [20] in 2.1.1, ultrafine carbon particles have been proved to be toxic to some extent. Deckers et al. [22] further compared the toxic effect of aluminum oxide, titanium oxide nanoparticles to multi-walled carbon nanotubes. Carbon nanotubes were more toxic than metal oxide nanoparticles. They also demonstrated significant difference in biological response as different functions of nanomaterials. Prevailing theories suggested that acicular or fiber-like particles induce enhanced toxicity over isotropic materials through hindrance of phagocyte-mediated clearance mechanisms and through the aggravation of proximal cells via mechanical interactions. Moreover, Lundborg et al. [23,24] found that rat and human alveolar macrophages had impaired function due to aggregates of ultrafine carbon particles, which may be linked to increased infection risk and decreased protection of sensitive lung cells.

2.1.3. Quantum dots (QDs)

Recently, researchers are more and more focused on the influence of size, crystalline structure, and chemical composition of nanoparticles in the investigation of their toxicities. Clift et al. [25] studied the uptake, kinetics and cellular distribution of different surface coated QDs and demonstrated that surface coating has a significant influence on the mode of nanoparticle interaction with cells, as well as the subsequent consequences of the interaction.

2.2. Risks of contacted nanoparticles

2.2.1. Metal oxide nanoparticles (TiO_2 and ZnO)

Apart from exposure by inhalation, dermal penetration of nanoparticles is a matter of interest for humans. The application of TiO_2 and ZnO nanoparticles in sunscreens, currently the most important use of ultrafine metal oxide particles in personal care products highlights the dermal penetration of nanoparticles. TiO_2 and ZnO particles sized ~15 to 50 nm can be photocatalytically active on exposure to sunlight [15]. According to a study of Dunford et al. [26], this also holds for coated particles that are actually applied in sunscreens.

Menzel et al. [27] demonstrated in experiments that TiO_2 nanoparticles can penetrate pig skin through the stratum corneum into the underlying stratum granulosum within the first 8 h after application. And studies with ZnO suggest that ZnO nanoparticles may penetrate deep into the rat and rabbit skin [26]. ZnO and TiO_2 nanoparticles may also become involved in damaging nucleic acids and other cell components by photocatalytic reactions on exposure to sunlight due to penetration into the stratum granulosum [26]. TiO_2 nanoparticles may furthermore become involved in causing allergic reactions [15,27].

Wu et al. [28] evaluated the potential toxicity of TiO_2 nanoparticles in hairless mice and porcine skin. Their results indicate that TiO_2 nanoparticles can penetrate through the skin, reach different tissues and induce diverse pathological lesions in several major organs. Topical application of nano- TiO_2 for a prolonged period can induce dermal toxicity, most likely associated with free radical generation, oxidative stress, and collagen depletion that can lead to skin aging.

2.2.2. Carbon nanotube

Dermal exposure of humans may also be important in handling nanoparticles in laboratories or industries. Glove deposits of single-walled carbon nanotube during handling were estimated by Maynard et al. [29]. They showed that substantial deposits on skin or gloves could originate in handling carbon nanotubes, and presented evidence that (unrefined) carbon nanotubes may cause dermal toxicity due to oxidative stress [15].

2.3. Risks of nanoparticles in the aquatic environment

2.3.1. C₆₀-fullerene

For aquatic animals, other routes of entry such as the passage across gill and other external surface epithelia act. Studies with fish by Oberdörster [30] indicated that C₆₀-fullerene may be internalized by these routes and induce lipid peroxidation in brain of juvenile largemouth bass. Zhu et al. [31] investigated different toxicities to daphnia magna between tetrahydrofuran (THF)-solubilized nC₆₀ and water-stirred-nC₆₀. There were 100% mortality in the THF-nC₆₀-exposed fish between 6 and 18 h, while the water-stirred-nC₆₀-exposed fish showed no obvious physical effects after 48 h. Kovochich et al. [32] found the same results that THF-solubilized nC₆₀ but not fullerol or aqueous nC₆₀ generated cellular toxicity in a mouse macrophage cell. These suggest that the toxicity of nanoparticles can be greatly affected by various factors.

2.3.2. Metal oxide nanoparticles (TiO₂, CeO₂, SiO₂ and Fe₂O₃)

Zhu et al. [33] found that nTiO₂ exerted minimal toxicity to daphnia within the traditional 48 h exposure time, but caused high toxicity when the exposure time was extended to 72 h. This demonstrated that exposure duration may be a contributing factor in nanoparticle-mediated toxicity. Moreover, upon chronic exposure to nTiO₂ for 21 days, daphnia displayed severe growth retardation and mortality, as well as reproductive defects. A significant amount of nTiO₂ was also found to be accumulated in daphnia, and these daphnia displayed difficulty in eliminating nTiO₂ from their body, presenting increased bioconcentration factor values. This high level of bioaccumulation may interfere with food intake and ultimately affect growth and reproduction.

Genotoxic and ecotoxic assessments of widely used nanoparticles, CeO₂, SiO₂ and TiO₂, have been conducted on two aquatic sentinel species, the freshwater crustacean daphnia magna and the larva of the aquatic midge chironomus riparius [34]. A statistically significant correlation was observed between DNA damage and mortality in the CeO₂-exposed chironomus riparius, which suggests that CeO₂-induced DNA damage might provoke higher-level consequences. Auffan et al. [35] observed a reduction of $21 \pm 4\%$ of the Ce⁴⁺ atoms localized at the surface of CeO₂ nanoparticles due to the interactions with organic molecules present in biological media. These particles induced strong DNA lesions and chromosome damage related to an oxidative stress. SiO₂ nanoparticles did not seem to affect the DNA integrity; whereas, the mortality of both the SiO₂-exposed daphnia magna and chironomus riparius increased. In addition, the TiO₂ nanoparticle did not lead to significant alterations in geno- or ecotoxic parameters of both species in the work of Lee et al. [34].

Furthermore, Zhu et al. [36] used early life stages of the zebrafish to examine the ecological effects of iron oxide nanoparticles on aquatic species. These nFe₂O₃ nanoparticles aggregated rapidly and settled out of the water column where they contacted directly with zebrafish embryos. These aggregation and sedimentation phenomenon of nFe₂O₃ is similar to that of other nanoparticles, including Cu, Ag, TiO₂, nZnO, nAl₂O₃, fullerene, and single-walled carbon nanotube [37–44]. Their studies also demonstrated that nFe₂O₃ aggregates caused a serious delay in embryo hatching, malformation in some zebrafish embryos and larvae, and eventually mortality. It is worth noting that the conditions in the present study were those of an “ideal” experimental situation, using standard zebrafish culture medium as a simulated aquatic environment. However, in a real environment such as lakes and rivers, nFe₂O₃ may behave differently.

2.3.3. Other nanoparticles (Ag, Si, CdSe and carbon nanotube)

Bilberg et al. [45] investigated acute toxicity of nanosilver to zebrafish (*Danio rerio*) in a 48 h static renewal study and compared with the toxicity of silver ions (AgNO₃). The study demonstrated that silver nanoparticles were lethal to zebrafish. Their observations also revealed increased rate of operculum movement and surface respiration

after nanosilver exposure, suggesting respiratory toxicity. Moreover, the silver ions were approximately 3.4 times more toxic than the silver nanoparticles by mass of silver added to the tanks, indicating that nanoparticles form of silver are less toxic than their soluble forms by mass added.

Ong et al. [46] used silicon (nSi), cadmium selenide (nCdSe), silver (nAg) and single-walled carbon nanotubes to assess nanoparticle effects on zebrafish hatch. Exposure of 10 mg/L nAg and nCdSe delayed zebrafish hatch, and 100 mg/L of nCdSe inhibited hatch and the embryos died within the chorion. Both the morphology and the movement of the embryos were not affected. It was determined that the main mechanism of hatch inhibition by nanoparticles is likely through the interaction of nanoparticles with the zebrafish hatching enzyme. It was concluded that the observed effects arose from the nanoparticles themselves and not their dissolved metal components.

In conclusion, recent studies have shown some relevancy between nanoparticles and pathologies by animal experiments. Although more precise data and the mechanism of their risks have to be further studied, it is important to take into account that many nanostructures may cause potential risks for human health.

2.4. Physico-chemical features relevant to particle toxicology

As mentioned above, toxicities of nanoparticles can be influenced by many factors. It is recognized that biologically available surface area is probably the most critical parameter for the effects of the nanomaterials. Additionally, particle surface chemistry, biodegradability, concentration, shape, solubility, particle size and surface charges are all found to be significant factors in determining harmful biological effects.

Generally, for the same mass of particles with the same chemical composition and crystalline structure, a greater toxicity was found from nanoparticles than from their larger counterparts. The higher surface area of nanoparticles causes a dose dependent increase in oxidation and DNA damage, much higher than larger particles with the same mass dose [47,48].

For concentration-dependent toxicity of nanoparticles, there are many contradictory results related to their toxic effects at different concentrations. Comparing these results of different studies, one must take into account that there are differences in the aggregation properties of nanoparticles in air and water, causing inherent discrepancies between inhalation studies and instillation or in vitro experiments. The aggregation of nanoparticles may reduce their toxicity, due to a more effective macrophage clearance for larger particles compared to smaller ones [49,50]. Thus, experiments performed with high concentrations of nanoparticles may not be as toxic as lower concentrations of the same nanoparticles, because most aggregates may be formed for a high concentration of nanoparticles [51,52].

Particle chemistry is another critical in determining nanoparticle toxicity. It is especially relevant from the point of view of cell molecular chemistry and oxidative stress. Other words, depending on their chemistry, nanoparticles can show different cellular uptake, subcellular localization, and ability to catalyze the production of ROS [53]. For example, rutile TiO₂ nanoparticles (200 nm) were found to induce oxidative DNA damage in the absence of light, but anatase TiO₂ nanoparticles of the same size did not [51].

Furthermore, particle surface plays a critical role in toxicity as makes contact with cells and biological materials. Surfactants can drastically change the physicochemical properties of nanoparticles, affecting their cytotoxicity. Functional groups are usually attached either covalently or non-covalently onto the nanoparticles by chemical processes [54]. For example, place-exchange reaction is the most versatile and widely used method for introducing functional groups to Au nanoparticles. Although some findings showed that functionalized Au nanoparticles are not cytotoxic, a slight reduction in the reactive oxygen and nitrite species can be caused by them [55]. Additional, nano-TiO₂ has been reported to show adsorption behavior towards metals such as Cu (II),

Cr (III), Mn (II), Ni (II), Zn (II), Cd (II), Mo (VI) [56]. However, when an aqueous suspension of bacteria and other micro-organisms is in the presence of TiO₂ in the dark, a slight reduction for nano-TiO₂ to adsorb metals in the concentration of colonies was found due to the possible agglomeration of TiO₂ with the bacterial cells and subsequent sedimentation [57].

2.4.1. The challenge to relate the physicochemical properties of colloidal nanoparticles to their cytotoxicity

Until now, researchers cannot agree with each other on the dose at which nanoparticles cause a biological response. Some of them measured the dose of toxicity by total weight, some others by the number of particles per volume. Beckman¹ found that the best way to pinpoint how toxic the particles are to cells was to calculate the dose based on the total surface area of the nanomaterial. Brown et al. [21] investigated the shape-driven toxicity of amorphous silica and showed that this may be the main reason for the pathogenesis of lung disease. Zhu et al. [33] proposed that exposure duration has to be considered in nanoparticle-mediated toxicity. And Auffan et al. [35] pointed out that chemically stable metallic nanoparticles have no significant cellular toxicity, whereas nanoparticles able to be oxidized reduced or dissolved are cytotoxic and even genotoxic for cellular organisms.

It seems that different parameters play major roles under different conditions, complicating the toxicity evaluation of nanoparticles. Consequently, there would be little pressure to defend or treat wastewaters containing such particles that may present novel toxicity.

2.4.2. Predicting nanoparticle interactions in human bodies

The impact of nanomaterials on living cells can be broken down into the interactions between the nanomaterial and the individual cell components. The membrane interface is the first interactional medium between a material and a cell [58]. Foley et al. [59] demonstrated that a fullerene derivative could cross the external cellular membrane and it localizes preferentially to the mitochondria. Yang et al. [60] pointed to possible negative impacts of nanomaterials in daphnia magna. They concluded that long-term exposure (21 days) of low-level C₆₀ caused significant cellular damage, leading to cell dysfunction and cell lysis or necrosis in daphnia magna.

Nanomaterials that interact with proteins may alter protein structure as well. Highly selective protein adsorption on nanoparticles, added to the fact that particles can reach subcellular locations, results in significant new potential impacts for nanoparticles on protein interactions and cellular behavior. The loss of secondary structure and consequent changes in the activity of proteins upon binding to nanoparticles could be seen as a drawback or a potential source of nanoparticle toxicity [61].

Other literature focuses on the detrimental effects of nanomaterial-DNA interactions [58]. For example, hydroxyl radicals ($\cdot\text{OH}$) associated with TiO₂ nanoparticle induced cytotoxicity and oxidative DNA damage in fish cells [62]. A novel fullerene-lysine conjugate has been synthesized and was found to cleave the supercoiled DNA; superoxide radical generated on photoirradiation seems to be the ROS behind the DNA cleavage, which may give negative effects [63].

Finally, besides the potential hazards of nanoparticles, their occurrence and fate in aqueous system are also important in determining their final toxicity to public.

3. Occurrence and fate of nanoparticles in water

Nanoparticles are expected to be present in water environments with very low concentration from mg/L to $\mu\text{g/L}$ according to modeling studies [64–67]; but it still lacks of data reporting the realistic concentration ranges of nanoparticles in natural aqueous system, due to accelerating introduction of nanoparticles into various applications.

The aggregation and sedimentation of nanoparticles may occur naturally in the presence of suspended or dissolved substances in water (e.g. nature organic matter), which would favor the removal of nanoparticles from suspensions [68]. Fig. 1 gives the general schema of interactions in governing environmental colloidal processes and stability.

However, the combined effect of pH, ionic strength, electrolyte species and concentrations, and other characteristics of water would either make nanoparticles aggregated by charge neutralization, bridging, electrical double layer compression and by other mechanisms [70], or may cause nanoparticles to be more stable [71,72]. Thus, uptake of nanoparticles by animals and biomagnification in the food-chain is always possible.

Recently, silver nanoparticles (AgNPs) are used increasingly in consumer products such as water treatment for their antimicrobial properties. This increased use raises ecological concern because of the release of AgNPs into the environment. Once released, zero-valent silver may be oxidized to Ag⁺ and the cation liberated, or it may persist as AgNPs [73]. Aggregation of silver nanoparticles appears to strongly influence other processes, including precipitation, adsorption and dissolution, and thus is particularly important in determining the transport of the particles in aquatic systems. However, studies of aggregation stability of silver nanoparticles showed that aggregation is confined or limited to very slow rate and the particles in the system stay suspended for a relatively long term [74].

Furthermore, the dispersion stability of nanoparticles is also important in determining their potential exposure to organisms, which will depend on their intrinsic properties, including sizes, shape, core composition, surface properties and concentrations [75]. Since most of the engineered nanoparticles are surface-modified, functionalized, or coated during manufacturing, their stability against aggregation and deposition may increase [76]. For example, in China and Taiwan, silica nanoparticles are commonly used as abrasive in chemical mechanical polishing (CMP) industries for the manufacture of integrated circuits and electronic chips. The effluents of these factories are mainly composed of silica nanoparticles (1.3–8.5 g/L which correspond to 0.05%–0.36% in volume ratio) with an average size around 100 nm. These particles present a negative charge at the surface, and the suspensions are very stable [77–83].

Other fates of aquatic nanoparticles include adsorption/desorption, degradation, reaction and so on; but it is likely for nanoparticles (maybe even bind with toxic pollutants during their exposure) to enter into aquatic animals, and then accumulate into human body before their removal. Therefore, it is reasonable to begin considering how to remove nanoparticles from water, especially from wastewater such as the CMP effluents that has an important total solid content in the nano-range and has been produced in large quantities.

4. Technologies of nanoparticle separation

The conventional wastewater treatments including chemical, physical and biological methods may not be adapted to the recovery of nano-scaled particles, first of all due to their size, but also due to their original properties [13,15]. In the last few years, some researchers [84–88] have begun to study how to separate nanoparticles from waters, but compared to their plentiful applications and toxicities explorations, separation researches of nanoparticles are still limited.

4.1. Coagulation and electrocoagulation (EC) processes

Chang et al. [89] studied the treatment of nanoparticles by chemical coagulation as it exists in the unity of wastewater treatment plant. Their structural researches on the nanoparticle agglomeration due to coagulation have demonstrated the interest of coagulant addition for a good recovery, but its effect on nanoparticle removal (<9%) was still not satisfying. Chuang et al. [90] investigated colloidal silica removal in

¹ M. Beckman, *Nanoparticle toxicity doesn't get wacky at the smallest sizes*, Pacific Northwest National Laboratory, 2009.

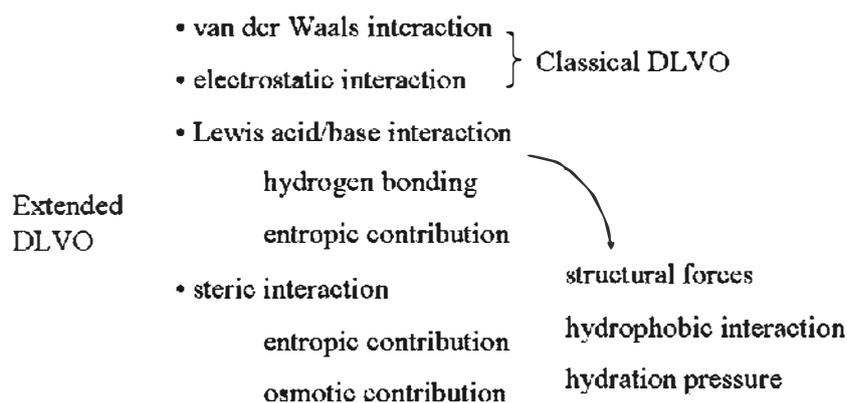


Fig. 1. General schema of interactions in governing environmental colloidal processes and stability (adapted from Grasso et al. [69]).

coagulation processes for wastewater reuse in another high-tech industrial park. Experimental results illustrated two coagulants (PACl and $Al_2(OH)_nCl_{6-n}$) demonstrated the same capacity on silica nanoparticle removal (approximately 80%). Chemical coagulation and flocculation processes have the advantages to benefit a fast increase of particle size and an easy removal of particles by sedimentation, but the high quantities of coagulant and sludge are their shortcomings.

EC was then tested as an alternative to chemical coagulation because it does not require the direct addition of a chemical coagulant [71,80]. Lai and Lin [77] investigated the treatment of copper CMP wastewater from a semiconductor plant by EC. The test results indicated that EC with Al/Fe electrode pair was very efficient and able to achieve 99% copper ion and 96.5% turbidity removal in less than 30 min. Another group [78] used electro-coagulation-flotation (ECF) process with surfactant to treat CMP wastewater. The addition of surfactant CTAB that could both increase the particle size and produce positive-charged bubbles (particles are negative-charged) effectively increased the removal of the turbidity. The sludge volume and settling time were significantly less in the solution containing CTAB than in the one without CTAB. Comparing with chemical coagulation process, EC process has less sludge and no preliminary pH adjustments. Main disadvantage of EC is the dissolution of electrodes into wastewater streams as a result of oxidation. Thus electrodes need to be regularly replaced. Other disadvantages contain the relatively high usage of electricity, and high conductivity of the water suspension required.

At the present time, excellent coagulation/flocculation performances have been reached using organic reagents such as polyamines and polyDADMACs authorized by the Directorate General for Health of several countries. After optimization of the aggregating process with cationic organic polymers, the size distributions of SiO_2 nanoparticles (about 80 nm) can reach between 10 μm and 1 mm, with fractal dimensions (compactness) ranging from 2.3 to 2.5. The performances obtained show that the use of these organic reagents is a promising potential route to treat other types of nanoparticles. The treatment also proposed to reach a ratio of average diameters d_{Floc}/d_{NP} of 3500, and therefore it facilitates the elimination of these nanoparticles agglomerated by filtration [91].

4.2. Flotation process

Lien and Liu [81] tested the treatment of CMP effluents by dissolved air flotation (DAF). Very effective removal of particles (turbidity decrease > 98%) from wastewater was found when CTAB was used as a collector. It is proposed that both the change of interface properties and the aggregation of nanoparticles contributed to flotation removal of particles.

Tsai et al. [83] studied nano-bubble flotation with coagulation by PACl/sodium oleate (NaOl) as a combination of activator/collector for the cost-effective treatment of CMP wastewater. Their work increased

the wastewater clarification efficiency by 40% as compared with traditional coagulation/flocculation process. More than 95% of the turbidity, total solids and total silica removal efficiencies were observed.

Furthermore, Liu et al. [92] tested the flotation of nanosilica suspensions in a new designed continuous DAF system. They showed that flotation had an interesting separation efficiency (removal of 99% of nanoparticle concentration) only when additives were added to overcome the hydrophilic behaviors of silica. In the conditions tested in their work, the quantities of additives were a little more than the ones necessary to perform aggregation and settling separation, but the flotation combined with coagulation process needed much less time to achieve the separation purpose.

4.3. Filtration process

Due to the small size, the separation of nanoparticles from liquid medium by conventional filtration without pre-coagulation could be difficult [93]. In the last few years, coagulation or electrocoagulation with filtration was then explored by many researchers [94–95].

Zhong et al. [96] used the tubular ceramic membranes to remove nickel catalysts from slurry, indicating a separation efficiency of 100%. Springer et al. [97] evaluated the feasibility of membrane ultrafiltration for the removal of SiO_2 nanoparticles (78 nm mean hydrodynamic diameter), the 10 kDa membrane showed the highest expectable retention rates (>99.6%). Additionally, it was demonstrated that approximately 98% of fullerol could be removed by a polyamide nanofiltration membrane [98].

Based on several studies, the removal efficiencies for nanoparticles could be greatly improved by using membrane filtration as the final process. However, membrane filtration process is mainly hindered by membrane fouling, leading to flux decline and the increase of operating costs.

4.4. Biological process

During conventional wastewater treatment process, the nanoparticles could be incorporated into the sewage sludge through aggregation and sorption and further accumulated in sewage sludge over time. Once attached to biomass, the removal of nanoparticles is associated with the setting and removal of the biomass [99]. A recent full-scale wastewater treatment test indicated that TiO_2 nanomaterials were trapped in biomass, which could then be settled and removed by secondary sedimentation or membrane filtration process, and more than 96% of the TiO_2 could be finally removed [100]. Adsorption to activated sludge seems to be the major removal mechanism for nanoparticles in this study.

However, Limbach et al. [87] investigated the capture of nanoparticles by clearing sludge. Their study demonstrated a significant influence of the nanoparticle surface charge and the addition of dispersion stabilizing surfactants as routinely used in the preparation of nanoparticle

derived products. A detailed investigation on the agglomeration of oxide nanoparticles in wastewater streams revealed a high stabilization of the particles against clearance (adsorption on the bacteria from the sludge). Their present results indicate a limited capability of the biological treatment step to completely remove oxide nanoparticles from wastewater.

Another study suggested that the predominant mechanisms of engineered nanoparticle removal (95% of nano-copper were removed) were aggregation and settling rather than biosorption in activated sludge biomass [101]. The different conclusion may be attributed to the different types of nanoparticles investigated in these studies. It should be noted that some nanoparticles entrapped within the sludge materials may still have an effect on the activity of the essential bacteria or may re-enter the environment through application of sewage sludge to fields, incineration or landfilling [102]. More experiments will be required for in depth studies on the detailed mechanism of nanoparticle adsorption to sludge.

4.5. Other processes for nanoparticle separation

Zarutskaya and Shapiro [84] applied magnetic filters to capture nanoparticles with permanent magnetic moments. The influence of filtration operating conditions and particle diameters on their behavior and magnetic capture efficiency was investigated numerically, but this work was limited to the separation of magnetic nanoparticles.

Chin et al. [79] used synthesized magnetite nanoparticles to aggregate target nanoparticles by the electrostatic attraction between the two oppositely charged particles. By optimizing experimental conditions, the residual turbidity could be removed until less than 1 NTU, but large amount of magnetic nanoparticles had to be used.

Michael and Armstrong [103] summarized separation and analysis of nanoparticles by capillary electrophoresis. The advantage of this method is that the separation of different colloids is possible. However, all of the above technologies have obvious disadvantage for a large scale wastewater (containing nanoparticles) treatment.

5. Conclusion

As we all know, the potential advantages of nanomaterials are immense, but so are the potential dangers. More attention on the risk assessment and waste management associated with nanomaterials are required. Nevertheless, the knowledge about occurrence, fate and toxicity of nanoparticles are still lacking. The pathways of nanoparticle penetration into bodies by food (fish and shellfish) are still uncertain. Consequently, characterization and quantification of nanoparticles may be firstly crucial to evaluate their potential risks and to compare different research results.

Until now, a wide number of techniques including microscopy techniques (transmission electron microscopy, confocal laser scanning microscopy, scanning electron microscopy and atomic force microscopy), static and dynamic light scattering (SLS, DLS), X-ray diffraction (XRD), inductively coupled plasma (ICP-OES and ICP-AES), X-ray photoelectron spectroscopy (XPS) have been developed for detection and characterization of nanomaterials. However, it is still a great challenge to directly detect engineered nanoparticles in natural water due to their low concentrations.

In order to promote the feasibility of these analytical techniques, several key issues are needed to be addressed: (i) minimizing the alteration of samples and loss of components from sampling to analysis; (ii) minimizing artifacts in estimation of size distribution during fractionation process; (iii) ensuring the representativeness of samples; (iv) distinguishing between engineered nanomaterials and their naturally occurring counterparts; (v) validating detected results by several methods.

On the other hand, the development of wastewater treatment containing nanoparticles is urgent for hazard reduction in aquatic environment. It

may be difficult for one type of method to treat the complex matrix containing nanoparticles, different techniques are usually required to complement one another for achieving better removal efficiency. Although some methods are effective in removing specific types of nanoparticles at laboratory scale, their efficiencies for different nanoparticles in full scale are still unknown. It might be a good news that nanoparticles could be stabilized by sewage sludge in nature, even if the interaction between nanoparticles and sewage sludge has not been clear. More researches and funds are required to fill these knowledge gaps even though the regulations have not yet been imposed.

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