NASS Journal of Agricultural Sciences
http://ojs.nassg.org/index.php/NJAS

REVIEW

Nanomaterials in Soil Environment: A Review

Satya Sundar Bhattacharya[1*] **Subhasish Das**[2]

1. Soil and Agro Bio-engineering Lab, Department of Environmental Science, Tezpur University, Tezpur, 784028, India
2. Department of Environmental Science, Pachhunga University College, Mizoram University, Aizawl, 796001, India

ARTICLE INFO

Article history
Received: 5 July 2019
Accepted: 15 July 2020
Published Online: 31 July 2020

Keywords:
Nanomaterials
Toxicity
Soil
Stress
Biomagnification

ABSTRACT

Nanomaterials (NMs) have become an integral part of our daily life, and their extensive production will only increase with the increasing time. These NMs exhibit significant contrast regarding dimension, reaction, and structure. The most important aspect of the NMs is that these can be easily manipulated and engineered to custom-suit different functions/industries. Owing to their dynamic nature, these NMs behave differently when introduced in any medium. In soil, the behavior of NMs is significantly controlled by the interactions of nanomaterials with soil phases. Although NMs are deemed beneficial for human-use, yet these also carry lethal effects. Moreover, there is a dearth of adequate research for the interactions among nanomaterials and soil physicochemical properties; their accumulation-dissolution dynamics in soil-plant systems; and their long term influence on soil health. Several NMs induce physiological stress when introduced inside the body. Thus, various researchers have devised green pathways for producing NMs, although their wide applicability is still questionable. Although the domain of nanotechnology is greatly explored, yet there remain several grey areas which need to be addressed for sustainable utilization of these unique materials in the benefit of humankind.

1. Nanotechnology and Nanomaterials

Nanotechnology is the branch of science that deals with materials spanning 1-100 nm in size. These materials are produced after altering the physical architecture at the atomic, molecular, and supra-molecular scale [1]. Nanomaterials (NMs) are popularly termed as 0D, 1D, 2D, and 3D based on their physical dimensions [1,2]. Nanoparticles are abundant in nature, say the fragments of colloidal particles (1-1000 nm) which possess at least one dimension in the range 1-100 nm are termed as natural nanoparticles [3]. These natural nanoparticles are formed by geological processes like volcanic eruptions, weathering, microbial action, etc. and can be biological (*e.g.* viral cages, biomolecules, complex carbohydrates, etc.) or inert/non-living in origin *viz.* Al-silicates, O-hydroxides, etc. [4]. On the other hand, artificially produced NMs also known as Engineered NMs (ENM) are significantly different structurally and chemically from their natural counterparts [5]. Recently, great focus has been put on ENMs due to their plethora of applications in the health-care, food, industrial, and environmental sectors [6].

Generally, ENMs bear unique structure and a large

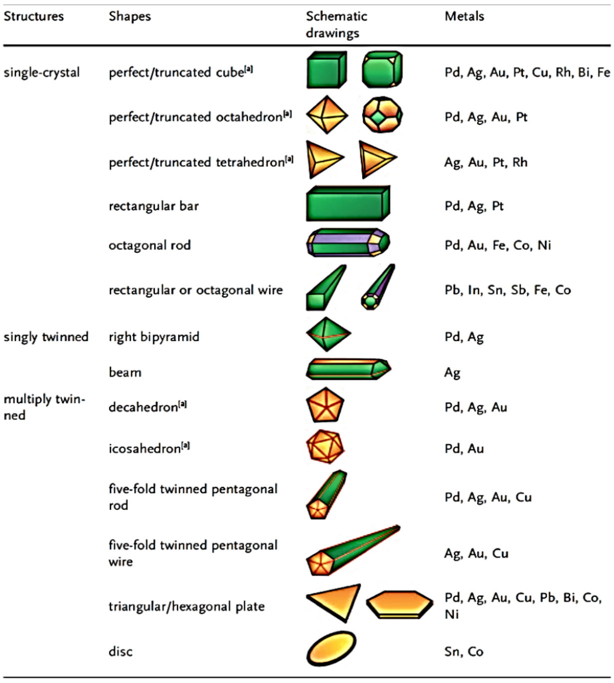
**Corresponding Author:*
Satya Sundar Bhattacharya,
Soil and Agro Bio-engineering Lab, Department of Environmental Science, Tezpur University, Tezpur, 784028, India;
Email: satya72@tezu.ernet.in; satyasundarb@yahoo.co.in

DOI: https://doi.org/10.36956/njas.v1i2.11

area-to-volume ratio which give rise to the special character and behavioral attributes. These unique features also allow scientists to produce different types of ENMs custom-suited for specific applications [7,8]. Owing to their large scale production several ENMs are now being synthesized on a large-scale. Speaking from a production point of view, ENMs may be either metal based or oxides/oxyhydroxides of different metallic precursors [8].

2. Metal-based ENMs

The NMs of metallic origin are termed as metallic NMs (MNMs) and these are the most widely used NMs owing to their easy synthesis and utility in various industries [9].



Structures	Shapes	Schematic drawings	Metals
single-crystal	perfect/truncated cube[a]		Pd, Ag, Au, Pt, Cu, Rh, Bi, Fe
	perfect/truncated octahedron[a]		Pd, Ag, Au, Pt
	perfect/truncated tetrahedron[a]		Ag, Au, Pt, Rh
	rectangular bar		Pd, Ag, Pt
	octagonal rod		Pd, Au, Fe, Co, Ni
	rectangular or octagonal wire		Pb, In, Sn, Sb, Fe, Co
singly twinned	right bipyramid		Pd, Ag
	beam		Ag
multiply twinned	decahedron[a]		Pd, Ag, Au
	icosahedron[a]		Pd, Au
	five-fold twinned pentagonal rod		Pd, Ag, Au, Cu
	five-fold twinned pentagonal wire		Ag, Au, Cu
	triangular/hexagonal plate		Pd, Ag, Au, Cu, Pb, Bi, Co, Ni
	disc		Sn, Co

Figure 1. A gist of different structural conformations of metallic NMs

Source: Reproduced from Xia et al. [10] with permission (© 2009, John Wiley and Sons, USA).

Also, the metallic precursors of these NMs cover more than two-thirds of the periodic table making them an interesting subject for novel discoveries in material science. Fascinatingly, the metallic NMs exhibit great diversity in their structural properties which not only renders them unique characters but also influences their applicability to a large extent [9]. A summary of various possible structural conformations of the metallic NMs has been provided in Figure 1 [9,10].

In their work, Bratlie et al. [11] elaborated the importance of NM's structure on their catalytic properties. In any catalytic reaction, it is quintessential to attain perfect binding between the reagent molecules and the catalyst (here NM) to form new bonds *i.e.* the product molecules. This condition relies on: (1) the available orbitals of the reagent molecules, and (2) atomic arrangement of the NM surface. Hence, manipulating the structural arrangement of NMs could be a major step towards designing more efficient metallic NMs [9].

3. Metal-oxide NMs

Recently a lot of interest has cropped up on metal-oxide NMs (MONMs) which is mainly credited to their diverse applicability in medicine, agriculture, and engineering [12]. The MONMs exhibit unique physico-chemical properties attributed by their high density and limited corner/edge size on the surface sites. Thus the MONMs duly fill the gap between bulk materials and atomic/molecular structures which attests their importance in nanotechnological applications [13]. In many MONMs *viz*. CuO, ZnO, TiO_2, SnO_2, Al_2O_3, MgO, AgO, CeO_2, ZrO_2 etc. it was observed that reduction in size increased surface strain/stress and concomitant structural perturbations [14-16]. Apart from size and shape attributes, some other important parameters that determine NM properties and application are (i) ionic strength, (ii) zeta potential, and (iii) valency of the metallic precursors in the NMs [17].

(1) Ionic strength: The ionic strength of the electrolyte is an important parameter which determines the behavior of the NMs in solutions. French et al. [18] reported that TiO_2 NMs form stable aggregates at 0.0045 M NaCl solution which changed to micro-aggregates within 15 min when the ionic strength was increased to 0.0165 M. Comparatively, it was noticed that the same NMs (TiO_2) when introduced in 0.0128 M $CaCl_2$ solution form micro-aggregates in 5 min.

(2) Electrical charge and zeta-potential: In general, M NMs bear negatively charged surfaces. This may be provided by the negatively charged hydroxyl ions. Moreover, the high negative surface charge facilitates easy binding of the NMs with moieties. Although, the efficiency of forming bonds is significantly influenced by the inherent reaction (pH), the concentration of the NMs, as well as constituents of the medium [8]. In many MNMs, "double-charged layer" is characteristically present. The double-charged layer is formed by a charged surface layer and a diffused charged layer. The latter is formed by the adhered ions that the NMs attract from the medium. As a result, the difference in the electrical potential originates between the diffused layer and the medium which is termed as zeta-potential.

(3) Valency: The combining power of any NM with other elements to form nano-complexes is influenced

DOI: https://doi.org/10.36956/njas.v1i2.11

by the valency. According to Pieters et al. [19], a proper understanding of valency of NMs is of utmost importance to yield efficient catalytic NMs. Similarly, it is also very vital to know about the valence band and the conduction band which modulate the structural properties of NMs [20]. Figure 2 presents a typical 1D band scheme for direct and indirect bandgap semiconducting metal-based NMs where the direction of the wave vector is fixed irrespective of the magnitude.

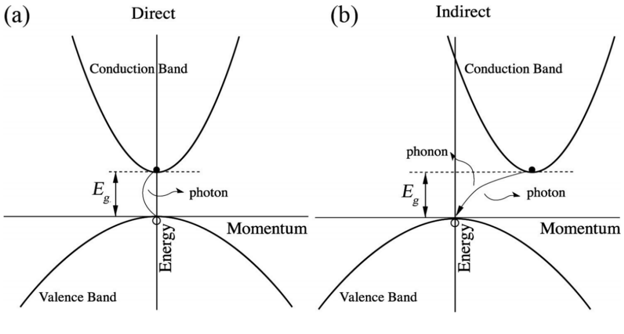


Figure 2. One-dimensional band diagrams containing (a) direct and (b) indirect bandgaps

Source: Martin-Palma and Lakhtakia [20].For further reading please visit: https://www.spiedigitallibrary.org/ebooks/TT/Nanotechnology-A-Crash-Course/3/Properties-of-Nanostructures/10.1117/3.853406.ch3?SSO=1 (© 2010, Society of Photographic Instrumentation Engineers, USA)

Au-NMs are widely used as physical vectors for drug delivery systems and such property is duly induced by the multivalent characteristics of Au nanomaterials [19]. Today, with the advancement in nanotechnology it is possible to produce poly-valent NMs. Such poly-valent NMs have the speciality to change their valency depending on the charge of the target [19].

3.1 Silver NM

Silver is a transition metal with a soft texture and white-lustrous color. It has properties like high electrical and thermal conductivity. Generally, Ag-NMs is very popular due to its anti-microbial activity [21]. Due to their novel properties, the incorporation of silver nanoparticles into different materials like textile fibers and wound dressings can extend their utility on the biomedical field while inhibiting infections and biofilm development [22]. Several workers reported different synthetic pathways for Ag-NM *viz.* physical, chemical, and biological. Evaporation-condensation and laser ablation are the most used physical approaches for Ag-NM synthesis [21]. According to Wiley et al. [23], laser ablation offers pure and clean metallic Ag-NMs without using chemical reagents in solution. Chemical reduction is the mostly used chemical method of Ag-NM production. In this method, several reducing agents *viz*. sodium borohydride, N, N-dimethylformamide, ascorbic acid, hydrazine, etc. are used to reduce Ag^+ in aqueous or nonaqueous solutions [21]. However, due to the contingent toxic nature of these chemical precursors, Ag-NMs are deemed highly toxic for living organisms. In this regard, biologically assisted green synthesis of Ag-NMs has gained a lot of momentum recently. Green synthetic systems use any biological microorganisms such as bacteria, fungi (yeast) and plant extracts for preparing nanoparticles. The interesting review by Pandian et al. [24] elaborated several bio-assisted synthetic methods of silver nanoparticles with a special emphasis on plant-leaf extract mediated synthesis of AgNMs to be an emerging area in the field of nanotechnology.

3.2 Iron oxide NM

Naturally, Iron oxide is found as a mineral with a polymorphic crystalline structure and magnetic properties [25]. The three major polymorphs of Fe-oxide are magnetite (Fe_3O_4), hematite (α-Fe_2O_3), and maghemite (γ-Fe_2O_3). The maghemites mainly in the forms of β-Fe_2O_3 and ε-Fe_2O_3 are generally prepared in laboratory conditions as Fe-oxide NMs [26]. Although several methods are followed for the lab-scale synthesis of Fe-oxide NMs, the most widely used methods are co-precipitation, sol-gel, microemulsion and thermal decomposition methods [26]. The co-precipitation pathway involves dissolving a stoichiometric mixture of Fe (II) and Fe (III) salts in a basic aqueous medium of sodium hydroxide (NaOH) or ammonium hydroxide (NH_4OH). Experimental conditions are critical and depend on the type of Fe-salt precursors *viz.* chlorides, sulphates, nitrates or perchlorates and also on the ratio of Fe^{2+}/ Fe^{3+} [26,27]. The co-precipitation method can yield Fe-oxide NMs in the range of 5-20 nm diameter. However, optimizations of synthesis parameters like pH, temperature, and ionic force of the medium are vital towards controlling the size and surface properties of the synthesized Fe-ox NMs [26].

In the sol-gel synthesis method, the surface of the Fe-ox NMs are coated with organic molecules, polymers (*e.g.* poly(vinyl alcohol), poly(lactide-co-glycolide), polyethyleneimine, polymethyl-methacrylate and poly(ethylene glycol), biomolecules (*e.g.* gelatin, chitosan and dextrosan) or inorganic molecules such as silica [26,28]. Generally, water is used as the solvent and the metallic precursors are hydrolyzed by either by the addition of acid or a base. Factors like rate of reaction, temperature, nature of precursors and pH are optimized to control the size of iron oxide NMs. For example, nano-maghemite (γ-Fe_2O_3) particles with size ranging from 6 to 15 nm are produced at 400°C [29]. Microemulsion method is primarily used to produce catalytic Fe-oxide NMs. This process yields cubic or spherical particles with characteristic narrow pore size ranging from 4 to 15 nm and high surface area (~315 $m^2\ g^{-1}$) [30,31]. Water-in-oil microemulsion consisting of a cationic or non-ionic surfactant (Triton-X), a co-surfactant (glycols, hexanol, 1-butanol), oil phase (n-octane, cyclohexane) and the aqueous phase is generally used to prepare magnetic iron oxide nanoparticles with controlled size and morphology [32]. The microemulsion is formed through the addition of an aqueous solution with iron salt precursors. Experimental parameters *viz.* temperature, pH, reaction medium, washing cycles, etc. are pivotal in the execution of this process [26,28,30]. The water-in-oil microemulsion methods hold much interest in Fe-ox NM synthesis due to its precise control on size and size distribution of the synthesized nanoparticles (range: 7 - 10 nm) [26,33].

Thermal decomposition of precursors *viz*. ferric acetylacetonate, iron nitroso phenylhydroxylamine or iron pentacarbonyl in octyl ether and oleic or lauric acid followed by oxidation, leads to the formation of Fe-oxide nanoparticles with a size distribution between 4 and 16 nm. The reaction of ferric acetylacetonate in phenyl ether at 538 K in the presence of alcohol, oleic acid and olamines produc Fe_3O_4 nanoparticles that may easily be transformed in γ-Fe_2O_3 by annealing at 523 K and oxygen for 2 h. This preparation method produces monodispersed particles with a narrow size distribution but has a great disadvantage that the resulting particles are always dissolved in non-polar solvents [26,28].

Maghemite (γ-Fe_2O_3) particles are extensively used in pollution control due to their ability to consume secondary pollutants and chemicals from industrial wastewater [26]. The Fe-oxide NMs in the size distribution range of 10-80 nm are also used as solid-gas-liquid phase catalysts in industries for enhanced production of styrene, photocatalytic production of hydrogen and oxygen, catalytic conversion of methane in aromatic compounds, fuel cells and production of biodiesel [26]. Iron oxides are commonly applied as ballistic additives in composite solid propellant formulations in order to accelerate the combustion at the burning surface and so to increase the propellant burn rate and its thrust-time curve. In the field of solid propulsion, Fe-ox NMs like hematite (α-Fe_2O_3) and maghemite (γ-Fe_2O_3) are effectively used as burn catalysts to fuel propellers [26,34]. Moreover, Fe-ox NMs are also applied in several biomedical operations (*e.g.* drug delivery), and nuclear magnetic resonance imaging [35].

3.3 Copper Oxide (CuO) NM

CuO is a higher oxide of Cu naturally found as the mineral tenorite. The compound has a characteristic black color and a melting temperature >1200°C. Generally, it is formed by burning Cu in O_2 available environment as:

$$2Cu+O_2=2CuO$$

In laboratory conditions, CuO NMs are generally prepared through precipitation method [36]. Metallic salts *viz.* $CuCl_2$ and $Cu(NO_3)_2.3H_2O$ dissolved in deionized water are adjusted to pH 14 by adding NaOH till a black precipitate occurs. This precipitate is then washed with deionized water and absolute alcohol until neutral reaction (pH=7) is attained. Later the residue is dried at 80°C and calcined at 500°C for 4 h to yield CuO NMs. Copper (II) oxide is used as a glazing and coloring agent in the ceramic industry and also to sanitize materials for its superb anti-bacterial properties [37]. Cu-oxide NMs in the form of Cu-ammonium hydroxide is utilized used in the production of rayon.

The Copper (II) oxide NMs are effectively used as catalysts in rocket propellants due to its superior properties like uniform propellant combustion rate and low-pressure index. Considering its narrow bandgap (~1.2 eV), Cu-oxide NMs are extensively used as p-type semiconductors. Other important applications of Cu-oxide NMs are seen in the preparation of batteries (both dry and wet cell) and as polishing agent for optical instruments. Additionally, this nanomaterial is extensively utilized during welding operations with copper alloys [38].

3.4 Magnesium Oxide (MgO) NM

Magnesium oxide (MgO) also called magnesia, is a solid white hygroscopic mineral that occurs in nature as ‘periclase’. It consists of a lattice of Mg^{2+}ions and O^{2-} ions linked by ionic bonds. The general reaction can be seen as under:

$$MgO + H_2O \leftrightarrow Mg(OH)_2$$

Magnesium hydroxide is produced in the presence of water and this reaction can reversely yield MgO by heating it to separate moisture. Due to its high boiling point (~3600°C), Mg-ox NMs are widely used in the refractory industry. There are few dense engineering ceramics of the structural type made from pure magnesia [39]. Mg-oxide NMs are also used in chemical, construction, environmental and electrical appliance industries.

3.5 Zn-oxide (ZnO) NM

ZnO is known to be a highly functional, and versatile inorganic material in nanotechnology due to its unique properties *viz.* optical, chemical sensing, semiconducting, electric conductivity, and piezoelectric properties [40]. Zn-

DOI: https://doi.org/10.36956/njas.v1i2.11

oxide NMs are prepared through different routes but the most followed methods include thermal evaporation of ZnO powders at 1400°C, hydrothermal synthesis, sol-gel technique, simple thermal sublimation, self-combustion, polymerized complex method, vapor-liquid-solid technique, double-jet precipitation, and solution synthesis [40-42]. Interestingly, different production methods yield variable structural configuration of the ZnO-NMs and thus selection of production method varies greatly on the basis of the desired application. Moreover, the optimization of vital parameters *viz*. solvent type, salt precursors, pH, and the temperature is important for a controlled yield of this NM. As mentioned earlier, several successful structural re-arrangements of ZnO-NMs have been synthesized by changing the physic-chemical parameters of the synthesis method. Some of the major configurations of the ZnO nanostructures are nanorods, nanosphere, nanotubes, nanowires, nanoneedles and nanorings [42].

Zn-oxide NMs are very popular as an antibacterial/ antimicrobial agent and hence used widely in medicine and cosmetic industries. The “calamine” lotion is prepared out with Zn-oxide powder. ZnO is also utilized in the manufacture of rubber and cigarettes. It is recently used as a preservative of food items and as a coating agent in paint industries. Other important applications of ZnO NMs are in the manufacturing of concrete and ceramics where it is used as an additive.

4. NMs in Soil Environment

Increased demand of NMs has severely escalated their production and as a result, most of these NMs are released into the environment, leading to nano-pollution [43,44]. According to Keller et al. [45], about 9~37% and 63~91% of NMs are directly introduced into the air and landfills respectively as byproducts of industrial activities every year. The major source of NP deposition onto land is currently through the disposal of wastewater treatment (WT) sewage sludge, where NPs that are released from consumer products into wastewaters may partition into sewage sludge during the wastewater treatment process [8,46]. Figure 4 represents a schematic diagram of the different routes of NM introduction to the environment. For instance, the textile industry releases Ag-NMs during washing. According to Benn and Westerhoff [47], the amount of washed Ag-NM is directly related to the agents used for washing as well as the method which is utilized for impregnating the textile with Ag-NM. Similarly, TiO_2-NMs, popularly used in the paint industry is easily leached as effluents into the water bodies [48]. Such industrial effluents eventually end up in a treatment facility and finally sludge is obtained that is loaded with NMs [49]. According to Johnson et al. [50], about 99% of TiO_2-NMs entering the environment are mediated through water treatment sludge.

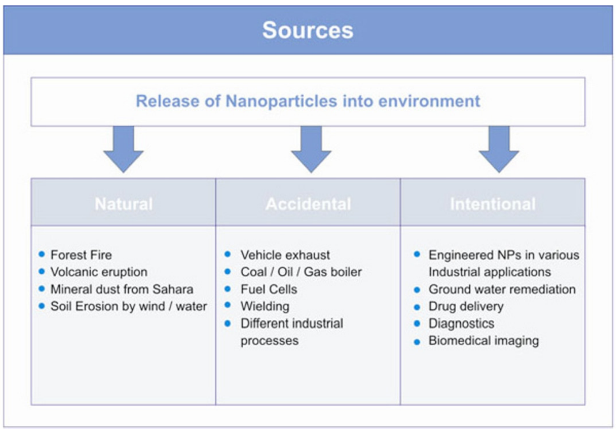


Figure 3. Routes of contribution of engineered NMs (ENM) into the environment

Source: Smita et al. [51] (Permission not required under the open access agreement) (© 2012, BioMed Central, UK)

NMs are introduced in the soil environment mainly through land-disposal of sludge and effluents [46,50,52]. Nanoparticles are unlikely to enter into the soil in their original form, however, because of the organically rich and reactive environments of WTs [53]. In a reduced environment, AgS-NMs are also formed in the sewage sludge after Ag-NMs react with sulfide [54]. Recently, several models are used to predict the fate and final concentration of several NMs into the environment. For instance, according to one model about 1 mg kg^3 and 120 mg kg^3 of Ag and TiO_2-NMs are annually introduced to arable lands when sewage sludge is used as an organic amendment [55]. On the contrary, the production of Ag-NMs should be checked as Ag concentration should be less in all environmental compartments [49,50]. However, TiO_2 is abundantly found in the environment naturally. According to Tourinho et al. [8], about 0.02 to 5.5% TiO_2 is present in 845 top-soils in Europe. Although it is difficult to predict the actual estimates, but TiO_2 and ZnO are the most abundant NMs in the environment matrices owing to their wide applicability [49,50].

5. Behavior of NMs in Soil

Soil is a porous and biologically active natural medium which acts as a sink for moisture, nutrients, and organic matter. The dynamic nature of soil makes it one of the best platforms for understanding the physico-chemical behavior of NMs. Soil comprises of mainly liquid and solid phases and NMs when introduced into soil interact differently with these phases, i.e. NMs either tend to aggregate or disperse when introduced into solid/liquid phases. From an ecotoxicological perspective, it is pivotal to understand how specific organisms would react when exposed to NMs in different phases (i.e. soil or soil water). As stated, attributes *viz*. agglomeration/aggregation, dissolution rate, area-charge -surface chemistry of the NMs should be learned to enumerate their eco-toxicity potential. According to Stone et al. [56] information about behavior of NMs in environmental matrices is vital in order to ascertain their stability as well as transport on a spatiotemporal scale.

5.1 Aggregation and Agglomeration of NMs in Soil Matrix

The property of the NMs whereby these bind strongly together by the core is called aggregation. On the other hand, when the bond is formed between the NM surfaces by weak Van der Waals it is termed as agglomeration [8,57]. Generally, agglomeration arises when the kinetic energy of attraction exceeds the repulsive energy [58]. However, when attached by the cores the NMs resemble flocks of particles eventually settled down by gravity [59]. According to Tourinho et al. [8] these particle flocks vary significantly in regard to size and this is mostly dependent on two factors: (1) concentration of the NM in the medium, and (2) size of each NM. Figure 4 presents a schematic view of the major factors that influence agglomeration/aggregation and dissolution processes of NMs.

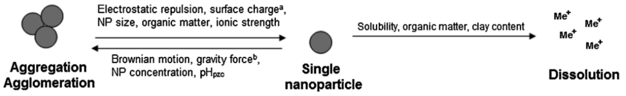


Figure 4. Factors affecting the processes of aggregation/agglomeration and dissolution of single nanoparticles. ^{a} Considering similar surface charge. ^{b} Acting only on larger particles

Source: Reproduced from Tourinho et al. [8] with permission (©2012, John Wiley and Sons, USA)

Iron oxide NMs readily aggregate with the increase in their concentrations and such aggregations are quite stable[60]. Zn-oxide NMs also tend to form stable aggregates of varied shapes and sizes at higher concentrations [61]. Moerz et al. [62] reported that when Au-NMs were introduced into the hemoglobin solution, the NMs tend to form agglomerates. Moreover, they observed that the extent of agglomeration was influenced by the ratio of Hemoglobin and Au NM concentration in the solution. A pictorial interpretation from their study has been shown in Figure 5.

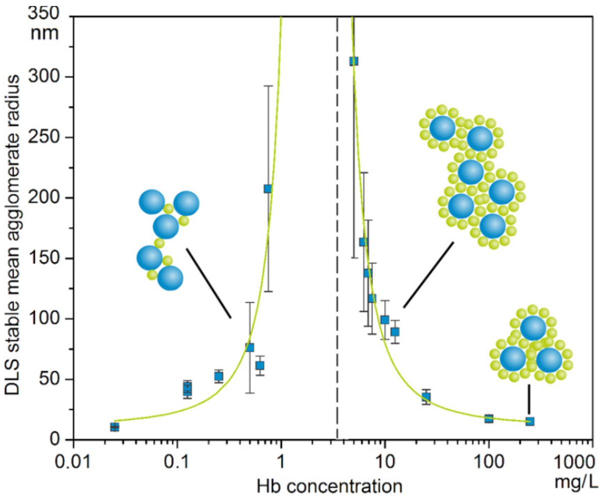


Figure 5. Mean agglomerate radii of stable AuNP clusters from DLS as a function of Hb concentration at a constant AuNP concentration of 16.15 mg/L

Note: Error bars indicate the size distributions calculated from DLS. The green line is a guide to the eye. The Hb concentration theoretically required for monolayer coverage of the AuNP is indicated as a vertical dashed line. Blue spheres represent AuNP, green spheres represent Hb, and both are not to scale.

Source: Moerz et al. [62]. For further reading please visit https://pubs.acs.org/doi/abs/10.1021/acsnano.5b01043 (© 2015, American Chemical Society, USA)

However, the agglomeration/aggregation in NMs varies greatly with the type of NMs. For example, TiO_2-NMs form aggregates of uniform sizes while whereas aggregates of varied sizes are formed when Zn-oxide NMs are introduced in a solution [8,61,63].

5.2 Surface Properties

The surface of NMs is a major attribute that not only dictates its reactivity but also its stability in any medium. Nowadays several materials are used for coating NMs which significantly modify the characteristics and behavior of the NMs in the environment. Hence, studying the time-dependent stability of coated NMs is an important step. Recently, several coated NMs are used as adsorbents for several environmental pollutants [8].

The stability of NMs is duly explained by the DLVO (Derjaguin, Landau, Verwey, and Overbeek) theory. According to this theory the particle-to-particle repulsion as well as attraction phenomena greatly regulate the stability of NMs in various mediums [8]. This theory can also be applied to understand the behavior of NMs in the aqueous medium [64,65]. Although this theory is applicable to most of the NMs, it has been less applied to interpret the behavior of colloidal NMs in soil matrices.

DOI: https://doi.org/10.36956/njas.v1i2.11

5.3 Dissolution and Transport

Dissolution of NMs signifies the movement of ions from the core through the electrical double layer into the medium [8,66]. The dissolution of NMs is greatly influenced by the thermodynamic instability of the NMs and also by properties of the medium. Hence, Tourinho et al. [8] advocate the importance of understanding the dissolution patterns of NMs to gauge their toxicity on organisms over time.

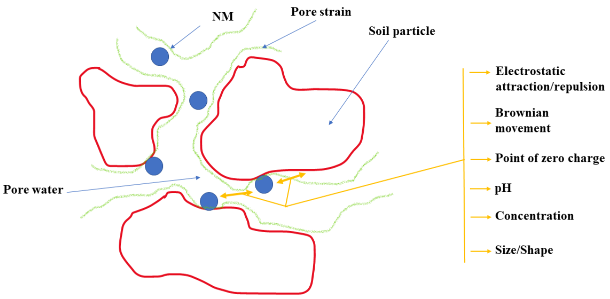


Figure 6. Schematic diagram representing the factors which effect the dissolution/transport of nanomaterials between soil and pore water

Zhang et al. [67] opined that MONMs which are mostly utilized in industries like ceramics, catalysts, coatings, powders, and metal should magnify by 100 folds by 2020. In the UK, several industries like medicine, electronics and sensors, cosmetics, fuel additives, catalysts, paints, etc. utilize huge quantities of metal oxide based NMs [68]. According to Schmid and Riediker [69], the Swiss food and paint industry use MONMs like Al-Ox, Fe-Ox, SiO_2, TiO_2, and ZnO at 1 ton per year per company.

6. Bioaccumulation of Metal based NMs

Mostly, the NMs released/introduced into the environment eventually enter the food chain and get accumulated in the living organisms [6]. In general, plants are used as potential models for studying the toxic behavior of the NMs in terrestrial and aquatic environments. *Brassica juncea* exposed to Mo-NM tend to imbibe the particles culminating into significant inhibition in growth [70]. According to Larue et al. [71], plants can also imbibe NMs through the leaves leading to phyllosphere mediated NM transport. They observed that foliar application of TiO_2 and Ag-NMs in *Lactuca sativa* induced no lethal effects with regular glutathione (GSH) and phytochelatin activity.

Fishes are deemed as potential models for studying the toxicological aspects of NMs in animals. However, there have been numerous studies of NM exposure to nematodes and their fate over time. Recently, biomagnification of Au-NMs was observed in hornworms when they were fed tobacco leaf impregnated with Au-NMs [72]. Their study revealed that the dissolution of Au-NMs mostly varied on the basis of their sizes and less on the zeta-potential. Similarly, TiO_2 NMs form stable aggregates in soil solution and subsequently accumulate in the body of organisms. These NMs bind with lipids and carbohydrates and get biomagnified at each trophic level [8,18]. In nematodes, the negatively charged cuticle attracts NMs and makes dermal route a very convenient way for metal-based NMs to enter [73]. However, oral intake is the most common or major pathway for NMs to enter inside any organisms body via contaminated food/feed [8]. Interestingly, the response of different organisms when exposed to NMs is significantly different from one another. Similarly, different NMs interact differently with various organisms. For instance, earthworms when exposed to ZnO and TiO_2 NMs tend to accumulate higher amount of ZnO than TiO_2, resembling selective uptake [74]. According to Tourinho et al. [8] the niche of soil organisms may also be another key factor which determines the extent of NM exposure. For example, the collembolans will mainly be exposed to NMs dispersed in soil pore water while earthworms will be interacting with both pore water and soil particles, and woodlice to food (decaying leaf material).

Ag-NMs in higher concentrations create oxidative stress in organisms. *Eisenia fetida* specimens when exposed to both nano-Ag and Ag-salt could accumulate higher amount of nano-Ag into their bodies. Shoults-Wilson et al.[75] (94.21 mg kg(-1reported that such accumulation of NMs is facilitated by the dissolution pattern of both nano-Ag and Ag-salt. Similar reports also illustrate higher toxicity of Ag-NMs when compared to $AgNO_3$ in *Caenorhabditis elegans* [76]. In general, Ag-MN enter the body and rupture the reproductive organelles of the worms. Moreover, beyond a concentration limit of 55 ppm, significant dermal abnormalities occurred in the exposed worm [76].

Although less research has been conducted on Fe-oxide NMs these NMs bear significant potential in biomedical industry [77]. According to Gonzalez-Moragas et al. [78] citrate-coated Fe-oxide NMs induce lethal effects to soil nematodes like *Caenorhabditis elegans.* it was observed that at higher concentration ($500 \mu g\ ml^{-1}$) Fe-oxide NMs trigger oxidative stress evidenced through upregulation of genes *viz. sod1, sod 2chc-1, dyn-1, eps-8, act-5*, and *elt-2*. A higher expression of metal-chelating proteins (metallothioneins) is also prominent when these nematodes are exposed to higher concentration of Fe-oxide NM. Moreover, Fe-NMs tend to accumulate in the body of *Caenorhabditis elegans* when exposed for longer time periods and this led to significant disruption in locomotory power of the organism [79].

Cu-oxide NMs applied in soil (at the rate of 65 mg kg^{-1}) induced non-lethal effects on *Eisenia fetida* [80]. Gomes et al. [81] observed that Cu-NM at 1g L^{-1} induced no toxic effects to *Enchytraeus albidus.* However, higher concentration (>100 ppm) of Cu-NMs accelerated deterioration of biomolecules (*i.e*. carbohydrate, lipid, and protein) in *E. albidus* after 6 weeks of exposure. Gomes et al. [81] proposed that Cu-induced toxicity was mainly driven by the undissolved Cu-NMs. They even traced damage at the molecular level (gene expression) suggesting the deleterious impact of Cu-NMs on exposed organisms. Generally, oxidation of Cu-NMs yields Cu-ions which might be the cause of such toxic effects [8].

ZnO is a highly investigated NM regarding ecotoxicity enumerations in living organisms [8]. Several workers have observed genetic and physiological changes (mainly stress enzymes *viz.* catalase, superoxide dismutase, peroxidase) in *Eisenia fetida* exposed to ZnO NMs [8,74]. Hooper et al. [82] compared the toxicity of ZnO NM and $ZnCl_2$ on growth and proliferation of *E. veneta*. They reported that soil spiked with ZnO NM reduced the reproduction of *E. veneta* by 30% but did not hamper their immunity. It was confirmed through SEM and EDX that ZnO-NMs got accumulated in the body tissue through an internal mechanism [82]. A similar report by Canas et al. [83] also elaborated on the deleterious effects of ZnO NMs to *E. fetida* at higher concentrations, especially in the form of oxidative stress. In case of the isopod *Porcellio scaber,* nano-Zn accumulation was primary routed through the dissolution of ZnO-NMs rather than direct accumulation of the particles [61,84]. Contrarily, Manzo et al. [84] extended information on the accumulation of dissolved-Zn species *in lieu* of particulate-Zn in the body of *Folsomia candida* exposed to ZnO-NMs.

7. Summary

Although the use nanomaterials are going on for quite a few years, the environmental fates of purposefully synthesized nanoscale materials are drawing greater attention recently because of their widespread use. Numerous metal-based nanomaterials are used in various applications in the fields of information technology, electronics, catalysis, medicine, and energy owing to their electronic, thermal, optical, and photoactive properties. As such, synthesized vis-à-vis engineered metal based nanoparticles are widely used in consumer goods and industrial processes. Consequently, the invisible release of engineered nanomaterials to the environmental matrix is significantly increasing; thereby leading to long range contamination and/or alteration of the natural resources of our planet. Soils being the ultimate sink of all terrestrial biotic and abiotic substances, gradual piling up of nanoscale metal based materials in soils is inevitable. To date, there is very little understanding of how such discharged nanomaterials influences the soil physicochemical properties as well as the life forms dwelling in the land ecosystems. Hence, it is become imperative to carry out in-depth research on how nano-materials interact with the biological factors so that efficient and non-lethal nano-materials could be synthesized.

References

[1] Khan, I., Saeed, K., Khan, I. Nanoparticles: Properties, applications and toxicities. Arabian Journal of Chemistry, 2017, 12(7): 908-931.

[2] Tiwari, J.N., Tiwari, R.N., Kim, K.S. Zero-dimensional, one-dimensional, two-dimensional and three-dimensional nanostructured materials for advanced electrochemical energy devices. Progress in Materials Science, 2012, 57(4): 724-803.

[3] Baalousha, M., Lead, J.R. Characterization of natural and manufactured nanoparticles by atomic force microscopy: Effect of analysis mode, environment and sample preparation. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2013, 419: 238-247.

[4] Heiligtag, F.J., Niederberger, M. The fascinating world of nanoparticle research. Materials Today, 2013, 16(7): 262-271.

[5] Handy, R.D., von der Kammer, F., Lead, J.R., Hassellov, M., Owen, R., Crane, M. The ecotoxicology and chemistry of manufactured nanoparticles. Ecotoxicology, 2008, 17(4): 287-314.

[6] Goswami, L., Kim, K.-H., Deep, A., Das, P., Bhattacharya, S.S., Kumar, S., Adelodun, A.A. Engineered nano particles: Nature, behavior, and effect on the environment. Journal of Environmental Management, 2017, 196: 297-315.

[7] Auffan, M., Rose, J., Wiesner, M.R., Bottero, J.-Y. Chemical stability of metallic nanoparticles: a parameter controlling their potential cellular toxicity in vitro. Environmental Pollution, 2009, 157(4): 1127-1133.

[8] Tourinho, P.S., van Gestel, C.A.M., Lofts, S., Svendsen, C., Soares, A.M.V.M., Loureiro, S. Metal-based nanoparticles in soil: fate, behavior, and effects on

DOI: https://doi.org/10.36956/njas.v1i2.11

soil invertebrates. Environmental Toxicology and Chemistry, 2012, 31(8): 1679-1692.

[9] Gentile, A., Ruffino, F., Grimaldi, G.M. Complex-Morphology Metal-Based Nanostructures: Fabrication, Characterization, and Applications. Nanomaterials, 2016, 6(6): 1-10.

[10] Xia, Y., Xiong, Y., Lim, B., Skrabalak, S.E. Shape-controlled synthesis of metal nanocrystals: simple chemistry meets complex physics? Angewandte Chemie, 2009, 48(1): 60-103.

[11] Bratlie, K.M., Lee, H., Komvopoulos, K., Yang, P., Somorjai, G.A. Platinum nanoparticle shape effects on benzene hydrogenation selectivity. Nano Letters, 2007, 7(10): 3097-3101.

[12] Corr, S.A. Metal oxide nanoparticles. in: Nanosci. Nanostructures through Chem., The Royal Society of Chemistry, 2013, 1: 180-207.

[13] Oskam, G. Metal oxide nanoparticles: synthesis, characterization and application. Journal of Sol-Gel Science and Technology, 2006, 37(3): 161-164.

[14] Rodriguez, J.A., Liu, G., Jirsak, T., Hrbek, J., Chang, Z., Dvorak, J., Maiti, A. Activation of Gold on Titania: Adsorption and Reaction of SO2 on Au/TiO2(110). Journal of the American Chemical Society, 2002, 124(18): 5242-5250.

[15] Schoiswohl, J., Kresse, G., Surnev, S., Sock, M., Ramsey, M.G., Netzer, F.P. Planar Vanadium Oxide Clusters: Two-Dimensional Evaporation and Diffusion on Rh(111). Physical Review Letters, 2004, 92(20): 206103.

[16] Song, Z., Cai, T., Chang, Z., Liu, G., Rodriguez, J.A., Hrbek, J. Molecular Level Study of the Formation and the Spread of MoO3 on Au (111) by Scanning Tunneling Microscopy and X-ray Photoelectron Spectroscopy. Journal of the American Chemical Society, 2003, 125(26): 8059-8066.

[17] Bizmark, N., Ioannidis, M.A. Effects of Ionic Strength on the Colloidal Stability and Interfacial Assembly of Hydrophobic Ethyl Cellulose Nanoparticles. Langmuir: The ACS Journal of Surfaces and Colloids, 2015, 31(34): 9282-9289.

[18] French, R.A., Jacobson, A.R., Kim, B., Isley, S.L., Penn, R.L., Baveye, P.C. Influence of Ionic Strength, pH, and Cation Valence on Aggregation Kinetics of Titanium Dioxide Nanoparticles. Environmental Science & Technology, 2009, 43(5): 1354-1359.

[19] Pieters, G., Pezzato, C., Prins, L.J. Reversible Control over the Valency of a Nanoparticle-Based Supramolecular System. Journal of the American Chemical Society, 2012, 134(37), 15289-15292.

[20] Martin-Palma, R.J., Lakhtakia, A. Properties of Nanostructures. in: Nanotechnol. A Crash Course. SPIE Digital Library, 2010: 31-36.

[21] Beyene, H.D., Werkneh, A.A., Bezabh, H.K., Ambaye, T.G. Synthesis paradigm and applications of silver nanoparticles (AgNPs), a review. Sustainable Materials and Technologies, 2017, 13: 18-23.

[22] Marin, S., Vlasceanu, G.M., Tiplea, R.E., Bucur, I.R., Lemnaru, M., Marin, M.M., Grumezescu, A.M. Applications and toxicity of silver nanoparticles: a recent review. Current Topics in Medicinal Chemistry, 2015, 15(16): 1596-1604.

[23] Wiley, B.J., Im, S.H., Li, Z.-Y., McLellan, J., Siekkinen, A., Xia, Y. Maneuvering the Surface Plasmon Resonance of Silver Nanostructures through Shape-Controlled Synthesis, The Journal of Physical Chemistry B, 2006, 110 (32): 15666-15675.

[24] Pandian, A.M.K., Karthikeyan, C., Rajasimman, M., Dinesh, M.G. Synthesis of silver nanoparticle and its application. Ecotoxicology and Environmental Safety, 2015, 121: 211-217.

[25] Machala, L., Tuček, J., Zbořil, R. Polymorphous Transformations of Nanometric Iron(III) Oxide: A Review. Chemistry of Materials, 2011, 23 (14), 3255-3272.

[26] Campos, E.A., Pinto, D.V.B.S., Oliveira, J.I.S. de, Mattos, E. da C., Dutra, R. de C.L. Synthesis, Characterization and Applications of Iron Oxide Nanoparticles - a Short Review. Journal of Aerospace Technology and Management, 2015, 7: 267-276.

[27] Sun, S., Zeng, H. Size-Controlled Synthesis of Magnetite Nanoparticles. Journal of the American Chemical Society, 2002, 124(28): 8204-8205.

[28] Wu, W., He, Q., Jiang, C. Magnetic Iron Oxide Nanoparticles: Synthesis and Surface Functionalization Strategies. Nanoscale Research Letters, 2008, 3(11): 397-415.

[29] Laurent, S., Forge, D., Port, M., Roch, A., Robic, C., Vander Elst, L., Muller, R.N. Magnetic Iron Oxide Nanoparticles: Synthesis, Stabilization, Vectorization, Physicochemical Characterizations, and Biological Applications. Chemical Reviews, 2010, 110(4): 2064-2110.

[30] Bumajdad, A., Ali, S., Mathew, A. Characterization of iron hydroxide/oxide nanoparticles prepared in microemulsions stabilized with cationic/non-ionic surfactant mixtures. Journal of Colloid and Interface Science, 2011, 355(2): 282-292.

[31] Gupta, A.K., Gupta, M. Synthesis and surface engineering of iron oxide nanoparticles for biomedical applications. Biomaterials, 2005, 26(18): 3995-4021.

[32] Fernandes, M.T.C., Garcia, R.B.R., Leite, C.A.P., Kawachi, E.Y. The competing effect of ammonia in the synthesis of iron oxide/silica nanoparticles in

microemulsion/sol-gel system, Colloids and Surfaces A: Physicochemical and Engineering Aspects. 2013, 422: 136-142.

[33] Guardia, P., Pérez, N., Labarta, A., Batlle, X. Controlled Synthesis of Iron Oxide Nanoparticles over a Wide Size Range. Langmuir, 2010, 26(8): 5843-5847.

[34] Joshi, S.S., Patil, P.R., Krishnamurthy, V.N. Thermal Decomposition of Ammonium Perchlorate in the Presence of Nanosized Ferric Oxide. Defence Science Journal, 2008, 58(6): 721-727.

[35] Wang, Y., Deng, L., Caballero-Guzman, A., Nowack, B. Are engineered nano iron oxide particles safe? an environmental risk assessment by probabilistic exposure, effects and risk modeling. Nanotoxicology, 2016, 10(10): 1545-1554.

[36] Phiwdang, K., Suphankij, S., Mekprasart, W., Pecharapa, W. Synthesis of CuO Nanoparticles by Precipitation Method Using Different Precursors. Energy Procedia, 2013, 34: 740-745.

[37] Ananth, A., Dharaneedharan, S., Heo, M.-S., Mok, Y.S. Copper oxide nanomaterials: Synthesis, characterization and structure-specific antibacterial performance. Chemical Engineering Journal, 2015, 262: 179-188.

[38] Gawande, M.B., Goswami, A., Felpin, F.-X., Asefa, T., Huang, X., Silva, R., Zou, X., Zboril, R., Varma, R.S. Cu and Cu-Based Nanoparticles: Synthesis and Applications in Catalysis. Chemical Reviews, 2016, 116(6): 3722-3811.

[39] Aksel, C., Rand, B., Riley, F.L., Warren, P.D. Mechanical properties of magnesia-spinel composites. Journal of the European Ceramic Society, 2002, 22(5): 745-754.

[40] Sirelkhatim, A., Mahmud, S., Seeni, A., Kaus, N.H.M., Ann, L.C., Bakhori, S.K.M., Hasan, H., Mohamad, D. Review on Zinc Oxide Nanoparticles: Antibacterial Activity and Toxicity Mechanism. Nano-Micro Letters, 2015, 7: 219-242.

[41] Xu, Z., Hwang, J.-Y., Li, B., Huang, X., Wang, H. The characterization of various ZnO nanostructures using field-emission SEM. JOM, 2008, 60(4): 29-32.

[42] Yahya, N., Daud, H., Tajuddin, N.A., Daud, H.M., Shafie, A., Puspitasari, P. Application of ZnO Nanoparticles EM Wave Detector Prepared by Sol-Gel and Self-Combustion Techniques. Journal of Nano Research, 2010, 11: 25-34.

[43] Barua, S., Konwarh, R., Bhattacharya, S.S., Das, P., Devi, K.S.P., Maiti, T.K., Mandal, M. and Karak, N. (2013), Non-hazardous anticancerous and antibacterial colloidal "green" silver nanoparticles. Colloids and Surfaces B: Biointerfaces, 105, 37-42.

[44] Maurer-Jones, M.A., Gunsolus, I.L., Murphy, C.J., Haynes, C.L. Toxicity of engineered nanoparticles in the environment. Analytical Chemistry, 2013, 85(6): 3036-49.

[45] Keller, A.A., Wang, H., Zhou, D., Lenihan, H.S., Cherr, G., Cardinale, B.J., Miller, R., Ji, Z. Stability and aggregation of metal oxide nanoparticles in natural aqueous matrices. Environmental Science & Technology, 2010, 44(6): 1962-1967.

[46] Mueller, N.C., Nowack, B. Exposure Modeling of Engineered Nanoparticles in the Environment. Environmental Science & Technology, 2008, 42(12): 4447-4453.

[47] Benn, T.M., Westerhoff, P. Nanoparticle Silver Released into Water from Commercially Available Sock Fabrics. Environmental Science & Technology, 2008, 42(18): 7025-7026.

[48] Kaegi, R., Ulrich, A., Sinnet, B., Vonbank, R., Wichser, A., Zuleeg, S., Simmler, H., Brunner, S., Vonmont, H., Burkhardt, M., Boller, M. Synthetic TiO2 nanoparticle emission from exterior facades into the aquatic environment. Environmental Pollution, 2008, 156(2): 233-239.

[49] Gottschalk, F., Nowack, B. The release of engineered nanomaterials to the environment. Journal of Environmental Monitoring, 2011, 13(5): 1145-1155.

[50] Johnson, A.C., Bowes, M.J., Crossley, A., Jarvie, H.P., Jurkschat, K., Jürgens, M.D., Lawlor, A.J., Park, B., Rowland, P., Spurgeon, D., Svendsen, C., Thompson, I.P., Barnes, R., Willaims, R.J., Xu, N. An assessment of the fate, behaviour and environmental risk associated with sunscreen TiO2 nanoparticles in UK field scenarios. Science of The Total Environment, 2011, 409(13): 2503-2510.

[51] Smita, S., Gupta, S.K., Bartonova, A., Dusinska, M., Gutleb, A.C., Rahman, Q. Nanoparticles in the environment: assessment using the causal diagram approach. Environmental Health : A Global Access Science Source, 2012, 11 Suppl 1 (Suppl 1): S13-S13.

[52] Gottschalk, F., Sonderer, T., Scholz, R.W., Nowack, B. Modeled Environmental Concentrations of Engineered Nanomaterials (TiO2, ZnO, Ag, CNT, Fullerenes) for Different Regions. Environmental Science & Technology, 2009, 43(24), 9216-9222

[53] Gallego-Urrea, J.A., Tuoriniemi, J., Pallander, T., Hassellöv, M. Measurements of nanoparticle number concentrations and size distributions in contrasting aquatic environments using nanoparticle tracking analysis. Environmental Chemistry, 2010, 7(1): 67-81.

[54] Kim, B., Park, C.-S., Murayama, M., Hochella, M.F. Discovery and Characterization of Silver Sulfide

DOI: https://doi.org/10.36956/njas.v1i2.11

Nanoparticles in Final Sewage Sludge Products. Environmental Science & Technology, 2010, 44(19): 7509-7514.

[55] Barnes, R.J., Riba, O., Gardner, M.N., Scott, T.B., Jackman, S.A., Thompson, I.P. Optimization of nano-scale nickel/iron particles for the reduction of high concentration chlorinated aliphatic hydrocarbon solutions. Chemosphere, 2010, 79(4): 448-454.

[56] Stone, V., Nowack, B., Baun, A., van den Brink, N., von der Kammer, F., Dusinska, M., Handy, R., Hankin, S., Hassellov, M., Joner, E., Fernandes, T.F. Nanomaterials for environmental studies: Classification, reference material issues, and strategies for physico-chemical characterisation. Science of The Total Environment, 2010, 408 (7): 1745-1754.

[57] Jiang, J., Oberdörster, G., Biswas, P. Characterization of size, surface charge, and agglomeration state of nanoparticle dispersions for toxicological studies. Journal of Nanoparticle Research, 2009, 11(1): 77-89.

[58] Shen, C., Jin, Y., Li, B., Ruckenstein, E., Shang, J., Huang, Y. Anomalous Attachment Behavior of Nanoparticles inside Narrow Channels. Vadose Zone Journal, 2018, 17(1): 1-9.

[59] Rosicka, D. and Sembera. J. Assessment of Influence of Magnetic Forces on Aggregation of Zero-valent Iron Nanoparticles, Nanoscale Research Letters, 2011, 6(1): 1-6.

[60] Phenrat, T., Saleh, N., Sirk, K., Tilton, R.D., Lowry, G. V. Aggregation and sedimentation of aqueous nanoscale zerovalent iron dispersions. Environmental Science & Technology, 2007, 41(1): 284-290.

[61] Pipan-Tkalec, Z., Drobne, D., Jemec, A., Romih, T., Zidar, P., Bele, M. Zinc bioaccumulation in a terrestrial invertebrate fed a diet treated with particulate ZnO or ZnCl2 solution, Toxicology. 2010, 269(2-3): 198-203.

[62] Moerz, S.T., Kraegeloh, A., Chanana, M., Kraus, T. Formation Mechanism for Stable Hybrid Clusters of Proteins and Nanoparticles. ACS Nano, 2015, 9(7): 6696-6705.

[63] Jemec, A., Drobne, D., Remskar, M., Sepcic, K., Tisler, T. Effects of ingested nano-sized titanium dioxide on terrestrial isopods (Porcellio scaber). Environmental Toxicology and Chemistry, 2008, 27(9): 1904-1914.

[64] Buettner, K.M., Rinciog, C.I., Mylon, S.E. Aggregation kinetics of cerium oxide nanoparticles in monovalent and divalent electrolytes. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2010, 366(1): 74-79.

[65] Stebounova, L. V, Guio, E., Grassian, V.H. Silver nanoparticles in simulated biological media: a study of aggregation, sedimentation, and dissolution. Journal of Nanoparticle Research, 2011, 13(1): 233-244.

[66] Borm, P., Klaessig, F.C., Landry, T.D., Moudgil, B., Pauluhn, J., Thomas, K., Trottier, R. and Wood, S. Research strategies for safety evaluation of nanomaterials, part V: role of dissolution in biological fate and effects of nanoscale particles. Toxicological Sciences, 2006, 90(1): 23-32.

[67] Zhang, Y., Leu, Y.-R., Aitken, R.J., Riediker, M. Inventory of Engineered Nanoparticle-Containing Consumer Products Available in the Singapore Retail Market and Likelihood of Release into the Aquatic Environment. International Journal of Environmental Research and Public Health, 2015, 12(8): 8717-8743.

[68] Aitken, R.J., Chaudhry, M.Q., Boxall, A.B.A., Hull, M. Manufacture and use of nanomaterials: current status in the UK and global trends. Occupational Medicine, 2006, 56(5): 300-306.

[69] Schmid, K., Riediker, M. Use of Nanoparticles in Swiss Industry: A Targeted Survey. Environmental Science & Technology, 2008, 42(7): 2253-2260.

[70] Aubert, T., Burel, A., Esnault, M.-A., Cordier, S., Grasset, F., Cabello-Hurtado, F. Root uptake and phytotoxicity of nanosized molybdenum octahedral clusters. Journal of Hazardous Materials, 2012, 219-220: 111-118.

[71] Larue, C., Castillo-Michel, H., Sobanska, S., Cécillon, L., Bureau, S., Barthès, V., Ouerdane, L., Carriere, M., Sarret, G. Foliar exposure of the crop Lactuca sativa to silver nanoparticles: Evidence for internalization and changes in Ag speciation. Journal of Hazardous Materials, 2014, 264: 98-106.

[72] Judy, J.D., Unrine, J.M., Bertsch, P.M. Evidence for Biomagnification of Gold Nanoparticles within a Terrestrial Food Chain. Environmental Science & Technology, 2011, 45(2): 776-781.

[73] Wang, H., Wick, R.L., Xing, B. Toxicity of nanoparticulate and bulk ZnO, Al2O3 and TiO2 to the nematode Caenorhabditis elegans. Environmental Pollution, 2009, 157(4): 1171-1177.

[74] `Hu, C.W., Li, M., Cui, Y.B., Li, D.S., Chen, J., Yang, L.Y. Toxicological effects of TiO2 and ZnO nanoparticles in soil on earthworm Eisenia fetida. Soil Biology and Biochemistry, 2010, 42(4): 586-591.

[75] Shoults-Wilson, W.A., Zhurbich, O.I., McNear, D.H., Tsyusko, O. V, Bertsch, P.M., Unrine, J.M. Evidence for avoidance of Ag nanoparticles by earthworms (Eisenia fetida). Ecotoxicology, 2011, 20(2): 385-396.

[76] Kim, S.W., Nam, S.-H., An, Y.-J. Interaction of silver nanoparticles with biological surfaces of Caenor-

habditis elegans. Ecotoxicology and Environmental Safety, 2012, 77: 64-70.

[77] Patil, R.M., Thorat, N.D., Shete, P.B., Bedge, P.A., Gavde, S., Joshi, M.G., Tofail, S.A.M., Bohara, R.A. Comprehensive cytotoxicity studies of superparamagnetic iron oxide nanoparticles. Biochemistry and Biophysics Reports, 2018, 13: 63-72.

[78] Gonzalez-Moragas, L., Yu, S.-M., Benseny-Cases, N., Stürzenbaum, S., Roig, A., Laromaine, A. Toxicogenomics of iron oxide nanoparticles in the nematode C. elegans. Nanotoxicology, 2017, 11(5): 647-657.

[79] Gourgou, E., Zhang, Y., Mirzakhalili, E., Epureanu, B. Caenorhabditis elegans locomotion dynamics is affected by internally localized magnetic fields. BioRxiv, 2018, 248369: 1-54.

[80] Unrine, J.M., Tsyusko, O. V, Hunyadi, S.E., Judy, J.D., Bertsch, P.M. Effects of particle size on chemical speciation and bioavailability of copper to earthworms (Eisenia fetida) exposed to copper nanoparticles. Journal of Environmental Quality, 2010, 39(6): 1942-1953.

[81] Gomes, S.I.L., Novais, S.C., Scott-Fordsmand, J.J., De Coen, W., Soares, A.M.V.M., Amorim, M.J.B. Effect of Cu-nanoparticles versus Cu-salt in Enchytraeus albidus (Oligochaeta): Differential gene expression through microarray analysis. Comparative Biochemistry and Physiology Part C: Toxicology & Pharmacology, 2012, 155(2): 219-227.

[82] Hooper, H.L., Jurkschat, K., Morgan, A.J., Bailey, J., Lawlor, A.J., Spurgeon, D.J., Svendsen, C. Comparative chronic toxicity of nanoparticulate and ionic zinc to the earthworm Eisenia veneta in a soil matrix. Environment International, 2011, 37(6): 1111-1117.

[83] Canas, J.E., Qi, B., Li, S., Maul, J.D., Cox, S.B., Das, S., Green, M.J. Acute, reproductive toxicity of nano-sized metal oxides (ZnO and TiO(2)) to earthworms (Eisenia fetida). Journal of Environmental Monitoring, 2011, 13(12): 3351-3357.

[84] Manzo, S., Rocco, A., Carotenuto, R., Picione, F.D.L., Miglietta, M.L., Rametta, G., Francia, G.D. Investigation of ZnO nanoparticles' ecotoxicological effects towards different soil organisms, Environmental Science and Pollution Research International, 2011, 18(5): 756-763.

DOI: https://doi.org/10.36956/njas.v1i2.11