

CHAPTER 2

Review of Literature

2.1. Nanotechnology and nanomaterials

Richard P. Feynman coined the term “Nanotechnology” for the first time in 1959 while delivering a lecture at an American Physical Society meeting on a topic entitled, “*There’s Plenty of Room at the Bottom*” [1]. As such, nanotechnology offers the scope to synthesize nano-scale materials or simply nanomaterials (NM), via physico-chemical modifications (atomic, molecular, and supramolecular) of matters. Generally, it has been found that materials of 100 nm or lesser size are best for industrial or commercial applications [2,3]. Based on their architecture, these NMs may be classified as 0D, 1D, 2D, and 3D [1]. However, NMs are also formed through natural processes; for example, some fragments of soil colloids (1-1000 nm) that are of sized in the range 1-100 nm are denoted as natural nanoparticles [4]. These natural nanoparticles are formed by geological processes like volcanic eruptions, weathering, microbial action, etc. and can be organic (*e.g.* virus, proteins, polysaccharides, etc.) or inorganic *viz.* aluminosilicates, oxyhydroxides, etc. [5]. Contrary to the natural nanoparticles, artificially manufactured or engineered NMs (ENM) possess characteristic differences in their structure and overall chemistry [6]. The popularity in ENMs has sprung up mainly by dint of their application in medicine, industry, agriculture, and environmental engineering [7].

2.2. Metal-based ENMs

Metallic NMs are the most studied particles because of their potential application in various fields and also due to the simple synthetic methodology [8].















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

Fig. 2.1: A gist of different structural conformations of metallic NMs. Reproduced from Xia et al. [9].

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 [8]. A summary of various possible structural conformations of the metallic NMs has been provided in Fig. 2.1 [8,9].

In their work, Bratlie et al. [10] 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: (i) the available orbitals of the reagent molecules, and (ii) atomic arrangement of the NM surface. Hence, manipulating the structural arrangement of NMs could be a major step towards designing more efficient metallic NMs [8].

2.3. Metal-oxide NMs

Recently lot of interest has cropped up on metal-oxide NMs (MONMs) which is mainly credited to their diverse applicability in medicine, agriculture, and engineering [11]. 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 [12]. In many MONMs *viz.* CuO, ZnO, TiO₂, SnO₂, Al₂O₃, MgO, AgO, CeO₂, ZrO₂ etc. it was observed that reduction in size increased surface strain/stress and concomitant structural perturbations [13-15]. In addition the size-shape dependent attributes, some other important features that determine NM behavior are (i) ionic strength, (ii) zeta potential, and (iii) valency of the metallic precursors in the NMs [16].

- I. Ionic strength: The ionic strength of the electrolyte is an important parameter which determines the behaviour of the NMs in solutions. French et al. [17] showed that the aggregation-dispersion dynamics of NMS greatly vary depending on the ionic strength of aqueous matrix. On the basis of their in-depth experimentations with a typical TiO₂-NM they concluded that dispersion of NMs might accelerate with increment of the ionic strength of the solution up to a certain point and such relation is not exactly linear, rather curvilinear.
- II. Surface charge and zeta-potential: Generally, the metallic NMs have negative charge on their surfaces attributed by the -OH group which aid them to bind any metal ion or ligand present in a solution. The pH of the matrix (solid or aqueous) largely regulates the charge-mediated binding efficiency of NMs [3]. Interestingly, formation of a “double-charged layer” or “ionic double layer” could be evidenced with the dispersed metallic NMs, *i.e.* (i) the charged surface

layer of the NMs, and (ii) another layer with diffused charge could be formed by the attracted ions in the solution.

III. Valence: It is a key attribute in the field of nanotechnology, supramolecular chemistry, catalysis, etc. [18]. According to Martin-Palma and Lakhtakia [19] it is very important to understand the valence band and the conduction band which control the properties of many nanomaterials. Fig. 2.2 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.

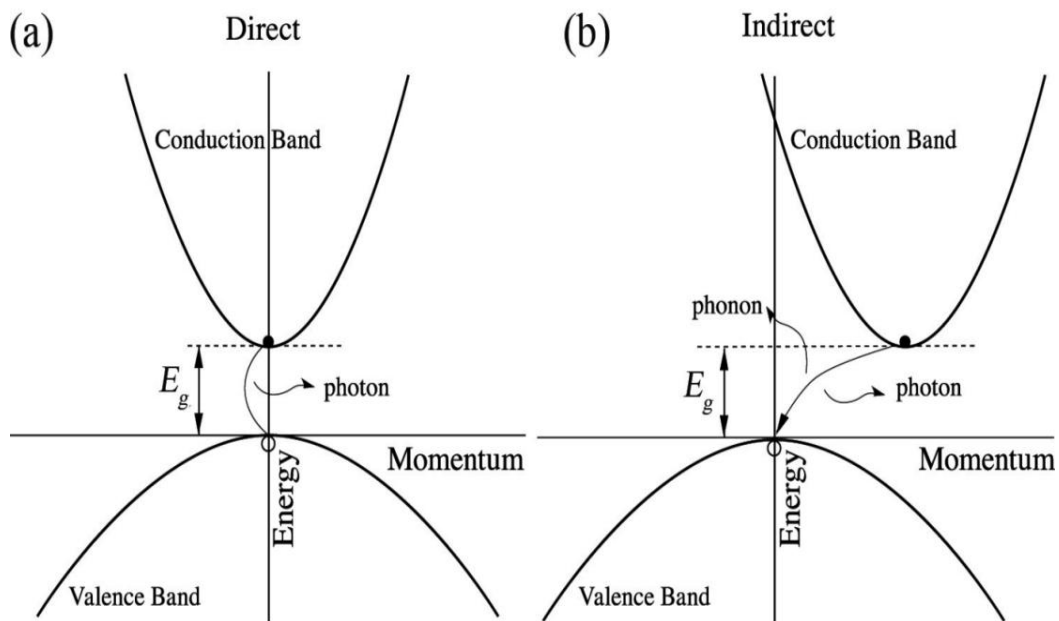


Fig. 2.2: One-dimensional band diagrams containing (a) direct and (b) indirect bandgaps. Reproduced from Martin-Palma and Lakhtakia, [19]

Pieters et al. [18] reported the multivalent characteristics of Au nanomaterials which are greatly utilized as nano-scaffolds in drug development. Enormous progress has been made in the development of multivalent NMs which can adapt their valence with the target spontaneously [18].

2.3.1. Silver NM

Silver is a transition metal with soft texture and white-lustrous color. It has properties like high electrical and thermal conductivity. Generally, Ag-NMs are very popular due

to its anti-microbial activity [20]. The silver nanoparticles are profusely used in textile fibres and wound healing and/or disinfectant ointments owing to the elevated activities of the nanoscale silver [21]. Several workers reported different synthetic pathways for Ag-NM *viz.* physical, chemical, and biological. Evaporation-condensation and laser ablation are the mostly used physical approaches for Ag-NM synthesis [20]. According to Wiley et al. [22], 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 [20]. 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 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. [23] elaborated several bio-assisted synthetic methods of silver nanoparticles with special emphasis on plant-leaf extract mediated development of AgNMs.

2.3.2. Iron oxide NM

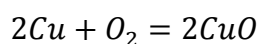
Polymorphic crystalline iron oxides with magnetic properties Can be found in many natural and anthropogenic processes [24]; among which hematite ($\alpha\text{-Fe}_2\text{O}_3$), maghemite ($\gamma\text{-Fe}_2\text{O}_3$), and magnetite (Fe_3O_4) are most abundant. The $\beta\text{-Fe}_2\text{O}_3$ and $\epsilon\text{-Fe}_2\text{O}_3$ forms of maghemites are generally prepared in laboratories as Fe-oxide NMs [25]. Among different chemical synthetic routes of Fe-oxide NMs sol-gel, thermal decomposition, co-precipitation, and microemulsion based preparations are predominantly followed by researchers because of the simplicity and reproducibility of these procedures [25]. Stoichiometric mixture of iron (Fe^{2+} and Fe^{3+}) salts are dissolved in any basic solutions (NaOH or NH_4OH) and this process is technically termed as ‘co-precipitation’; however, the nature of the basic solution (sulphates, chlorides, nitrates etc) and the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio largely govern the characteristics of end products [25,26]. The co-precipitation method can yield Fe-oxide NMs in the range of 5-20 nm diameters. However, optimization 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 [25].

In the sol-gel synthesis method, the surface of the Fe-ox NMs are coated with organic molecules, polymers (*e.g.* poly(ethylene glycol), poly(vinyl alcohol) etc), biomolecules (*e.g.* gelatin, chitosan, and dextran) or mineral molecules (*e.g.* silica) [25,27]. Generally, water is used as the solvent and the metallic precursors are hydrolyzed by either by the addition of acid or a base. Moreover, speed of reactions, pH, temperature, and precursor are altered to obtain the iron oxide NMs of size. For example, 6-15 nm sized nano-maghemite (γ -Fe₂O₃) particles are prepared at 400°C [28]. On the other hand, microemulsion method is primarily used to produce catalytic Fe-oxide NMs that yields cubic or spherical particles with narrow pore size (4-15 nm) and high surface area ($> 300 \text{ m}^2 \text{ g}^{-1}$) [29,30]. Moreover, water-in-oil microemulsion methods hold much interest in Fe-ox NM synthesis due to its unique command on the size distribution of the synthesized nanoparticles [25,31]. Sometimes, iron oxide nanoparticles (4-16 nm) are synthesized via thermal denaturation followed by oxidation of the precursors (*e.g.* Fe³⁺-acetylacetonate and iron nitroso phenylhydroxylamine) in organic solvents (*e.g.* oleic or lauric acids).

Maghemite (γ -Fe₂O₃) particles are extensively used in pollution control due to their ability to consume secondary pollutants and chemicals from industrial wastewater [25]. 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 [25]. Iron oxides are integral ingredients composite solid propellant formulations and render acceleration of the combustion that in-turn greatly improves the rate of burning of the propellant. Some Fe-ox NMs (hematite (α -Fe₂O₃) and maghemite (γ -Fe₂O₃)) are effectively used as burn catalysts to fuel propellers in the domain of solid propulsion [25,32]. Moreover, Fe-ox NMs are also applied in several biomedical operations (*e.g.* drug delivery), and nuclear magnetic resonance imaging [33].

2.3.3. 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 $>1200^\circ\text{C}$. Generally, it is formed by burning Cu in O₂ available environment as:



In laboratory conditions, CuO NMs are generally prepared through precipitation method [34]. Metallic salts *viz.* CuCl₂ and Cu(NO₃)₂.3H₂O 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. Then, drying of the at 80°C followed by high temperature calcination (about 500°C) for few hours yields the CuO NMs.

Copper (II) oxide is used as a glazing and coloring agent in ceramic industry and also to sanitize materials for its superb anti-bacterial properties [35]. Cu-oxide NMs in the form of Cu-ammonium hydroxide is utilized in the production of rayon.

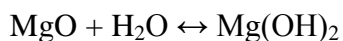
Table 2.1: Utility of different metal-oxide based nanomaterials

Sl. No.	Metaloxide NMs	Applications	References
1	CuO	Redox catalyst	[36]
		Microwave irradiation	[37]
		Photoconductive and photothermal applications	
2	ZnO	UV blockers	[36]
		Mixed varistors	[15]
		Solar cell and optoelectronics	[38]
		Gas sensors	
3	MgO	Catalysts	
		Industrial scrubber for gaseous pollutants (CO ₂ , NO _x , Sox)	[39]
4	ZrO ₂	Catalysts	
		Ceramics	[40]
		Solid electrolyte	[41]
5	CeO ₂	Gas sensors	
		Catalysts	
		Chemical catalysts	[42]
6	TiO ₂	Photocatalysts	[43]
		Electrolyte	
		Chemical catalysts	[44]
7	Al ₂ O ₃	Photocatalysts	[45]
		Industrial scrubber for air pollutants	
		Catalysts	[46]
		Coating agent	[47]

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 band gap (~1.2 eV), Cu-oxide NMs are extensively used as p-type semiconductor. 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 [48].

2.3.4. Magnesium oxide (MgO) NM

The solid and hygroscopic magnesium oxide (MgO) (i.e., magnesia) is often found in nature as periclase; remains in lattice form (series of ionic bonds of Mg²⁺ and O²⁻). The general reaction can be seen as under:



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. Mg-oxide NMs are also used in chemical, construction, environmental and electrical appliance industries.

2.3.5. 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 [49]. Zn-oxide NMs are prepared through different routes but the mostly 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 [49-51]. 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 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 [51].

Zn-oxide NMs are very popular as 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 preservative of food items and as a coating agent in paint industries. Other important applications of ZnO NMs are in manufacture of concrete and ceramics where it is used as an additive.

2.3.6 Ti-dioxide (TiO₂) NM

A wide range of application has been observed of TiO₂ nanoparticles as paints, toothpaste, sunscreen etc. Because of their photocatalytic activity they have tremendous expectation in the area of effective energy uses through utilization of solar energy based devices. They are found to be generally transparent in visible light region. But their optical sensitivity can be enhanced in visible light region by doping or sensitization [52]. Synthesis of this type of nanostructures can be attained through various approaches i.e., Sol-Gel method, Sol method, Hydrothermal method etc [52].

2.4. NMs in soil environment

World's land and water resources are considerably exposed to engineered nanomaterials [53,54]. Therefore, it is important to derive mechanistic interpretations through focused as well as holistic experimentations to ascertain the true impacts of NMs on soil environment. The behaviour and effects of nanoparticles in soil-plant systems are rather unpredictable because of influence of numerous factors (inherent soil chemistry, soil porosity, water retention capacity, size of NMs, coating materials, time and level of exposure) [7]. Very recent studies have revealed concentration driven agglomeration property of engineered nanomaterials in soil largely influences nitrogen metabolism, photosynthesis, and growth of crop plants [55,56]. The unique features of NMs (aggregation/agglomeration, dissolution, dispersibility, charge, surface area, and surface chemistry) greatly modify the stability and migration of the nanomaterials within soil system; which may also alter the physical and chemical

character of the contaminated soils [57]. Whereas, pH, organic matter, soil biota, colloidal composition, elemental solutes, ionic strength, porosity, and moisture contents of soils significantly alter behaviour of NPs within soil system [3]. As such, the distinctive physico-chemical properties of AgNPs are likely to affect microbial diversity in soil [53,58-60].

Soil represents a relatively complex medium for the understanding of the physicochemical behavior of manufactured NPs. In comparison with the dissolved phase, in which behavior can be understood largely in terms of particle stability against aggregation, soils present a solid matrix with which NPs may interact, as well as an aqueous phase, which may contain appreciable amounts of natural colloidal/particulate material. In the context of environmental toxicology, a key issue is the understanding of how specific organisms are exposed to NPs present in different phases (soil, soil water) and how the presentation of the NPs within these phases further influences exposure. As mentioned earlier some major attributes *viz.* agglomeration/aggregation, dissolution rate, area-charge -surface chemistry of the NMs need to be studied to ascertain their eco-toxicity potential. According to Stone et al. [61] these properties are instrumental in controlling the stability and subsequent transport of the NMs in the environmental matrices. The routes of contribution of engineered nanomaterials into the environment are represented in Fig. 2.3.

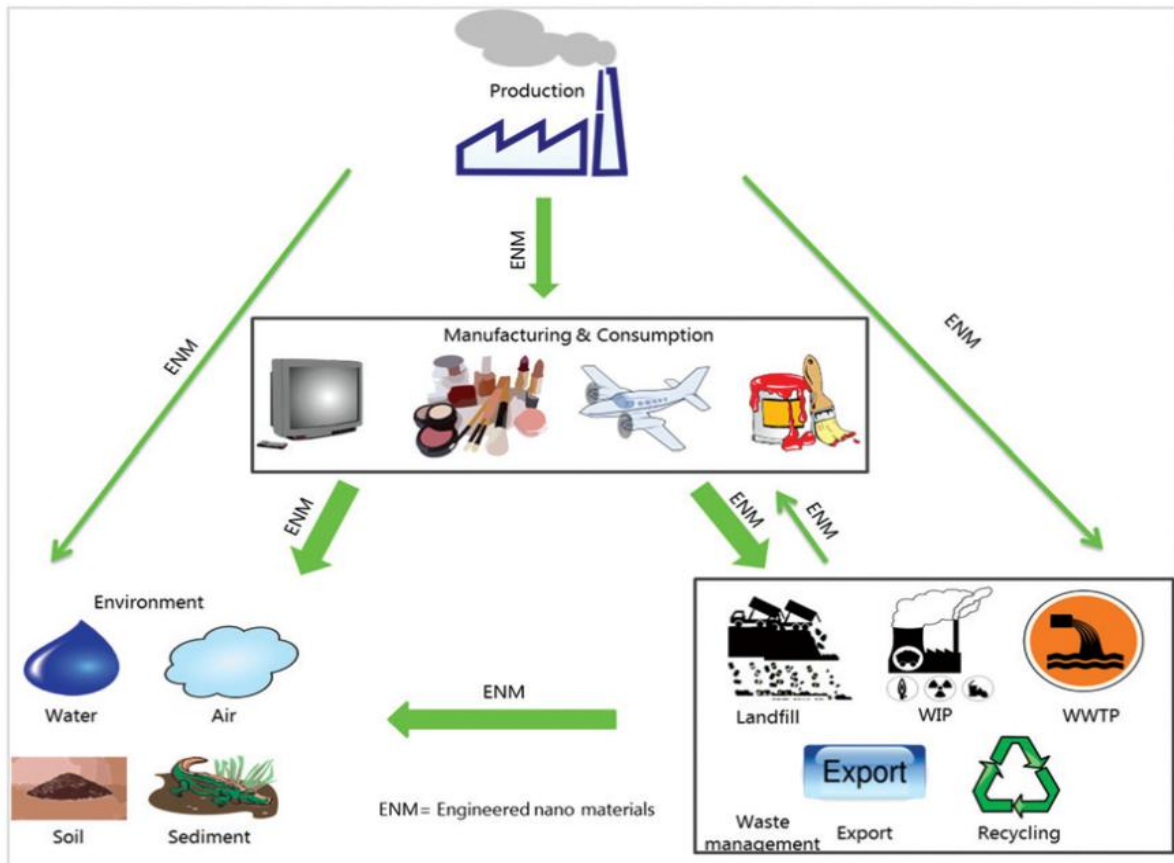


Fig. 2.3: Routes of contribution of engineered NMs (ENM) into the environment. Reproduced from Wang et al. [33].

2.4.1. Agglomeration/Aggregation of NMs in soil

The strong bonding between the core of the NMs is called aggregation while agglomeration implies to the weak Van der Waals force bonding among the NM surfaces [3,62]. According to Lin et al. [63], agglomeration occurs when the Brownian motion induced particles collide with each other creating a condition where energy of motion/attraction is greater than energy of repulsion. Contrarily, when the cores of the NMs collide they tend to aggregate forming “particle flocks” that settle down eventually due to gravity [64]. The size of NM aggregates varies mostly with the concentration of the NM in the solution and also with the initial size of the NMs [3]. Fig. 2.4 presents a schematic view of the major factors that influence agglomeration/aggregation and dissolution processes of NMs.

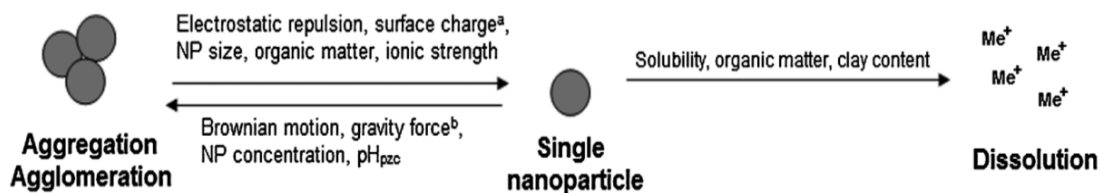


Fig. 2.4: Factors affecting the processes of aggregation/agglomeration and dissolution of single nanoparticles. ^a Considering similar surface charge. ^b Acting only on larger particles. Adapted from Tourinho et al. [3].

Phenrat et al. [65] observed that Fe-oxide NMs tend to form stable aggregates when the concentration of the solution is increased from 2 mg L⁻¹ to 10 mg L⁻¹. Similar studies on Zn-oxide NMs also revealed formation of stable aggregates at higher concentrations which were diverse in sizes and some aggregates were almost 10 times larger in size than the primary particles [66]. In their study with Au NMs in hemoglobin solution, Moerz et al. [67] cited that the extent of Au NM-Hemoglobin agglomeration depends greatly on the Hemoglobin: Au NM concentration ratio. A pictorial interpretation from their study has been shown in Fig. 2.5.

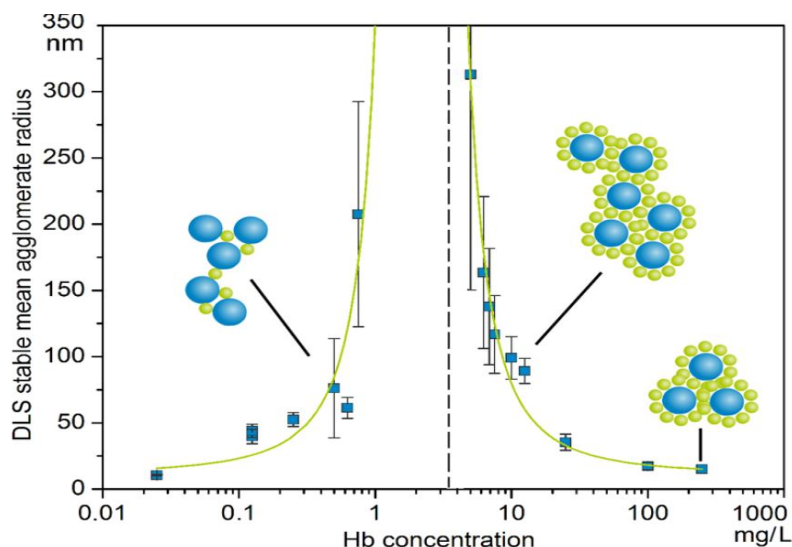


Fig. 2.5: A pictorial interpretation representing DLS stable mean agglomerate radius. Adapted from Moerz et al. [67].

However, the agglomeration/aggregation in NMs varies greatly with the type of NMs. For instance, Ti-oxide NMs form uniform sized aggregates whereas Zn-oxide NMs portray a variety of aggregate sizes when dispersed in solutions [3,66,68].

2.4.2. Surface characteristics

Presence or absence of coating greatly modifies the characteristics of the NMs in the environment. In case of coated NMs, determination of their stability over time is an important parameter to check. Considering the enhanced utilization of NMs as cleansing agents for several environmental pollutants it is important to check their coating stability and the (bio) degradability of the coating over time [3].

The DLVO (Derjaguin, Landau, Verwey, and Overbeek) theory classically explains the stability of NMs in any medium. Basically, this theory considers stability as a function of the repulsive (i.e., electrostatic) and attractive forces (i.e., Van der Waals) to which a particle is subjected [3]. However, the DLVO theory has been least applied to investigate colloidal behavior of NMs in natural environment. Although, the conceptual framework of the DLVO theory holds much promise in highlighting the behavioral trends of NMs in environment, especially in aqueous media [69,70].

2.4.3. Dissolution and transport

Thermodynamic instability is a characteristic of some types of metal-based NMs that eventually leads to their dissolution over time. Dissolution implies to the detachment of an ion from the particle, later migrating through the electrical double layer into the solution [3,71]. However, with such dissolution the probability of toxicity enhances due to higher introduction of ionic moieties from the metal-based NMs. Hence, it is important to learn on the extent of dissolution and the relative toxicities of both the nanoparticulate and dissolved forms to better understand the potential NP effects on organisms over time [3].

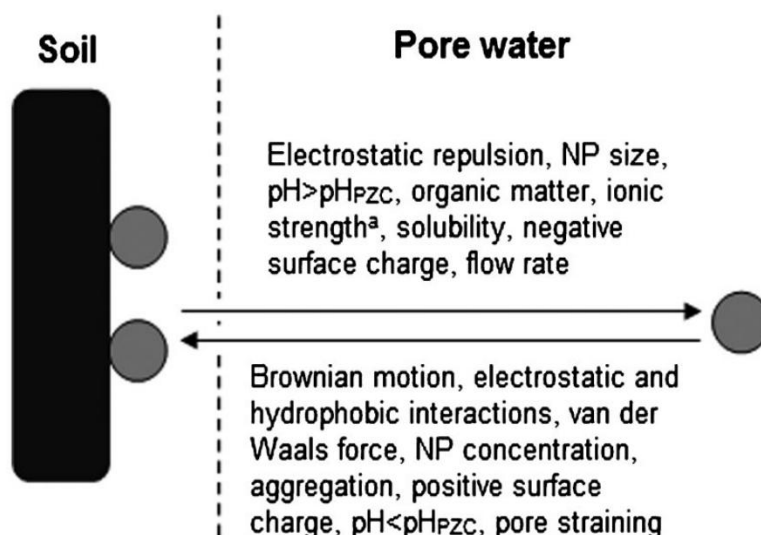


Fig. 2.6: Schematic diagram representing the factors which effect the dissolution/transport of nanoparticles between soil and pore water (pH_{PZC} =point of zero charge). Adapted from Tourinho et al. [3].

In the United Kingdom, MONMs find their extensive utility in medicine, electronics and sensors, cosmetics (mainly sun-screen lotions), fuel additives, catalysts, paints etc [72]. As per the report of Schmid and Riediker [73], the food and paint industry in Switzerland utilize Al-Ox, Fe-Ox, SiO₂, TiO₂, and ZnO NMs at 1 ton per year per company.

2.5. Bioaccumulation (mass concentration) of metal based NMs

Mostly, the NMs released/introduced into the environment eventually enter the food chain and get accumulated in the living systems [7]. Usually, plants have been recognized as a perfect model to study the toxicokinetic behavior of NMs because they represent both terrestrial and aquatic environment. In their study, Aubert et al. [74] highlighted the Mo-NM sorption by the roots of *Brassica juncea* leading to their significant growth inhibition. Several reports also other than roots, phyllosphere mediated NM transport is also possible for certain plants. For example, foliar application of TiO₂ and Ag-NM in *Lactuca sativa* induced no toxic effects with regular glutathione (GSH) and phytochelatin activity [75]. These studies reveal that metal-based NMs might enter plant system through both rhizospheric and aerial modes. In case of animals, mostly the environmental toxicology experiments have been studied on fish-models. Although there are reports on nematodes to observe the

toxicity of NM, insights on their bioaccumulation has not been addressed fully. Judy et al. [76] studied the biomagnification of Au-NMs in hornworms exposed to Au-NM fortified tobacco leaf diet. The authors found that the bioaccumulation of Au-NM was mostly related to their zeta-potential rather than their size or dissolution dynamics. Similarly, TiO₂ NMs are highly persistent in environment due to their very low dissolution in soil or aquatic media. It has been elaborately shown that the TiO₂ NMs form stable aggregates in soil solution and subsequently accumulate in the body of organisms (mainly by bonding with lipids and carbohydrates) at each trophic level [3,17]. In nematodes, metal based NMs may also enter through dermal contact. The negatively charged cuticle of nematodes greatly attracts metallic NMs [77]. Although, the primary route of NM into an organism's body is mainly through ingestion of contaminated food/feed [3]. Overall, the accumulation of NMs greatly varies with the metallic precursor of the NM and also with the type of organisms exposed. For example, earthworms exposed to both ZnO and TiO₂ showed more accumulation of ZnO [78]. Speaking of soil organisms, collembolans will mainly be exposed to NMs present in soil pore water, earthworms to both pore water and soil particles by dermal and oral contact, and woodlice to food (decaying leaf material) and soil particles by ingestion and to a limited extent to soil pore water [3].

Table 2.2 presents a summary of environmental toxicology studies on soil nematodes exposed to metal-based NMs. Ag-NMs are good anti-bacterial agents but in higher concentration they induce oxidative stress in organisms. *Eisenia fetida* greatly accumulate Ag in their tissue when exposed to nano-Ag rather than its salts (AgNO₃). According to Shoultz-Wilson et al. [79], this accumulation is mainly attributed to the non-dissolved nano-Ag and not the dissolved ionic form. Similar reports also vouch for the toxicity of Ag-NMs over silver nitrate in *Caenorhabditis elegans* exposed at a dose of 10-1000 mg L⁻¹ [80]. They confirmed that Ag-NM exposure primarily disrupts the reproductive capacity of the worms through significant free radical generation. Also, a lethal dose of 55 mg L⁻¹ was ascertained surpassing which significant dermal abnormalities were observed leading to 60% mortality of the exposed worms [80].

Fe-oxide NMs are one of the least studied particles in the domain of nanotechnology which has started to change considering their recently recognized potential in biomedical application [81]. Recent investigation by Gonzalez-Moragas et

al. [82] presented eco-toxicity potential of citrate-coated Fe-ox NMs to soil borne organisms like *Caenorhabditis elegans* at a dose of 100-500 ppm and duration was for 1 day. They coined that in higher concentration ($500\mu\text{g mL}^{-1}$) the oxidative stress marking genes (*sod1*, *sod 2*), and intestinal genes (*chc-1*, *dyn-1*, *eps-8*, *act-5*, and *elt-2*) significantly upregulate. They also noted a significantly high expression of metallothionein protein in the highly dosed specimen, although no prominent mortality was encountered. Gourgou et al. [83] illustrated significant accumulation of magnetic Fe-NMs (size 100 nm) in the body of *Caenorhabditis elegans* in Agar medium. They observed that the internalized NMs drastically reduced the locomotive ability (velocity) of the worms. They also found effects on survivability, fecundity, and growth.

Cu-NM exposure at concentration up to 1g L^{-1} showed no toxic effects to the enchytraeid *Enchytraeus albidus* [84]. They conducted their study with a concentration range of 400-1000 ppm, for 2 days period in soil medium. Contrarily, Amorim et al. [85] illustrated that Cu-NMs significantly deplete the carbohydrate, lipid, and protein contents (energy reserves) in *E. albidus* after 6 week exposure with Cu-NMs ($100\text{-}200\text{ mgL}^{-1}$). Application of CuO NMs in soil at the rate 65 mg kg^{-1} recorded no toxic effects on growth and proliferation of *Eisenia fetida* [86].

Table 2.2: A gist of available literature on response of soil-based nematodes in metal-based NM enriched environment

NMs	Size (nm)	Organisms	Concentration (ppm)	Exposure	Media	Indicators	Reference
Ag	<100	<i>Caenorhabditis elegans</i>	0.05–0.5	1-3 days	K-media	Survival, growth, and fecundity	[87]
	50.3	<i>Do</i>	10–1000	1-2 days	K-media+Agar	Survival and fecundity	[80]
	10-50	<i>Eisenia fetida</i>	10–1000	4 weeks	Soil	Survival, fecundity, and growth	[88]
	30-50	<i>Do</i>	1000	< 1 week	Soil	Reproduction/fecundity	[89]
	7-14	<i>Do</i>	10-50	4 months	Soil	Survival	[90]
Fe ₃ O ₄	5.6	<i>Caenorhabditis elegans</i>	100-500	1 day	Agar	Stress enzymes and health	[82]
	100	<i>Do</i>	-	-	Agar	Biochemical and genetic assessments	[83]
						Movement resistance	
						Survival, fecundity, and growth	
CuO	20-100	<i>E. fetida</i>	5–50	4-8 weeks	Soil	gene expression	[86]
	80	<i>Enchytraeus albidus</i>	400–1000	2 day	Soil	Gene expression	[84]
	80	<i>Do</i>	130-230	3-8 weeks	Soil	Energetic reserves	[85]
ZnO	<50	<i>Folsomia candida</i>	230	4 weeks	Soil	Survival and reproduction	[91]
	<100	<i>Do</i>	100–6400	4 weeks	Soil	Survival and reproduction	[92]
	<100	<i>Eisenia veneta</i>	6–96	1 d	Water	Survival	[93]
	<100	<i>Do</i>	250-750	21 d	Soil	Survival, immune activity, and life history trait	[93]
	1–2.5	<i>Caenorhabditis elegans</i>	10–1,625	1-3 days	Water	Survival, reproduction, mobility, genetic	[94]
	20	<i>Do</i>	0.4–8.1	1 day	Water	Survival, fecundity, growth, and feeding	[77]
	40–100	<i>Eisenia fetida</i>	0.1-10000	2 weeks	Filter paper-soil	Survival and reproduction	[95]
		<i>Eisenia Andrei</i>					
TiO ₂	10-50	<i>Lumbricus terrestris</i>	1-100	1 week	Manured soil	Rate of apoptosis and mortality	[96]
	5-21	<i>Eisenia fetida</i>	20-10000	1-17 weeks	Soil	Survival, fecundity, growth, and avoidance	[97]
		<i>Eisenia Andrei</i>					
CeO ₂	15-45	<i>Caenorhabditis elegans</i>	1.0	1 day	K-media	Apparent growth, survival, gene expression	[98]

Gomes et al. [84] 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 [3].

ZnO is a highly investigated NM regarding environmental toxicology enumerations in living organisms [3]. Several workers have observed genetic and physiological changes (mainly stress enzymes *viz.* catalase, super oxide dismutase, and peroxidase) in *Eisenia fetida* exposed to ZnO NMs [3,78]. Hooper et al. [93] compared the toxicity of ZnO NM and ZnCl₂ on growth and proliferation of *E. veneta*. For this experiment 6-96 ppm concentration range was exposed and duration of the study was 1 days in water medium. 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 [93]. Similar report by Canas et al. [95] also elaborate the deleterious effect 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 dissolution of ZnO-NMs rather than direct accumulation of the particles [66]. Contrarily, Manzo et al. [91] extended information on accumulation of dissolved-Zn species *in lieu* of particulate-Zn in the body of *Folsomia candida* exposed to ZnO-NMs

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