Transformation and bioavailability of metal oxide nanoparticles in aquatic and terrestrial environments. A review[☆]

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ABSTRACT

Metal oxide nanoparticles (MeO-NPs) are among the most consumed NPs and also have wide applications in various areas which increased their release into the environmental system. Aquatic (water and sediments) and terrestrial compartments are predicted to be the destination of the released MeO-NPs. In these compartments, the particles are subjected to various dynamic processes such as physical, chemical and biological processes, and undergo transformations which drive them away from their pristine state. These transformation pathways can have strong implications for the fate, transport, persistence, bioavailability and toxic-effects of the NPs. In this critical review, we provide the state-of-the-knowledge on the transformation processes and bioavailability of MeO-NPs in the environment, which is the topic of interest to researchers. We also recommend future research directions in the area which will support future risk assessments by enhancing our knowledge of the transformation and bioavailability of MeO-NPs.

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1. Introduction

Nanomaterials (NMs) are nano-objects having a size range of 1–100 nm, at least in one dimension (Batley et al., 2013; Kumar et al., 2012), and a novel physical and chemical properties which may vary according to their size, distribution, morphology and phase. NMs comprise a variety of materials classified as carbonaceous, metal oxides, semiconductors, polymers, clays, emulsions, and metals (Batley et al., 2013) which can be engineered from a combination of identical or different elements. They have attracted wide applications in various areas of science and technology due to their unique properties, limited size and high surface area/sites, respect to their bulk counterparts.

Metal oxide nanoparticles (MeO-NPs) are metallic oxides having a size within a nanoscale range, which include both deliberately synthesized and naturally occurring particles resulting from natural and anthropogenic processes. Hitherto, numerous MeO-NPs

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which are attractive nominees from the scientific and technological perspective, due to their variety of crystal structure and the nature of the metal-oxygen bonding (varies from nearly ionic to covalent or metallic) (Niederberger and Pinna, 2009) have been engineered and well documented. MeO-NPs also exhibit a fascinating electronic and magnetic properties, and are among the most utilized engineered NPs (Hendren et al., 2011; Piccinno et al., 2012) in different areas such as commercial products (e.g. fuel cells, plastics, consumer products) (Devener and Anderson, 2006; Lagaron and Lopez-Rubio, 2011; Lee et al., 2010; Mu and Sprando, 2010), environmental application (e.g. environmental analysis, sensing, remediation, amendments) (Amde et al., 2016, 2015; Bai and Zhou, 2014; Corr, 2013; Gan et al., 2016; Ghasemi et al., 2017; Ju-Nam and Lead, 2016; Lee et al., 2016; Mahdavi et al., 2014; Mirzaei et al., 2016; Parga et al., 2012; Park et al., 2016; Rahman et al., 2017; Singhal et al., 2017; Trujillo-Reyes et al., 2014; Vuong et al., 2016), sustainable chemistry (e.g. catalysis) (Almukhlifi and Burns, 2016; Gawande et al., 2016; Montini et al., 2016; Navalon et al., 2016; Peng et al., 2016), and health (e.g. antimicrobial, cancer treatment) (Al-Ajmi et al., 2016; Ansari et al., 2015; Applerot et al., 2009; Chauhan et al., 2015; Padmavathy and Vijayaraghavan, 2008; Saba and Amini, 2017; Salata, 2004; Tuli et al., 2015; Yang et al., 2016). For a quick overview, the

properties, recent preparations techniques, applications, and coatings of selected MeO-NPs have been compiled and tabulated as provided in the supporting information (Table S11).

Consumption of MeO-NPs in these activities, in large and/or small amounts, open the door for their intentional and unintentional (Fig. 1) release to the environment (Batley et al., 2013; Holden et al., 2016; Kaegi et al., 2008; Keller et al., 2013; Kiser et al., 2012, 2009; Tolaymat et al., 2017) with unidentified consequences, and their possible presence in the environmental systems have been reported (da Silva et al., 2011; Gottschalk et al., 2009; Mueller and Nowack, 2008; Sun et al., 2016), even though limited information exists, currently, on their released quantity (Bauerlein et al., 2017; Ju-Nam and Lead, 2016). There might be also the possibility to become a threat to drinking water supplies in the future due to the fact that consumption quantities of engineered NPs are expected to increase significantly (Troester et al., 2016) and, consequently, increases the quantity of nano-wastes (Bystrzejewska-Piotrowska et al., 2009).

In the environment, MeO-NPs are subjected to various chemical and/or physical processes (Auvinen et al., 2017; Garner et al., 2017) that will drive them away from their pristine state toward different products having distinct physicochemical properties (Wang et al., 2013a). Sources, introduction routes, and the major transfer and transformations that MeO-NPs experience in the environment is represented in Fig. 1.

On the other hand, bioavailability and deleterious effects of

MeO-NPs towards aquatic and terrestrial organisms have been reported in recent (Chen et al., 2012b; Ma et al., 2013a; Miao et al., 2015; Mouneyrac et al., 2014; Poynton et al., 2011; Skjolding et al., 2016; Zhao et al., 2012b). Even though their toxicity mechanisms are not exactly known, it might be attributed to the formation of reactive oxygen species (ROS) and various hazardous entities of the particles due to the transformation processes which shall also affect their fate, transport, bioavailability and toxicity in the environmental systems. It should be also noted that the transformation pathways (e.g. adsorption) may also decrease the toxic-effects and persistence of MeO-NPs in the environment.

Therefore, a formative review, based on recent studies, on the transformations and their effects on the fate and bioavailability of MeO-NPs in the environment is highly important from the environmental point of view. Although there are some review papers (Cornelis et al., 2014; Cross et al., 2015; Dwivedi et al., 2015; Dwivedi and Ma, 2014; Klaine et al., 2008; Lowry et al., 2012; Peijnenburg et al., 2015; Tourinho et al., 2012) addressing fate of NMs in the environment before this one, most of these papers are general, and condensed all engineered NMs together, while some others have discussed few topics on limited environmental systems. Also, none of these papers has discussed the aforementioned behaviors related to MeO-NPs, separately, and no critical review has been done on MeO-NPs alone to the best of our knowledge. Moreover, MeO-NPs have unique properties such as high specific surface area, superparamagnetic property, relatively dissolvable

Fig. 1. Sources, introduction routes, and summary of the transformations that MeO-NPs experience in the environment.

property and excellent sorption capacity which can affect their transformation in the environment compared to other NMs, and also they yield dissolved metal ions in the processes which exacerbate their environmental impacts. Therefore, this critical review was designed to provide the state-of-the-art on the transformations of MeO-NPs that can affect their fate, toxicity/bioavailability, and persistence in the environment, which is the topic of interest to researchers and thus to highlight future research gaps in the area.

2. Transformations of metal oxide nanoparticles in the environment

Transformations of MeO-NPs in the environment is the result of various physical, chemical, and biologically mediated processes. The commonly occurring processes in environmental and biological systems such as aggregation/agglomeration, adsorption, deposition, dissolution, sulfidation, mineralization, redox reactions (e.g. photo-oxidation and photo-reduction), and others, as depicted in Fig. 1, can be stated as the essential processes impacting fate of the materials in aquatic and terrestrial environments. In this section, current research reports in the area have been reviewed. Since the transformations of MeO-NPs strongly dependent on the chemistry of the environment, and thus, extent of the processes may vary with types of the compartments, the discussion has been made in separate sections for the aquatic and terrestrial environments.

2.1. Transformations in aquatic environment

Waste water discharge is one of the intentional pathways for the release of MeO-NPs to the environmental systems, soil, water and sediment. As the main recipient, most of the processes (Fig. 1.) occur in the aquatic environment during their transport from their discharge source to water, soil, and sediment, and then to other recipients (e.g. aquatic plants and organisms, benthos). Furthermore, a lot of advancement in fate assessment of the materials has been made on the aquatic compartments (Peijnenburg et al., 2016).

2.1.1. Physical transformations

Aggregation/agglomeration, adsorption, and deposition (Fig. 2) are the physical processes which have lasting implications on the fate, bioavailability, and toxicity of MeO-NPs in the aquatic environment.

2.1.1.1. Aggregation/agglomeration. Aggregation, formation of a cluster of NPs that has come together, is one of the processes which has a significant effect on the fate of MeO-NPs in aquatic environment (Buffet et al., 2011; Cross et al., 2015; Lowry et al., 2012; Mouneyrac et al., 2014; Wang et al., 2016b). According to Derjaguin–Landau–Verwey–Overbeek (DLVO) theory (Adamczyk and Werofiski, 1999), aggregation of aqueous dispersions results from the combined effect of van der Waals attraction and electrostatic repulsion due to the electric double layer of the counter ions. Other interactions such as hydration force, magnetic and hydrophobic interactions which are not DLVO theory interactions, also have significant contribution in the aggregation process (Dwivedi et al., 2015; Sendra et al., 2017a). If the aggregation is formed due to the interaction between same NPs, homo-aggregation occurs and if it is between NPs and the cocktail of other components in the environment, hetero-aggregation results (Hotze et al., 2010; Lowry et al., 2012; Quik et al., 2012) as schematically represented in Fig. 2. Due to trace realistic amount of NPs in the environment, hetero-aggregation is more probable than homo-aggregation (Schultz et al., 2015).

Aggregation usually decreases the concentration of NPs in the suspensions and the aggregate size increases through time, which may favor the deposition process (Quik et al., 2012). In the work of Mouneyrac et al. (2014) the rapid aggregation/agglomeration of CuO-NPs (size, 1–100 nm) and ZnO-NPs (size, 21–34 nm) in the marine system lead to larger-sized aggregates, >810 and 250–800 nm, respectively. Therefore, aggregation can mitigate the transport/mobility of MeO-NPs in a water body, and further facilitate their homo- and/or hetero-aggregation (until equilibrium) and sink to the sediment. On the other hand, an increase in size due to the aggregation process may cover the active sites and accessible surface area of the MeO-NPs, and hence decrease their chemical reactivity and toxicity. The persistence and bioavailability of MeO-NPs can be also affected, significantly by the aggregation process,

Fig. 2. Common physical transformations that MeO-NPs undergo in the aquatic environment based on the literature.

even though cannot be clearly delineated.

Aggregation/agglomeration processes depend on the type and physicochemical behavior of the NPs themselves and the various conditions of the suspension medium (Cross et al., 2015; Lowry et al., 2012; Peng et al., 2017). The aggregation kinetics of ZnO-NPs with different morphology, spherical and nano-rod, was investigated by Zhou and Keller (2010) and their report depicted that the aggregation kinetics of the NPs depend on their shape and size, in addition to the solution chemistry such as ionic strength (IS), pH and natural organic matter (NOM) (Lin et al., 2017; Peng et al., 2017; Zhou and Keller, 2010). The variation in aggregation kinetics with the morphology of NPs may be ascribed to its effect on the diffusion coefficient, the effectiveness of the attachment and the presence of different crystal phase with the shape. The initial concentration of the NPs in the suspension may also have a paramount effect on the aggregation process. At higher concentration, there is enhanced collision frequency which leads to rapid aggregation, which is also a thermodynamic-driven process in which particles reduce their surface energy by forming larger aggregates. This was confirmed as faster aggregation rate of TiO₂-NPs (Botta et al., 2011), ZnO-NPs (Yung et al., 2015) and CeO₂-NPs (Marie et al., 2014; Quik et al., 2012, 2014) were reported at higher dosage than lower concentrations, and larger aggregate size is also expected as concentration of the NPs increases (Marie et al., 2014). The presence of coating materials can also alter the aggregation (homo- and hetero-aggregation) behavior of MeO-NPs. For example, 10 mg/L CeO₂-NPs (size, 3–4 nm) was found to aggregate (hydrodynamic size (R_D), 900 nm) within few minutes unlike citrate-coated CeO₂-NPs (initial size, 3–4 nm) which took about three days to obtain lesser sized aggregate (R_D , 600 nm) (Marie et al., 2014). In addition, surface functionalization of MeO-NPs can also have a significant effect on their aggregation and deposition behaviors. As reported by Vikesland et al. (2016), tetramethylammonium hydroxide functionalized Fe₂O₃-NPs (size, 4 nm) aggregate more rapidly than unfunctionalized Fe₂O₃-NPs (size, 5 nm). Similarly, steric stability (lower aggregation) of TiO₂-NPs in aqueous suspension was achieved upon surface coating the NPs with dodecyl succinic anhydride and poly acrylic acid (Elbasoney, 2017).

Aggregation and stability of MeO-NPs in the aquatic environment depends to a large extent on the IS. High IS in the surrounding water results in compressed electric double layer and reduced electrostatic repulsion, and it also affects the particle surface charge and thus, increases the aggregation process. For example, in 0.1 and 1 mM NaCl solution (pH, 8.1), no cluster aggregation of ZnO-NPs (size, 20 nm) was observed (time, >160 min), but large aggregate (size, above 1 μ m) was formed in 25 mM NaCl (pH, 8.1) within 15 min (Zhou and Keller, 2010). As reported by Yung et al. (2015), on the effect of salinity on the aggregation of ZnO-NPs (size, 20 nm), the aggregate size was found to increase (0.84–1.46 μ m) as the IS of the solution increases (range, 12–22 practical salinity unit (PSU)). In recent, Odzak et al. (2017) reported the high agglomeration behavior of ZnO-NPs (size, $\leq$ 130 nm) at high IS. High aggregation of TiO₂-NPs in the presence of 45 mg/L Ca²⁺ and 5 mg/L Mg²⁺ ions (Loosli et al., 2015a) was also reported which is in good agreement with the recent reports on the increased hetero-aggregation behavior of TiO₂-NPs with montmorillonite (Zhou et al., 2012), microalgae cells (Sendra et al., 2017a) and extracellular polymeric substances from *Bacillus subtilis* (Lin et al., 2017) as the IS increases. Similarly, exacerbated homo- and hetero-aggregation of CeO₂-NPs (R_D , 175 nm) in water with high IS was reported (Quik et al., 2014). It should be also noted that the effect of salinity is dependent on the concentration of the NPs in the suspension, and lower concentrated suspensions are highly affected by the IS (Yung et al., 2015).

The aggregation of MeO-NPs also depends on pH of the solution,

since it affects the surface charge of the materials which strongly affects their aggregation behavior. High homo- or hetero-aggregation is expected around the pH point of zero charges (pH_{zpc}) of the particles (Lin et al., 2017; Peng et al., 2017; Zhou and Keller, 2010). Stable ZnO-NPs suspension, the less aggregation, was reported at pH of 7.45 (far from pH_{zpc}) than at 8.65 (near pH_{zpc}), where more aggregation is expected (Zhou and Keller, 2010). Higher agglomeration of TiO₂-NPs was reported to form around its pH_{zpc} (6.2) (Loosli et al., 2014, 2015a), and the suspension is stable at pH <5 and >8, zeta-potential (ζ -potential) become $\geq +40$ and ≤ -43 mV, respectively (Loosli et al., 2015a). Therefore, the pH has a significant effect on the aggregation based transformation of TiO₂-NPs in the environment.

Another factor which can affect the aggregation of MeO-NPs in waters is the presence of NOM and other colloids. Even though it seems challenging to exactly delineate the effect of NOM, which is ubiquitous in environmental systems, it is certain that the materials adsorb to the surface of the NPs, and provide charge and steric stabilization (Chen et al., 2012a; Gallego-Urrea et al., 2014; Keller et al., 2010; Loosli et al., 2014; Omar et al., 2014; Peng et al., 2017; Zhou and Keller, 2010). Furthermore, bridging flocculation (at a lower concentration of NOM) and disaggregation (Fig. 2) are likely in the presence of NOM (Loosli et al., 2014, 2015a; Lowry et al., 2012; Miao et al., 2015; Zhou and Keller, 2010). Zhou and Keller observed complete mitigation of ZnO-NPs aggregation in the presence of 10 mg/L NOM (Zhou and Keller, 2010) which agree with the recent report of Peng et al. (2017) in which high stability, lower aggregation, of ZnO-NPs was observed in the presence of Suwannee River humic acid (HA) (10 mg/L). Decrease in the aggregation behavior of TiO₂-NPs in the presence of HA (Chen et al., 2012a; Chowdhury et al., 2012), montmorillonite (Zhou et al., 2012), bacteria (Chowdhury et al., 2012), carbomer (Englehart et al., 2016), alignate (Loosli et al., 2014, 2015a) and dye stuff (Mahlalela et al., 2016) were reported, and alignate showed significant effect in the disaggregation of larger (micro sized) aggregates of the NPs (Loosli et al., 2014). Low aggregation of CeO₂-NPs was also reported in a water solution containing 5 and 10 mg/L HA (Lv et al., 2014). In general, the stability of MeO-NPs suspensions, lower aggregation behavior, in the presence of organic colloids such as NOM may be rendered due to the surface coating e.g. as confirmed from change in the overall zeta potential of the NPs to negative (Mahlalela et al., 2016) which cause the particle-particle repulsion.

2.1.1.2. Deposition. Deposition, the behavior to settle on a bottom surface from a solution, is mainly favored by aggregation/agglomeration of the MeO-NPs in the aquatic environment. The aforementioned NPs properties and environmental conditions which enhance the aggregation process could also favor the sedimentation. The NP type also affects the deposition behavior, as the extent of NPs aggregation changes with their nature. For example, CeO₂-NPs undergo depletion more easily (>95% undergo deposition within 7 days) (Van Koetsem et al., 2015) than ZnO-NPs (fast in dissolution) in natural waters. This indicates that the type of NPs should be considered while studying the deposition behavior of MeO-NPs in the environment. Besides, since electrostatic interactions play a great role in the deposition process, at least during initial surface deposition, surface chemistry (e.g. surface charge) of the solid materials where the NPs reside also have a significant effect on the process (Ikuma et al., 2014).

In general, aggregation, agglomeration and deposition processes are interrelated processes. Deposition increases when aggregation is higher, and eventual stability and deposition processes of MeO-NPs are likely determined by properties of the NPs (to some extent) and a combination of physicochemical parameters of the medium. These physical processes could affect the fate,

bioavailability and persistence of MeO-NPs in waters and sediments. However, the trend cannot be exactly generalized since the effect of physical transformations on the NPs depends on the type of the NPs and organisms in the environment.

2.1.2. Chemical transformations

Owing to various active entities on their surface, it is certain that MeO-NPs are susceptible to various chemical transformations like dissolution, redox reaction, and others. The basic chemical-based transformation processes of MeO-NPs in aquatic environment have been schematically represented in Fig. 3 based on the literature.

2.1.2.1. Dissolution. Dissolution is one of the transformation processes which can affect the fate, reactivity, toxicity, persistence and bioavailability of MeO-NPs in the environment (Cross et al., 2015; Lowry et al., 2012). Like other processes, dissolution of MeO-NPs also depends on their physicochemical properties and chemistry of the environmental system.

Size and morphology of the MeO-NPs have a significant effect on their dissolution property due to the difference within surface area to mass ratio, smaller NPs have higher specific surface area than the larger ones (Soenen et al., 2015). For instance, Mudunkotuwa et al. (2012) investigated size-dependent dissolution of ZnO-NPs (particle diameters, 4–130 nm) at circumneutral pH (pH, 7.5), and their results showed that the dissolution is higher in smaller-sized than the larger-sized NPs which is in good agreement with other reports (Bian et al., 2011; Odzak et al., 2014). Besides, it was also reported that the presence of citric acid can enhance the extent of ZnO-NPs dissolution, and the effect is more significant for the case of smaller

sized NPs which confirm the significant effect of particle size on the NPs dissolution. Similar size effect was observed on the dissolution of Fe₂O₃-NPs, smaller size (8 nm) NPs exhibited 3.3–10 fold dissolution (based on the reaction conditions) than the larger size (40 nm) NPs (Lanzl et al., 2012). Moreover, using stabilizing agents for a different purpose can drastically minimize the dissolution of MeO-NPs (Gelabert et al., 2014; Merdzan et al., 2014). For example, an organic coating of ZnO-NPs drastically modifies its stability, lower dissolution rate in synthetic water (maximum dissolution reached in 7 days) compared to uncoated NPs (maximum dissolution in the first hour) (Gelabert et al., 2014). On the other hand, the high dissolution behavior of citrate-coated CeO₂-NPs (size, 3.9 nm) in water column compared to uncoated CeO₂-NPs (size, 31 nm), as the report of Tella et al. (2015), could be attributed to the surface complexation with citrate in addition to the significance difference in their nominal size.

The dissolution of MeO-NPs also depends on the chemistry of the medium, such as pH (Bian et al., 2011; Li et al., 2013; Odzak et al., 2014; Omar et al., 2014; Son et al., 2015), NOM, (Bian et al., 2011; Jiang et al., 2015; Li et al., 2013; Omar et al., 2014; Wang et al., 2016b), IS (Li et al., 2013; Odzak et al., 2015; Yung et al., 2015), temperature (Majedi et al., 2013), and the presence of other reactive species (Kent and Vikesland, 2016; Lv et al., 2012). The dissolution of MeO-NPs such as ZnO- and CuO-NPs have been reported to depend on pH of the medium (Bian et al., 2011; Li et al., 2013; Miao et al., 2010; Odzak et al., 2017; Omar et al., 2014; Son et al., 2015), and lower pH enhance the dissolution of the NPs (Li et al., 2013; Odzak et al., 2014, 2015, 2017; Omar et al., 2014). In the work of Miao et al (Miao et al., 2010), ZnO-NPs dissolution was found to decrease as the pH value increases (Zn²⁺ concentration,

Fig. 3. Basic chemical transformations of MeO-NPs in aquatic environments. Text can be referred for the detail.

5.03×10^{-4} M and 5.63×10^{-6} M at 7 and 9 pH values, respectively). Similarly, higher dissolution of ZnO-NPs (size, ≤ 130 nm) at lower pH values (pH, < 6.5) was reported in recent (Odzak et al., 2017). This might be due to the interaction among the NPs which is favored at high pH, and hence, reduces the dissolution.

The dissolution of MeO-NPs also depends on the IS of the sample solution, and high and rapid dissolution of the NPs is expected at low IS (Li et al., 2013; Odzak et al., 2015; Son et al., 2015) which might be attributed to the precipitation processes (Reed et al., 2012). Yung et al. (2015) investigated the effect of salinity on the dissolution of ZnO-NPs and found that the ion release decreases as the IS of the solution (range, 12–22 PSU) increase. In addition to this, the dissolution of CuO-NPs in seawater is reported to be insignificant (Buffet et al., 2013, 2011; Gomes et al., 2011; Heinlaan et al., 2011).

The presence of NOM may also affect the dissolution-based transformation of MeO-NPs in environmental systems (Bian et al., 2011; Jiang et al., 2015; Li et al., 2013; Miao et al., 2015; Odzak et al., 2015; Wang et al., 2016b). Enhanced complexation of free metal ions of the NPs with NOM might be the mechanism for their effect on the dissolution process (Omar et al., 2014; Son et al., 2015). In the work of Jiang et al. (2015) the dissolution of ZnO-NPs was reported to increase with NOM concentration (0–40 mg/L). In the report, the aromatic carbon content of the NOM was proposed as a key factor in determining the rate of NOM-promoted dissolution of the NPs. However, as the report of Odzak et al. (2015), high dissolution of ZnO- and CuO-NPs under freshwater conditions was reported at a low concentration of DOM which is in line with other reports (Bian et al., 2011; Li et al., 2013). Hence, NOM-promoted MeO-NPs dissolution might be limited to a specific concentration range of the NOM in the system, and the effect of NOM on the dissolution of MeO-NPs in waters is also pH dependent (Omar et al., 2014).

Even though rarely studied, the temperature and light (UV and/or visible) may also affect the dissolution behavior of MeO-NPs in the aquatic environment. For example, the dissolution of ZnO-NPs (size, ~ 40 nm) was found to be temperature dependent, and high aggregation rate, and hence, low dissolution was found at higher temperature (35 °C) than lower temperatures (15 and 25 °C) (Majedi et al., 2013). Similarly, high dissolution of 100 mg/L ZnO-NPs suspension was reported to be higher at 20 °C than at 37 °C (Reed et al., 2012). The lowering of solubility as temperature increases could be attributed to the negative enthalpy of the NPs dissolution (Reed et al., 2012). In very recent, Odzak et al. (2017) reported that the dissolution of ZnO-NPs may be facilitated in the presence of UV (400–700 nm) and visible (300–400 nm) light which might be associated to the indirect effects of the parameters on the surface and surface coatings of the NPs which is in agreement with the previous reports on the impact of solar UV radiation on the dissolution behavior of ZnO-NPs (Ma et al., 2014a).

The presence of anions and chelating agents in the solution can also affect (either way) the dissolution of MeO-NPs in waters. Lv et al. (2012) investigated the influence of phosphate on the dissolution and microstructural transformation of ZnO-NPs (size, 40 nm) in the aquatic environment, and the report showed that the presence of low amount of phosphate in the system can drastically reduce the NPs dissolution. Similarly, high stability of ZnO-NPs was reported in the presence of 10 eq/L SO_4^{2-} which might be due to the surface neutralization or inverted surface potential (Peng et al., 2017). The high dissolution of Cu-based NPs such as metallic Cu and CuO-NPs in aquatic samples were reported and such NPs could short live unless affected by competing for a process such as sulfidation process (Kent and Vikesland, 2016; Ma et al., 2014c). On the other hand, the presence of metal binding ligands (e.g. Cl^- , SO_4^{2-}) (Miao et al., 2010) and pre-exposure to CO_2 and humidity can

accelerate the dissolution of MeO-NPs (Gankanda et al., 2016). The presence of extracellular polymeric substances in the waste water system can also increase the dissolution of CuO-NPs in aquatic environments probably due to their abundant functional groups and excellent metal-binding capacity (Miao et al., 2015). In the presence of *Botrytis cinerea*, a plant pathogenic fungi, the siderophores and organic acid secretion was reported to induce the dissolution and mobilization of Cu ions from the CuO-NPs (Kovacec et al., 2017). However, the presence of a layer of cells does not have significance influence on Co_3O_4 -NPs dissolution in water (Papis et al., 2009). This shows that the effect of foreign entities (e.g. polymeric substances in the media) on the dissolution of MeO-NPs vary with the NPs type.

2.1.2.2. Redox reactions. Redox reaction comprises two coupled processes, oxidation and reduction reactions, which involve the transfer of electrons among the reacting species. MeO-NPs may compose of various constituents that undergo reduction and/or oxidation in environmental systems. The coating materials may also have significant effect on the redox reactions of the NPs. For instance, solid silica coated Fe_3O_4 -NPs exhibited strong stability towards oxidation than the uncoated counterparts (Cendrowski et al., 2017). In addition to the MeO-NPs moieties, there are plenty of species in the environment which facilitate the redox process. For example, CeO_2 -NPs may contain both Ce(III) and Ce(IV) species, and in the environment, it interacts with macromolecules such HA and biological media, and undergo oxidation reaction which results in altered ratio of Ce(III)/Ce(IV) on the CeO_2 -NPs surface (Fig. 3) (Baalousha et al., 2010). Recently, a net reduction of CeO_2 -NPs in the intracellular environment was reported unlike in environmental systems (Cui et al., 2014; Szymanski et al., 2015), which indicate that the release of Ce(III) may contribute to the toxicity of CeO_2 -NPs (Cui et al., 2014). The presence of cellular molecules like proteins may involve in the redox reaction of MeO-NPs in an aqueous environment. For example, reduction of NiO-NPs to zero valence nickel was reported in the presence of soluble proteins (Gong et al., 2011). During sulfidation process (in the presence of sulfide), CuO-NPs may undergo reduction (Cu(II) to Cu(I)), coupled with sulfide oxidation to sulfate, and form copper sulfate hydroxides (Ma et al., 2014c). Moreover, when exposed to sunlight, photoactive MeO-NPs (e.g. TiO_2 , MnO_2) can undergo sunlight-catalyzed redox reactions to undergo dissolution or generate ROS. MnO_2 -NPs underwent photo-induced reduction and Mn(III) was obtained (Marafatto et al., 2015), which indicate its possible dissolution upon reduction.

It should be also noted that the type of the environmental system also affects the redox-based transformations of NPs, and oxidation is effective in natural waters and aerated soils, while sediments (carbon rich) and ground water (insufficient oxygen) are reducing environments. Kinetics of MeO-NPs redox reaction processes can be substantially affected by the presence of NOM in the aquatic environment, which may hinder the transfer of electrons among the reacting species.

Redox reactions may result insoluble surface coating which enhances stability of the NPs so that their persistence increases. On the other hand, it may also lead to the formation of active surface which facilitate the reaction between the NPs and other components existing in the environment and thus, their stability decreases. The oxidation process may also promote the dissolution behavior of NPs. Therefore, it is one of the processes which has significant effect on the fate of MeO-NPs in the environment.

2.1.2.3. Other chemical processes. The presence of other reactive organic and inorganic substances in the environment (e.g. surfactants capable of ligand exchange with NPs) can have a significant

effect on the transformations and fate of MeO-NPs. If the system comprises reduced sulfur species, it can react with MeO-NPs and form various products in aquatic environments (Brunetti et al., 2015; Lombi et al., 2012; Ma et al., 2014b, 2014c). The sulfidation of CuO-NPs (size, 40 nm) in waters in the presence of inorganic sulfur was reported in recent, and crystalline and amorphous Cu sulfide compounds were obtained as the major transformation products (Ma et al., 2014c). In the report of Brunetti et al. (2015) Zn sulfide was obtained as the major constituent (90%) of the transformation products while investigating the transformation of ZnO-NPs (size, 22.9 nm) within sewerage transfer networks. Similar studies also showed the formation of Zn sulfide in wastewater–sewage sludge in which anaerobic digestion process and post processing of the sewage sludge (which caused a significant change in Zn speciation) facilitated the conversion of all types of the ZnO-NPs (size, 30–40 nm) in the system (Lombi et al., 2012; Ma et al., 2014b). The extent of sulfidation process in aqueous solution depends on the sulfide concentration, and close to 100% conversion of the NPs can be achieved in a solution containing excessive sulfide (Ma et al., 2013b). In addition to Zn sulfide (the major product), the formation of Zn phosphate was also observed during anaerobic wastewater digestion (Brunetti et al., 2015; Lombi et al., 2012; Ma et al., 2014b). Ma et al. (2014b) examined the chemical speciation of Zn in sludge from a pilot wastewater treatment plant that had received 30 nm ZnO-NPs using X-ray absorption spectroscopy (XAS) and other supporting characterization methods. Accordingly, the transformation of Zn to three Zn-containing species, Zn sulfide, $\text{Zn}_3(\text{PO}_4)_2$, and Zn associated Fe oxy/hydroxides was observed, and the products were formed regardless of the form of Zn added (ZnO-NPs or dissolved metal ion). Upon composting/stockpiling the sludge for a longer time, Zn speciation could be significantly affected as the Zn sulfide undergo oxidation (aerobic condition exacerbate the oxidation of Zn sulfide) and the Zn speciation shift toward association with Fe oxy/hydroxides, and complexes with phosphate to form Zn phosphate (Lombi et al., 2012; Ma et al., 2014b).

In the presence of phosphate ions, the interaction between phosphate and ZnO-NPs (size, 40 nm) leads to the formation of Zn phosphate (Lv et al., 2012). Besides, change in morphology of the particles from structurally uniform nano-sized spherical to an anomalous and porous material containing mixed amorphous and crystalline phases of ZnO and Zn phosphate was reported in the presence of phosphate. Due to wide phosphate contamination in water and its strong metal-complexation capability, phosphate-induced transformations may play an important role in the behaviors, fate, and toxicity, of many other metal-based NMs in the environment. It should be also noted that phosphate-induced transformation of MeO-NPs (e.g. ZnO-NPs) is pH dependent. For example, in the work of Rathnayake et al. (2014) the formation of hopeite-like crystalline zinc phosphate ($\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$, size, $\sim 1.5 \mu\text{m}$) and nanoscale ZnO core with an amorphous $\text{Zn}_3(\text{PO}_4)_2$ shell (size, 30 nm) from ZnO-NPs (size, 30 nm) and different concentrations of phosphate (0–150 mg/L) was reported at pH values of 6 and 8, respectively. This indicates that the reactions between MeO-NPs and different ions are influenced by environmental conditions, including pH, and may ultimately result heterogeneous end products having diverse structure and morphology.

With macromolecules like NOM, chemical processes like ligand exchange are likely to occur, and these processes are among the mechanisms via which NOM attach on the surface of MeO-NPs (Yang et al., 2009) and the phenolic (e.g. OH, COOH) and/or aliphatic groups of the NOM are responsible for the ligand exchange with the surface of NPs. These issues have been discussed briefly in the next section (interaction with macromolecules).

2.1.3. Interaction with macromolecules

The presence of macromolecules such as NOM, proteins, polysaccharides, and other surfactants in the environmental system may interact (Ansari et al., 2014; Lynch and Dawson, 2008; Schwaminger et al., 2016; Vakurov et al., 2013; Wang et al., 2016b) and transform the surface, and significantly alter the physicochemical properties of NPs. Thus, macromolecules can also determine fate of the NPs in the environment (Kiser et al., 2012; Sheng et al., 2016; Son et al., 2015), and their toxic-effects (Ansari et al., 2014). There are various mechanisms proposed for interactions between the macromolecules and NPs (depend on the types and behavior of both materials) which include hydrophobic interaction, electrostatic and van der Waals interaction, chelation, ligand exchange, bridging, and hydrogen bonding (Fig. 4.), and these interaction processes are highly dependent on the pH of the medium (Philippe and Schaumann, 2014; Yang et al., 2009).

As mentioned earlier, macromolecules (e.g. NOM) in the environment can interact and co-aggregate with MeO-NPs and grant steric or electrostatic stability, which then reduces aggregation and deposition of the NPs (Chen et al., 2012a; Huangfu et al., 2015; Sheng et al., 2016; Zhou and Keller, 2010).

Among the constituting macromolecules in the environment, the amounts of NOM are orders of magnitude higher in concentration than the realistic concentrations of NPs in the system, and so are likely to substantially modify their properties. Chen et al. (2012a) observed possible transport of TiO_2 -NPs nanoparticles (pH dependent, high pH value, 9, limit the adsorption of HA), in the presence of HA. The increase in the negative surface charge of TiO_2 -NPs and combinations of increased electrostatic and steric interactions might be the main mechanisms for the enhanced stability at low and high HA adsorption densities, respectively. Similarly, the significant interaction between TiO_2 -NPs and macromolecules, HA, montmorillonite, alginate, bacteria and microalgae has been reported to affect the aggregation and transport of TiO_2 -NPs in aquatic environments (Chowdhury et al., 2012; Loosli et al., 2014, 2015a, 2015b; Sendra et al., 2017a; Zhou et al., 2012). Minimum aggregation and enhanced transport of CeO_2 -NPs was also observed in an aquatic system containing HA (5 and 10 mg/L), which could introduce a negative surface charge and steric repulsion between the particles, and this trend further exacerbates at lower IS (Lv et al., 2014). NOM interaction with NPs may also alter the surface chemistry of the particles. As an example, the interaction of CeO_2 -NPs with HA and biological media was reported to change their surface oxidation state (Baalousha et al., 2010). Therefore, macromolecules and MeO-NPs interactions can also affect the toxicological behavior of the NPs.

Interaction of extracellular polymeric substances with MeO-NPs (e.g. CuO-NPs) in water system may also increase their dissolution capacity (Miao et al., 2015) and the interactions of HA and surfactants (sodium dodecyl sulfate, and polyvinylpyrrolidone) with the NPs such as MnO_2 -NPs were reported to have a significant effect on the stability and reactivity of the particles (Huangfu et al., 2015).

In general, the numerous macromolecules existing in the environment surpass the released MeO-NPs (in number and concentration), and adsorb to the NPs and can alter their physical and chemical properties. Therefore, once released and exposed to the environment, it is the type and amount of the macromolecules which determine the behavior, fate, bioavailability and toxic-effects of the NPs.

2.2. Transformations in terrestrial environment

Besides to the waste management (e.g. waste water discharge and landfills), the main pathways through which NPs end up in the environment, MeO-NPs also enter to the soil environment

Fig. 4. Common interaction mechanisms of macromolecules with the surface of MeO-NPs based on literature.

intentionally (e.g. as fertilizers to amend metal deficiency and as pesticides to protect plant production) and unintentionally, during production and product consumption (Fig. 1) (Ju-Nam and Lead, 2016; Keller et al., 2013; Peijnenburg et al., 2016; Sun et al., 2014). Besides, the terrestrial compartment and sediment are considered to be the longer time residence of NPs (Peijnenburg et al., 2016). On the other hand, MeO-NPs and their corresponding metal ions behave differently in soils depending on soil properties and aging processes (Romero-Freire et al., 2017). There are various chemical (dissolution, redox reaction, and others) and physical transformations (change in size and morphology, diffusion, and aggregation) (Fig. 5) which could be initiated within the system (Pachapur et al., 2016; Peijnenburg et al., 2016), and these processes should be known and their effects on behavior of the NPs have to be identified to assess the fate and bioavailability of the materials in terrestrial environment.

There are limited reports on the fate of MeO-NPs in terrestrial systems, compared to the aquatic compartment, due to the underdeveloped analytical techniques to characterize, track, and perform studies on the transformation processes, and most of the available reports have been based on soil suspensions, rather than the soil (Ju-Nam and Lead, 2016).

Aggregation of MeO-NPs in soil systems is associated with their interactions among the particles and with other components in the system which lead to homo- and hetero-aggregations, respectively. Due to the numerous amount of materials, for the hetero-aggregation to occur, its formation is more probable than homo-aggregation (Cornelis et al., 2014). Aggregation is also one of the processes which can affect the fate and bioavailability of the NPs in terrestrial systems. For instance, the aggregation of TiO₂-NPs in soil can significantly lower its bioavailability (Dimkpa et al., 2013; Du et al., 2011), and hindered diffusion of ZnO-NPs in soils in its nano-form was also reported due to its hetero-aggregation with granules (Milani et al., 2015, 2012; Zhao et al., 2012a). On the other

hand, hetero-aggregation of MeO-NPs (e.g. ZnO-NPs) with mobile soil colloids, may also provide their colloidal mediated mobility in terrestrial systems (Zhao et al., 2012a).

Due to the fact that soil organic substances are negatively charged under environmental conditions, they sorb to MeO-NPs surfaces, predominantly via ligand exchange and hydrophilic interactions (Fig. 4), and enhance the NPs stability (Ju-Nam and Lead, 2016). For example, the stability of TiO₂-NPs (size, 35 nm) was reported to have a positive correlation with the dissolved organic carbon and clay content of the soils but negatively correlated with IS, pH and ζ -potential (Fang et al., 2009). On the other hand, high aggregation of CeO₂-NPs (reduced stability) was reported in soils with high clay content (Cornelis et al., 2010, 2011) which might be attributed to the adsorption of the NPs on the surface of natural colloid materials. Similarly, in the case of Al₂O₃-NPs, humic substances promoted its aggregation, particularly at low pH, due to the low charged and more hydrophobic (π - π interactions) nature (Ghosh et al., 2008).

MeO-NPs also interacts with the numerous pollutants such as herbicides, pesticides, anions and heavy metals within the soil systems (Pachapur et al., 2016), and the interactions could be favored by the large surface area of the contaminants and the high specific surface area of the NPs. For example, in phosphate containing soils, the anion adsorb to the NPs surface (e.g. CeO₂-NPs) (Cornelis et al., 2011) which changes the NPs surface charge, and hence increases the NPs mobility in the compartment. Therefore, effects of co-existing contaminants should be also considered in the study of the fate of MeO-NPs in the environment.

MeO-NPs (e.g. Al₂O₃-, TiO₂-NPs) may diffuse through sedimentary rocks and transport through the medium, and their mobility in the various medium depends on their behavior (surface charge, size, and stability against deposition), and surface charge and roughness of the medium components (Bayat et al., 2015). Particle straining expected to be lower on smaller sized MeO-NPs,

Fig. 5. Common transformations, transport and bioavailability of MeO-NPs in a terrestrial environment based on literature.

and hence are more mobile in soils than the larger counterparts. As stated earlier, MeO-NPs surface charge could be reversed due to their interaction with the complex soil components which enhance their mobility in the compartment. For instance, the positively charged ZnO-NPs is immobile in soils, but increased mobility was reported in the presence of HA (Yechezkel et al., 2016).

Dissolution is another transformation which MeO-NPs undergo in soils, due to soil-pore water, namely during rain. Upon dissolution in soils, MeO-NPs exhibit identical behavior with their corresponding ions. For example, ZnO-NPs undergo rapid dissolution in soils, so that the spiked NPs were not detected after 1 h of incubation time (Wang et al., 2013a). However, the dissolution kinetics is dependent on type and property of the soils in addition to NPs related properties, and way of its introduction to soils (as solution or powder). In soils with high pH and IS conditions, limited diffusion and dissolution of ZnO-NPs were reported (Milani et al., 2015, 2012). Similarly, in the work of Cornelis et al. (2011) the dissolution behavior of citrate-coated CeO₂-NPs (size, 8 nm) was found to be significant only in acidic media (pH, 4). Besides, the presence of plant roots has been reported to exacerbate the dissolution of MeO-NPs in the terrestrial environment (Dimkpa et al., 2013; Schwabe et al., 2015) which might be attributed to the root exudates like organic acids and siderophores (Dimkpa et al., 2013). For example, enhanced dissolution of CuO-NPs (from <0.3 to 1 mg/kg) and ZnO-NPs (from ≤0.6 to between 1 and 2.2 mg/kg) in the presence of *Triticum aestivum* roots was reported (Dimkpa et al., 2013). It should be also noted that there are MeO-NPs (e.g. TiO₂-NPs) which exhibit low solubility in soils (Du et al., 2011).

Other chemical processes such as ROS generation, surface oxidation, degradation of the coating materials and others are also processes which MeO-NPs undergo in terrestrial systems. These processes hence can affect the fate of the NPs.

3. Bioavailability of metal oxide nanoparticles

The common mechanisms such as passive diffusion, facilitated diffusion, active transport and endocytosis proposed for the cellular internalization of any materials may also be the pathways for the uptake of MeO-NPs and their transformation products (Schultz et al., 2015), and the importance of these ways are strongly dependent on the type of the organisms. Bioavailability of MeO-NPs depends on their stability in the environment (Auffan et al., 2009; Moos et al., 2014), and stable NPs are less bioavailable and also exhibit lower toxic-effect to cellular organisms (Auffan et al., 2009) as their interactions with plasma proteins are important upon introduction of the materials into a physiological environment (Aggarwal et al., 2009). For example, the reduction of CeO₂-NPs, Ce(IV) to Ce(III), in the environment enhances its bioavailability to plant materials (Cui et al., 2014). On the other hand, the presence of organisms in the environment may introduce enzymes and chelating agents (organic acids, amino acids, fatty acids, proteins, and sugars), which induce transformations of the NPs into more bioavailable forms (Bystrzejewska-Piotrowska et al., 2011; Cornelis et al., 2014; Schwabe et al., 2015; Zhao et al., 2012a). Coating materials commonly used during the synthesis and stabilization of the NPs (Zhang et al., 2015a), and size of the NPs (Mate et al., 2016; Singh et al., 2013) can also affect their bioavailability and therefore should be monitored, carefully. The aggregation processes, both homo- and hetero-aggregation, can also significantly affect the NPs bioavailability (Johnston et al., 2010) since large aggregation can limit their direct transport across the cell wall/membrane, and hence prevent the uptake. Interactions (Fig. 4) of the NPs with endless coexisting substances such as other NPs, humic materials, proteins, polysaccharides, and different types of ions can also affect the uptake property (Lowry et al., 2012; Wang et al., 2014).

After the uptake, NPs and its other forms may undergo various transformations like aggregation, dissolution, complexation,

Fig. 6. Uptake of pristine/transformed MeO-NPs, analytical techniques for the analysis after the uptake and some of the intracellular transformation processes.

reduction, and others (Fig. 6) in the physiological environment, and various microscopic and spectroscopic techniques have been employed to investigate the processes in organisms. For example, based on transmission electron microscopy (TEM) and soft X-ray scanning transmission microscopy technique, Zhang et al. (2012) reported that CeO₂-NPs may undergo various transformations such as a change in structure, and chemical forms in plants. Similarly, X-Ray fluorescence (Hernandez-Viezcás et al., 2013) and X-ray absorption near-edge spectroscopy (XANES) (Cui et al., 2014; Hernandez-Viezcás et al., 2013) instruments were employed to investigate the chemical forms of CeO₂- and ZnO-NPs in plant tissues, and it was reported that some part of Ce(IV) in CeO₂-NPs can undergo biotransformation to Ce(III). In the work of Lv et al. (2015) even though ZnO-NPs were located in the *Zea mays* roots, no ZnO-NPs were translocated to the shoots, possibly due to the dissolution and transformation of the NPs inside the plants. In very recent, the possible degradation of Fe₃O₄-NPs in a biomimetic media with a similar conditions to physiological medium was investigated based on atomic absorption spectroscopy and TEM techniques, and the results showed that structural and magnetic properties of the NPs changed, significantly, after the degradation process and the process depends on the pH, coating and size of the initial NPs (Briceno et al., 2017).

Various ecological receptors, bacteria, algae, invertebrates, plants and mammalian cells have been employed to investigate the bioavailability of MeO-NPs and their products in the environment (Table S12) and the reports indicated that the NPs bioavailability vary with the test models besides to the NPs behavior and conditions of the test environment.

In general, the bioavailability of MeO-NPs are strongly dependent on their transformations in the environment and those NPs which oxidize, reduce, dissolve, and interact with the cell surface can readily penetrate into the cells (Fig. 6), and these aspects have been discussed in brief under this section.

3.1. Bioavailability to plant materials

Due to the presence of cell walls in plants, the uptake of MeO-NPs occur differently compared to the uptake process by other organisms. MeO-NPs and their transformation products can penetrate and uptake towards plant cells, via endocytosis (Schultz et al., 2015), symplastic (Lin and Xing, 2008; Zhao et al., 2012a) and apoplastic pathways. (Iannone et al., 2016; Zhao et al., 2012a). It should be also noted that the uptake and translocation of MeO-NPs in plants may depends on the plant species, cultivars, and growth conditions (Rizwan et al., 2017).

Most of the time, MeO-NPs are readily bioavailable to plants after dissolution. For example, studies showed that ZnO-NPs is bioavailable mainly in its dissolved (Zn²⁺) form, which might be ascribed to its rapid dissolution (Dimkpa et al., 2013; Du et al., 2011). In the work of Dimkpa et al. (2013) it was reported that treating *Triticum aestivum* with ZnO-NPs lead to Zn-phosphate accumulation in the shoots (based on XAS analysis), likely due to the uptake of Zn²⁺ from the dissolved NPs. Wang et al. (2013a) showed that Zn²⁺ from ZnO-NPs and ZnCl₂ are equally bioavailable to the *Vigna unguiculata* plant and this indicate that dissolution plays a great role in the uptake of MeO-NPs. Identical results were reported using *Phaseolus vulgaris* (Garcia-Gomez et al., 2017), *Solanum lycopersicon* (Garcia-Gomez et al., 2017), *Prosopis juliflora-velutina* (Hernandez-Viezcás et al., 2011), *Glycine max* (Hernandez-Viezcás et al., 2013) and *Zea mays* (Lv et al., 2015) plants, and was ZnO-NPs not detected in the plant materials but in its form which resemble Zn-citrate (Hernandez-Viezcás et al., 2013) and Zn-phosphate (Lv et al., 2015), which also indicate the possible biotransformation of the NPs entities after the uptake. Wang et al. (2016a) also observed the presence of small amounts of Cu₂(OH)PO₄ (2.0%), Cu-acetate (3.2%) and Cu₂O (6.0%) in the seeds of *Arabidopsis thaliana* exposed to CuO-NPs (50 mg/L) and these constituents might be formed due to the uptake of solubilized NPs or the NPs dissolution after the uptake.

MeO-NPs can also penetrate the cell walls in their nano-form and enter to the plant roots, and even translocate to the shoots via xylem, particularly, in the case of NPs with limited solubility (e.g. CeO₂-, CuO-, TiO₂-NPs). Based on XANES analysis, Hernandez-Viezcás et al. (2013) reported that Ce remained mostly as CeO₂-NPs within the *Glycine max* plant grown in CeO₂-NPs (1000 mg/kg) amended soil. Besides to this, Yang et al. (2017) reported that CeO₂-NPs exhibit particle-specific toxicity and bioavailability to *Arabidopsis thaliana* plant. In very recent, uptake of CuO-NPs (size, 20–40 nm) in its nano-form by *Arabidopsis thaliana* was also reported (Wang et al., 2016a). According to the report, a significant amount of the NPs accumulated in the roots, leaves and flowers of the plant exposed to 50 mg/L suspension (time, 96 h), and based on XANES analysis, 88.8% of the Cu content in the harvested seeds was CuO-NPs. Similarly, direct uptake of particulate CuO-NPs by wheat was confirmed by XAS analysis, besides to the dissolved Cu²⁺ (Dimkpa et al., 2013). ZnO-NPs may also penetrate the root epidermis and cortex of *Zea mays* plant through the apoplastic pathway, as reported by Zhao et al. (2012a) based on confocal microscopic images. Similarly, the uptake of ZnO-NPs in the root cells of *Lolium perenne* was reported in the work of Lin and Xing (2008) based on scanning electron microscopy (SEM) and TEM

images. Al₂O₃-NPs can also have a significant effect on root growth and development of *Triticum aestivum* (Yanik and Vardar, 2015) which indicate its bioavailability to plants. Rajeshwari et al. (2015) also reported the uptake of Al₂O₃-NPs (R_D, 142.4–169.2 nm) by *Allium cepa* (exposure concentration, 0.01–100 µg/mL), and uptake of the nano-particulate may lead to ROS generation, which in turn contribute to the induction of chromosomal aberrations. Using high resolution TEM, Ansari et al. (2015) observed that Al₂O₃-NPs (size, 34.5 nm) can cross the cell membranes of *Pseudomonas aeruginosa* to become intracellular. CeO₂-NPs can be taken up in its nano-form from soils, and may exist as CeO₂-NP aggregates within a plant vascular tissues (Fig. 5) as investigated by Zhao et al. (2012b) using *Zea mays* plant. Furthermore, CeO₂-NPs can also have trans-generation impact on plants as reported by Wang et al. (2013b) using tomato plants, and second generation seedlings accumulated the higher amount of ceria than control seedlings under the same treatment conditions. On the other hand, the bioavailable CeO₂-NPs (at a lower concentration, 10 mg/L) may also cause changes in growth and physiology in plants, (e.g. *Brassica napus*), and also improves the plant salt stress (Rossi et al., 2016). It should be also noted that the surface charge (zeta potential) and the plants cell wall structure can affect accumulation of CeO₂-NPs in plants materials (e.g. within phytoplankton cytosol) as investigated using three algae species, *Phaeodactylum tricornutum*, *Nannochloris atomus* and *Chlamydomonas reinhardtii* (Sendra et al., 2017b). Co₃O₄-NPs (size, 60 nm) is also bioavailable to the root system and phytotoxic to *Allium cepa* (Ghodake et al., 2011). According to Faisal et al. (2016) the bioavailability of 1 mg/mL suspension of Co₃O₄-NPs (size, 21.3 nm) towards *Solanum melongena* was manifested by significantly reduced (85%) root length, and the NPs may also translocate to the cytoplasm and increase in ROS, membrane potential, and nitric oxide. Cobalt ferrite (CoFe₂O₄)-NPs (size, 17 nm (XRD-based)) is also bioavailable, and can also cause a decrease in catalase enzymatic activity and affect the nutrient uptake capacity of *Solanum lycopersicum* (Lopez-Moreno et al., 2016). The bioavailability of CoO-NPs (size, <100 nm) towards *Artemia salina* were also investigated and found that the particles can enter, accumulate, and cause toxic-effects to the organism (Ates et al., 2016). In recent, Iannone et al. (2016) observed the uptake of Fe₃O₄-NPs (size, 10 nm) by *Triticum aestivum* and using TEM, they detected the NPs in the epidermal cell walls of the plant roots. Similarly, Hu et al. (2017) found that Fe₂O₃-NPs could enter the *Citrus maxima* plant roots, even though its translocation was not observed. MnO_x-NPs are bioavailable to Lettuce (*Lactuca sativa*) and can significantly stimulate the growth of the seedlings (up to 68% at 50 mg/L) (Liu et al., 2016). The report of Oukarroum et al. (2015) showed the higher bioavailability and hence, higher toxicity of NiO-NPs (size, 30 nm) than NiO-bulk towards *Lemna gibba* plant. Moreover, it should be noted that the toxicity and bioavailability of NiO-NPs can be affected by the aggregation and redox processes (Gong et al., 2011). The bioavailability and possible accumulation (in the root), and translocation of small sized TiO₂-NPs (size, 14 nm) to other part of wheat (*Triticum aestivum*) (Larue et al., 2012) and cucumber (*Cucumis sativus*) (Servin et al., 2012) plants have been reported without dissolution and crystal phase modification (Table S12). This also indicates that the TiO₂-NPs may not bio-transform in the plant tissues, but can aggregate and form larger “coronas” than their original sizes (Fig. 6) (Du et al., 2011).

3.2. Bioavailability to other organisms

MeO-NPs are also bioavailable either in their dissolved or nano-form to various marine and terrestrial organisms (Table S12). In the work of Pakrashi et al. (2014a) the bioavailability of Al₂O₃-NPs (size, 40–100 nm) towards *Chlorella ellipsoidea* was investigated, and the

trophic transfer of the NPs to *Ceriodaphnia dubia* up on feeding the *Chlorella ellipsoidea* exposed to 20–120 µg/mL NPs was reported. Significant uptake/bioavailability and accumulation of CeO₂-NPs (size, <25 nm) in liver of zebrafish in aquatic environment was also reported in the work of Johnston et al. (2010). Marie et al. (2014) investigated the bioavailability of citrate-coated CeO₂-NPs (size, 3–4 nm) towards snail, *Planorbis corneus*, and observed the presence of Ce in the digestive gland of benthic organisms after weeks of exposure time. On the other hand, minimal bio-accumulation of CeO₂-NPs (size, 40 nm) in rat due to its ease retention in organs that typically remove circulating particles (slowly cleared from the lung) has been reported (Molina et al., 2014). Co₃O₄-NPs (size, <50 nm) are bioavailable to cells, can cross the plasma membranes via a non-endocytotic pathway and enter inside the cells (Bossi et al., 2016). Bioavailability and potential toxicity of Co₃O₄-NPs (size, 45 nm) towards human cells investigated by Papis et al. (2009) and their report showed that the NPs can enter to the cells, and cause rapid induction of ROS if supplied in its NPs-form rather than as ions. Similarly, using endothelial cell lines, Alinovi et al. (2015) reported that Co₃O₄-NPs (size, 17 nm) can pass through the cell membrane and accumulate within the cytoplasm surrounding the nucleus. Using marine invertebrates, *Scrobicularia plana* and *Hediste diversicolor*, CuO-NPs (size, 29.5 nm) were reported to be bioavailable to the organisms in its nano-form (Buffet et al., 2013, 2011). Using the same test materials, *Scrobicularia plana* and *Hediste diversicolor*, Mouneyrac et al. (2014) studied the bioavailability and bioaccumulation of CuO-NPs, and their result showed that the NPs can bioaccumulate as nanoparticulate forms in both organisms. Croteau et al. (2014) reported that high percentage (80–90%) of the bioaccumulated Cu in *Lymnaea stagnalis* originated from CuO-NPs (size, 7 nm), which indicate that dissolution has a negligible influence on Cu uptake from the NPs. Cronholm et al. (2013) also reported a high uptake and toxic-effect of CuO-NPs (size, 20–40 nm; concentration, 1–10 µg/mL) to the human lung cell lines in its nano-form compared to no, or low, uptake and toxic-effect of the corresponding soluble salts (concentration, 1–10 µg/mL). The bioavailability of CuO-NPs in its soluble (Cu²⁺) form may increase in the presence of another process like sulfidation (Ma et al., 2014c). Otero-Gonzalez et al. (2013) reported that Mn₂O₃-NPs (size, 30–60 nm) is bioavailable and can significantly (50% at 170 mg/L dosage) inhibit the O₂ consumption and can damage (30% at 1000 mg/L) the cell membrane of *Saccharomyces cerevisiae*. In the report of Gong et al. (2011) the bioavailability of NiO-NPs (size, 20 nm) towards algae, *Chlorella vulgaris*, were reported. Reports also showed that NiO-NPs are bioavailable to the human cells lines and cause significant effects (Ahamed et al., 2013; Duan et al., 2015; Horie et al., 2011; Pietruska et al., 2011). Ahamed et al. (2013) showed that 44 nm NiO-NPs are bioavailable to human liver cells and lead to cell death via ROS generation and induced apoptosis. Similarly, NiO-NPs (size, <50 nm) can enter to the human bronchial epithelial cells, undergo dissolution (Ni²⁺ forms) and inhibit cell viability (Duan et al., 2015). Similarly, NiO-NPs (size, 40–60 nm) was found to be bioavailable to *Artemia salina* (Ates et al., 2016). There are also reports on the definitive uptake of TiO₂-NPs by various organisms. In the work of Johnston et al. (2010) its bioavailability to fish from water column was demonstrated, and the report indicated that the TiO₂-NPs (size, <100 nm) can bio-accumulate in the gills and ionic Ti in the gut of trout. Based on TEM, SEM and EDS techniques, Picchiatti et al. (2017) reported that TiO₂-NPs could enter sea bass cell line and can cause different morphological changes. Using mud shrimp, *Corophium volutator*, Lerner et al. (2012) reported that the bioavailability of ZnO-NPs is primarily affected by the dissolved Zn ions, whereby the uptake occurs via the aqueous phase feeding and/or the ingestion of

sediment particles with adsorbed Zn^{2+} from the dissolved ZnO-NPs. Similar result, bioavailability of the ZnO-NPs in its dissolved form was also reported using *Daphnia magna* (Adam et al., 2015). On the other hand, Mouneyrac et al. (2014) investigated that the bioavailability and bioaccumulation of ZnO-NPs in two marine endobenthic species, the bivalve *Scrobicularia plana* and the ragworm, *Hediste diversicolor*, occurs in its both ionic and nano-forms. Indistinguishable uptake of Zn ions from ZnO-NPs and ZnCl_2 by the earthworm *Lumbricus rubellus* was also investigated and the uptake via dietary was dominant (~95%) than dermal uptake (~5%) (Laycock et al., 2016).

3.3. Factors affecting bioavailability of the MeO-NPs

As early stated, the transformations of MeO-NPs in the environment have a significant effect on their bioavailability. Therefore, while investigating the bioavailability of the materials, effects of associated to the environmental conditions should be put into consideration in addition to properties of the NPs.

The aggregation behavior and surface charge (Nur et al., 2015), and the presence of various macromolecules (Callegaro et al., 2015; Mwaanga et al., 2014) can also have a paramount effect on the bioavailability of TiO_2 -NPs in the environment. Aggregation usually decreases the ability of the NPs to penetrate into cells and hence lower its bioavailability (Du et al., 2011).

The size of the NPs is one of the parameters which can affect the transport and the NPs uptake. This is due to the fact that to enter into an organism cells, the materials should pass through the pores of cell membranes, which is directly dependent on the size of the NPs (Tripathi et al., 2017). In addition to this, size can also affect the NPs transformations such as aggregation, dissolution, redox reactions and others which have a significant effect on their bioavailability. For example, *Arabidopsis thaliana* plant can uptake CuO-NPs (size, 20–40 nm) but not bulk CuO (size, 1500 nm) when exposed to equal concentrations (50 mg/L) of the materials (Wang et al., 2016a) and the high uptake and accumulation of CeO_2 -NPs (size DLS, 155 nm) than its bulk counterparts (size DLS, 330 nm) in *Cucurbita pepo* roots was also observed (Hawthorne et al., 2014). In the work of Ates et al. (2015) higher bioavailability of smaller sized γ - and α - Al_2O_3 -NPs towards *Artemia salina* was observed. In the report of Hazeem et al. (2015) smaller sized (20 nm) magnetite (Fe_3O_4 -NPs) were found to be more bioavailable to algae than larger sized (40 nm) NPs and bulk Fe_3O_4 , and high accumulation of Fe_2O_3 -NPs (size, 80–90 nm) compared to Fe_3O_4 -NPs (size, 140–160 nm) in zebrafish (*Danio rerio*) were also reported (Zhang et al., 2015b) which might be attributed to the size difference among the two particles. The size of TiO_2 -NPs has been also found to affect its bioavailability towards various organisms. For example, Du et al. (2011) reported that smaller TiO_2 -NPs penetrate plants cell walls than the larger NPs. Similar results were reported using *Triticum aestivum* (Larue et al., 2012) and *Cucumis sativus* (Servin et al., 2012) plants. Larue et al. (2012) also reported that TiO_2 -NPs bioavailability is strictly size-dependent, where <36, 40–140, and >140 nm were translocated from the roots to the shoots, retained in the roots, and excluded from the plants, respectively. The low concentration of ZnO-NPs aggregates was investigated in corn tissues using confocal microscopy by Zhao et al. (2012a) which suggest that only smaller size NPs can enter the cell walls of the plant materials. These examples show that the smaller NPs can easily enter to the cell body than the larger NPs in size. The size of the NPs can also affect their translocation from the root to the shoot parts in plants and transportation to various organs in other organisms. On this regard, Collin et al. (2014) observed that smaller sized particles can be taken up from root to shoot easily than the larger sized particles. A lesser amount of 25 nm CeO_2 -NPs were transferred to the areal

parts of cucumber plants than the smaller sized (7 nm) CeO_2 -NPs (Zhang et al., 2011). Similarly, 10 nm CeO_2 -NPs were more translocated to the upper plant parts than 20 nm CeO_2 -NPs (Schwabe et al., 2015).

Besides to size of the NPs, their phase can also affect the uptake and accumulation processes in plants. For instance, α - Al_2O_3 -NPs showed lower toxicity than the γ - Al_2O_3 -NPs (both with comparable R_D , 280 and 256 nm for α - and γ - Al_2O_3 -NPs, respectively) towards *Bacillus licheniformis* at 0.05–5 $\mu\text{g}/\text{mL}$ exposure concentration (Pakrashi et al., 2014b). Similarly, in the presence of two phases of TiO_2 -NPs, anatase and rutile, Servin et al. (2012) reported that the former phase remained preferentially in the root tissues of *Cucumis sativus* whereas, the rutile phase translocated to the aerial tissues of the plant. In very recent, lower toxicity of anatase TiO_2 -NPs (size, 20–40 nm) towards macrophages was also reported compared to the corresponding rutile TiO_2 -NPs (size, 20–40 nm) at the same dosage, 50 mg/L, and the difference was suggested to be due to their different affinity towards the biomolecules (Yu et al., 2017).

The bioavailability of MeO-NPs may be also affected by the coating materials and stabilizing agents used for different purposes. On this regard, Merdzan et al. (2014) investigated the effects of polyacrylic acid and sodium hexametaphosphate coating materials on the bioavailability of ZnO-NPs towards *Chlamydomonas reinhardtii*, and high dissolution and hence bioavailability of uncoated ZnO-NPs followed by polyacrylic acid coated NPs were observed which agree with the report of Gelabert et al. (2014). On the other hand, the bioaccumulation of sodium hexametaphosphate stabilized ZnO-NPs was greater than could be attributed to the release of free Zn from the particles which might be attributed to the biological stimulation of the test model to phosphate from the particle coating. Besides, the alginate coated CeO_2 -NPs were found to be less bioavailable than uncoated NPs (uncoated NPs bioaccumulate more in the plant materials). The high bioavailability of Fe_3O_4 -NPs and nanoscale zerovalent iron (nZVI) than the suspended carboxymethyl cellulose stabilized nZVI and $\text{Fe}(\text{II})\text{aq}$ to fish were reported in the work of Chen et al. (2012b). As benthic organisms or fish accumulate metals through direct oral ingestion of aggregates and sediments, Fe_3O_4 -NPs and nZVI are more bioavailable to fish due to their high aggregation behavior than the stabilized counterparts.

Other factors such as pH, IS and DOM could also alter the extent of MeO-NPs bioavailability in the environment. pH, mainly affect the extent of NPs dissolution in the environment, and therefore, their bioavailability could vary with pH. The effect of pH on the bioavailability and toxicity of ZnO-NPs in soils to the terrestrial isopod *Porcellionides pruinosus* (Tourinho et al., 2013) and soil bacterial communities (Read et al., 2016) were reported, and a significant effect was observed with low and medium pH levels (4.8 and 5.9) (Read et al., 2016) might be due to the high dissolution of the NPs at lower pH values. Unfavorable deposition and aggregation increases with IS and hence decreases the NPs uptake (bioavailability). Yung et al. (2015) reported that salinity increases the aggregate size and decreases the dissolution, and consequently lower the bioavailable forms of the NPs. The presence of DOM probably increases the NPs bioavailability, especially when the coating due to DOM adsorption is biocompatible. Besides, being one of the parameters affecting the dissolution and aggregation of MeO-NPs in the environment, the presence of extracellular polymeric substances in wastewater system is one of the determinants affecting their bioavailability. In the report of Miao et al. (2015) the presence of NOM can suppress CuO-NPs aggregation and increase dissolution, which increases the bioavailability of the materials.

Furthermore, exposure roots (soil, water, and sediment), and application forms (dry powder or suspension spiking) may also affect the extent of NPs bioavailability. For example, the roots of *Vigna unguiculata* exposed to ZnO-NPs and ZnCl_2 solutions (25

mgZn/L) differ significantly in a solution culture, whereas similar in a soil culture regardless of the spiking solutions (Wang et al., 2013a). According to the report, high uptake was observed in solution culture. In the work of Ramskov et al. (2015) the effect of exposure routes (water and sediment) and Cu forms (aqueous and nanoparticulate) on the bioavailability and subsequent toxicity of CuO-NPs towards the freshwater oligochaete, *Lumbriculus variegatus*, has been investigated. In the work, it was found that both forms of Cu exhibited similar accumulation in the organism, and at realistic sediment to water partitioning in freshwater systems (i.e., K_d of 10^4 – 10^6), sediment was predicted to be the primary exposure and uptake pathway for both aqueous and CuO-NPs forms. Similarly, diet exposure to CuO-NPs towards *Lymnaea stagnalis* was reported to bioaccumulate and cause adverse effects more readily than waterborne exposures (Croteau et al., 2014). This indicates that researchers are highly recommended to pay attention to the environmental systems which are considered as exposure route (water, and sediment) while assessing the toxicity of such materials in aquatic systems.

In general, based on the studies conducted on various test materials, it can be said that MeO-NPs are mainly bioavailable in their either dissolved and/or nano forms to the biota (Pakrashi et al., 2013). The bioavailability of MeO-NPs in environmental system is affected by various factors such as the nature of the test materials, type and physicochemical behaviors of the NPs and their coating agents, the constituent materials (e.g. NOM) in the test medium, activity of the soil organisms application and exposure routes, and chemistry of the test conditions such as pH, IS and others. Due to the high aggregation behavior of MeO-NPs, mainly in waters, benthic organisms are highly exposed to the materials via oral exposure up on feeding the deposited NPs aggregates below the aqueous phase and sediments contaminated with NPs.

4. Future research directions

Investigation of the fate, stability, toxicity and transport of MeO-NPs in the environmental systems, and their interaction with macromolecules, tissues, and organs in biological systems *in vitro* and *in vivo* will provide an insight knowledge to design friendly nanomaterial for different application scenario (He et al., 2015). Based on the current knowledge, more research works are expected on the engineering of degradable and less toxic NPs to minimize their environment related issues. For example, due to the fact that organic solvents can alter the shape, size, and other physicochemical properties of NPs that ultimately modulate biological, chemical, and environmental properties (Ali et al., 2017), the toxicity and bioavailability of MeO-NPs can be tailored by modifying the synthesis parameters/conditions (Ali et al., 2017; Caramazana-González et al., 2017; Papadaki et al., 2017; Punnoose et al., 2014) or by coating with biologically inert compounds (Ortelli et al., 2016; Sotiriou et al., 2014). Punnoose et al. (2014) synthesized two ZnO-NP samples (size, 9.26 nm each) from the same precursor, zinc acetate, and modified their surface chemical structures using different reaction solvents, diethylene glycol and denatured ethanol, which led to major differences in the ζ -potential, R_D , photocatalytic rate constant, and more importantly, their cytotoxic effects on Hut-78 cancer cells (IC_{50} , 0.37 and 0.56 mM, using diethylene glycol and denatured ethanol reaction solvents, respectively). Besides, coated ZnO-NPs and TiO_2 -NPs (Ortelli et al., 2016) exhibited lower toxic-effects due to minimum dissolution and no direct contact with cellular bodies in the case of ZnO-NPs and avoid the ROS generation for the case of TiO_2 -NPs. In the report of Papadaki et al. (2017), a ZnO-NPs synthesis route based on electricity and renewable energy can improve the environmental sustainability of the nanoparticles by 25%. Besides, a

precursor selection in preparation of NPs also plays a great role in determining cradle-to-gate environmental impacts. For instance, simple precursors such as titanium oxysulphate showed the lowest global warming potential and cumulative energy demand than the complex organic precursors like titanium bis(ammonium-lactato) dihydroxide (Caramazana-González et al., 2017). Therefore, further research works are expected on designing experimental procedures, appropriate precursors and coating materials which lead to the synthesis of environmentally friendly NPs, while preserving their attractive properties.

On the hand, careful consideration should be rendered and strategies and regulations should be developed for the application in various areas and consumption of the different products comprising the NPs. Particularly, future researches should focus on developing techniques for the recycling of the materials to minimize their release to the environmental systems (Joo and Zhao, 2017). In addition, effective techniques should be developed for the removal of NPs from wastes before their release, particularly, clogging and subsequent short circuiting may be considered as they can decrease the overall treatment processes.

Most of the current studies are laboratory based (used synthetic media), and the considered concentration of the NPs are incomparable with their amounts in the natural environment. Obviously, it is a challenging work to undertake studies on transformations, fate, and bioavailability of NPs in the environment at concentrations that are realistic and environmentally relevant due to the complexity of the transformation processes (multiple processes may occur in parallel) and inadequacy of the instrumental techniques to track the particles behavior at various transformation stages (Lowry et al., 2012). However, to avoid artifacts associated with the very high concentrations considered in various reports, such studies are highly recommended from an environmental point of view.

There are numerous macromolecules (natural and anthropogenic) existing in the environment compared to the limited amounts of released MeO-NPs. After adsorption (interaction) of these molecules to the surface of the NPs, the particles own different property. Therefore, to exactly elucidate the property, impact, persistence and bioavailability of MeO-NPs in complex media, the probable interactions between these counterparts and the exact behavior of the transformed NPs should be researched more.

5. Conclusions

MeO-NPs are introduced to the environment via different pathways, such as waste removal (effluents, solid waste removal), intentional applications for different purposes, accidental release during production and consumptions. Among these routes, waste water discharge is the main pathway for the NPs release to the environment. Consequently, various NPs are being detected in various environmental systems across the world. After being released, NPs can interact with different environmental components, undergo transformations and exhibit different behavior from their pristine form. The main transformation processes are aggregation/agglomeration, adsorption, deposition, dissolution, redox reactions, and interaction with macromolecules via various mechanisms, and these processes are interlinked phenomena of NPs in the environment. The processes are affected by behaviors of the NPs (e.g. size, morphology, surface charge), and conditions of the medium such as IS, pH, temperature, and the presence of various components (NOM, proteins, polysaccharides, radicals, surfactants).

There are MeO-NPs which are bioavailable in their nano-form to the biota. However, most of the NPs transform to other forms (their

corresponding metal ions and other products) which are more bioavailable than their sources. More or less, stable NPs are less bioavailable than the one which undergoes various transformations in the environment. The bioavailability of MeO-NPs in the environment depends on parameters such as physicochemical property of the NPs (e.g. type of the NPs, size, phase and morphology), type of coating materials and stabilizing agents (if used), chemistry of the medium, application modes, route of exposure, and the considered test materials.

Disclosure statement

No potential conflict of interest was reported by the authors.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.envpol.2017.06.064>.

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