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Review article

THE EFFECT OF NANOPARTICLE ZnO ON ENVIRONMENT AND DIFFERENT ORGANIZMS (Review)

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ABSTRACT: Nanotechnology has noticeably developed with potential effects in every science specially by using nanoscale chemical element. Among nano material ZnO is more attention due to its special properties and its less hazard to environmental impact. ZnO like most of nanoparticles is toxic in organiam, however the toxicity of this nanoparticles can be used for antibacterial, antifungal, antiviral and antialga. To reduce the hazard effect of nanoparticles some manufact or chemical particles such as Nanoscale zero-valent iron are introduce that can be used for environmental remediation of polluted water, soil and sediments. In the present study, the effect of Nanoparticle ZnO on environment and different organisms from virous to fish has been reviewed and the application of nanoscale material in treatment of water are discusse

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INTRODUCTION

Applying nanotechnology have occurred rapidly, and the use of nanoparticle is being used in all sciences in area of chemistry, physics, medicine and biology. Because of their high flexibility and strength, it is becoming increasingly important in modern industry. Nanotechnologies have huge potential for solving numerous problems for example from increasing the treatment efficiency and diagnosis of various diseases to economizing materials and energy resources [1]. There are intensive investigations in the direction of applying nanoparticles in biomedicine [2], studying the physicochemical properties of polymers [3], and wide applications in agricultural and aquaculture.

Metal-based nanoparticles are produced from iron, titanium and a variety of other metals and their oxides. Nanoparticles characteristically have very high surface area to volume ratios [4], which means that, compared to their bulk counterparts, the properties of nanoparticles (NPs) can vary dramatically under different electrical, photological, and thermodynamic conditions [5]. Of these properties, the ability to affect the redox potential of the nanoparticles by altering the state of the free radical has received considerable attention in the literature [6].

There are many types of NPs having environment and ecotoxicity effect. Natural NPs have existed in the environment and can be found in waters, soils and sediments. Some chemical factors such as pH, ionic strength, water hardness and the presence of organic matter will alter chemistry properties of these elements influence its toxicity. Manufactured NPs is also sources of pollution and its release to environment should be control.

The rapid development of nanotechnology holds great promises for application in nutritional science in fish. The toxicity of NPs to fish depends on the chemical form of NPs and the condition of animal, type of species, physiological state, nutrition and dietary interactions, dosage and time of administration. For minimizing the effect of nanoparticles in aquaculture and protecting the environment the application of Nanoscale zero-valent iron (nZVI) is under investigation. Nanoscale zero-valent iron (nZVI) has been used increasingly over the last decade to clean up polluted waters, soils and sediments [7]. The nZVI particles reduce toxic-chemicals through oxidation of the Feo core and subsequent allocation of electrons to the pollutant [8]. Controlling the activity of harmful microorganism or inactivation of them by different materials were examined by many scientists and many objects. In the present review the effect of Nano-iron in as well as the property of nZVI on different organism are discussed.

EFFECT ON ENVIRONMENT

In environment the important object is the effect of nanomethal to the organism as well as the associated environmental hazards and risks. It is well known that organisms need trace methal at a very low dosage. For example fish have essential nutrition requirements for trace metals e.g. copper, zinc, and iron [9], but the amount and available dosage of metal in environment is very important. Excess of these element causes problem in kidney and liver of fishes.

Mechanisms of respiratory toxicity are also possible with metals, and for example, excess iron (irrespective of bioaccumulation) can result in iron flocs on the gills which can clog the gills resulting in respiratory distress [10]. The use of nanoscale materials is growing exponentially, but parallely there are also concerns about the environmental hazard to aquatic biota. Metal-containing engineered nanoparticles (NPs) are an important group of these new materials, and are often made of one metal (e.g., Cu-NPs and Ag-NPs), metal oxides (e.g., ZnO and TiO NPs), or composite of several metals. The physiological effects and toxicity of trace metals in the traditional dissolved form are relatively well known and metal toxicity in fish were reviewed by Benjamin et al. [11].

Nano particle may be used in environment for treatment of soil or water. Generally In the environment, iron exists naturally either in the dissolved phase as ferric or ferroussalts or in the solid phase as iron oxides such as goethite and hematite [12], while nZVI is a manufactured material with special properties that are advantageous in remediation processes [13]. Also, nZVI can be anchored on a solid matrix and used for water, wastewater or gaseous stream treatments [14].

GENOTOXICITY EFFECT

Authigenesis or neoformation is a the reverse process that it takes place when chemical degradation eventually results in high enough concentrations of certain dissolved species to exceed the saturation in solution of a phase, leading to its nucleation and growth. The early forming nuclei of authigenic or neoformed phases are sub-nanometric in size and may either re-dissolve, grow to form larger particles, or remain nanosized. The nanoscale particles can be stabilised in solution by organic species such as humic substances [15], or simply because it is not thermodynamically possible to grow larger particles. Many common soil and water components contain natural NPs that are grown by authigenesis/neoformation including clay minerals and iron oxyhydroxides.

There are fewer data for metal based engineered nanomaterials and only a few reports focusing on genotoxicity. Iron nanoparticles including bare iron particles and polyaspartic acid modified iron particles were genotoxic, while iron modified with dextran was not [16]. These data suggest that metal nanoparticles may be genotoxic and indicate the need for further study. In cytotoxic and genotoxic study of fish cells, Cell culture studies confirm the toxicity of engineered nanoparticles reporting cytotoxicity, decreased cell viability, and the production of proinflammatory agents (Monteiro-Riviere et al., 2005). These cell culture studies indicate that size and particle composition can dramatically modify toxicity, with some sizes and forms highly toxic and others nontoxic [17].

Effect on bacteria

The effect of NPs on bacteria is very important since bacteria constitute the lowest level and hence the entrance to the food chain in many ecosystems. Heinlaan et al. [18] reported the ecotoxicity to bacteria *Vibrio fischeri*, *D. magna* and *Thamnocephalus platyurus* on product formulations (nano or bulk oxides) and solubilization of particles. Suspensions of nano and bulk TiO₂ were not toxic even at 20 g/L. Zn formulations exhibited the following toxicities (EC₅₀ expressed as mg/L) for bulk ZnO, nanoparticles of ZnO and ZnSO₄·7H₂O: 1.8, 1.9 and 1.1 for *V. fischeri*; 8.8, 3.2 and 6.1 for *D. magna*; and 0.24, 0.18 and 0.98 for *T. platyurus*, respectively. A study with both volunteers and laboratory animals showed that nano- particles taken up passively and actively by cells such as macrophages or cells of lung epithelium may end up in mitochondria and disrupt cellular processes [4].

Brayner and his colleques report preliminary studies of biocidal effects and cellular internalization of ZnO nanoparticles on *Escherichia coli* bacteria. The results confirmed that *E. coli* cells after contact with DEG and ZnO were damaged showing a Gram-negative triple membrane disorganization. This behavior causes the increase of membrane permeability leading to accumulation of ZnO nanoparticles in the bacterial membrane and also cellular internalization of these nanoparticles [19].

Recently, the effect of 1-hour exposure of a wild-type, in the rare situation when bioavailable iron is in excess, it might induce oxidative stress, and a mutant bacterium *E. coli* to nanoparticulate Fe₂O₃, Fe₃O₄ and nZVI. Transmission electron microscopy showed morphological changes of bacterial cells, and also changes of the nZVI shape [20]. Pristine nZVI showed an inhibitory effect on bacteria at concentrations of 5 mg L⁻¹. When applied under aerated conditions, the toxic effect was lower than under anaerobic conditions. This result was predictable because nZVI oxidizes under aerobic conditions. Natural organic matter coating and polymers decreased the toxicity of nZVI significantly, probably due to a thick layer formed by the polymer preventing adhesion to the cell surface [21]. The anaerobic dechlorinating bacteria *Dehalococcoides* spp. Was sensitive to nZVI exposure by the bioremediation of trichloroethylene using a mixture of bacterial species [22].

Effect on plant and Algae

In experiment with the plant, root elongation in all plants was completely inhibited by 2,000 mg/l of nanozinc and nanozinc oxide. Among the nanomaterials tested only Zn and ZnO had significant inhibition on germination and root growth of the plant species. Inhibition was predominant in the seed incubation process rather than the seed soaking process [23].

In an study for toxicity experiments using the freshwater *Iga Pseudokirchneriella subcapitata* revealed comparable toxicity for nanoparticulate ZnO, bulk ZnO, and ZnCl₂, with a 72-h IC₅₀ value near 60 µg Zn/L, attributable solely to dissolved zinc. Care therefore needs to be taken in toxicity testing in ascribing toxicity to nanoparticles perse therefore needs to be taken in toxicity testing in ascribing toxicity to nanoparticles perse when the effects may be related, at least in part, to simple solubility [24].

In using bioactive Iron, in the rare situation when bioavailable iron is in excess, it might induce oxidative stress, which affects algal growth and has a negative impact on natural phytoplankton. Estevez et al. [25], studied the effect of surplus redox-active iron on oxidative stress in *Chlorella vulgaris*. When culture medium was supplemented with 500 µM iron, the cells showed elevated levels of membrane lipid peroxidation and other oxidative stress signs. It is likely that nZVI can show similar or stronger effects on algae than micro scale iron due to their higher specific surface area.

In an another experiment Kobayashi et al. [26], examined the possible function of Fe²⁺ as a ROS generator in the unicellular green alga *Haematococcus pluvialis*. Addition of 450 µM Fe²⁺ enhanced the formation of hydroxyl radicals in the cells via the Fenton reaction. *H. pluvialis* responded by producing the carotenoid antioxidant astaxanthin, which was localized in cytosolic lipid bodies. With excess addition of 600 µM Fe²⁺, carotenoid formation was reduced, probably due to severe ROS injuries [27].

Effect on Microscopic fungi

In spite of its importance very few articles are available about the effect of nanoparticles in fungi. Nanoparticles might have direct and indirect effects on fungi that should be study. In experiment by Diao, and Yao (28) on the direct effects of nZVI on fungi, using *Aspergillus versicolor*, the authors tested the capacity of nZVI to inactivate bacteria and *A. versicolor*. Even when the fungal culture was treated with a relatively high concentration of nZVI, the effect on its viability was zero. Possible explanations for this might be the very short exposition time; the fungus had been in contact with nZVI for only five minutes. Regarding indirect effects, symbiotic fungi or bacteria may be harmed by nanoparticles as parts of mycorrhizas and lichens, which may cause reduced nutrient availability for plants [29]. Mycorrhizal fungi can protect host plants against oxidative stress, but this beneficial role might be affected by nanoparticles. In experiments with the application of nZVI to soil prior to or during the growth of mycorrhizal plants, resulted in severe reduction (30-50%) in plant growth without mycorrhiza being able to alleviate the stress or toxicity caused by nZVI. Such stress alleviation by mycorrhizas is commonly observed with other abiotic stressors [30].

Effect on Zooplankton

Study of the effect of nano particle ZnO also is very rare in zooplankton. In an experiment, the nanoparticles of TiO₂, Al₂O₃, and ZnO were detected in the gut of the daphnias kept in suspensions of nanoparticles for 48 h [31]. In this process, titanium dioxide nanoparticles rapidly accumulated over 12 h, whereas their excretion was slowed and a considerable part of these nanoparticles still remained in the daphnia body 72 h later [32].

The acute toxicity on *D. magna* of different NPs including ZnO, SiO₂ and TiO₂ was also studied by Adams et al. [33]. ZnO NPs were found to be the most toxic with EC₅₀ values of 0.5 mg/L. Particle size was not found to be related to the toxicity.

Effect on macrophages

Manufactured Single-walled carbon nanotubes (SWCNT) usually contain significant amounts of iron that may act as a catalyst of oxidative stress. Because macrophages are the primary responders to different particles that initiate and propagate inflammatory reactions and oxidative stress, Kagan and his colleagues utilized two types of SWCNT: (1) iron-rich (non-purified) SWCNT (26 wt.% of iron) and (2) iron-stripped (purified) SWCNT (0.23 wt.% of iron) to study their interactions with RAW 264.7 macrophages. SWCNT with different iron content displayed different redox activity in a cell-free model system as revealed by EPR-detectable formation of ascorbate radicals resulting from ascorbate oxidation. In the presence of zymosan-stimulated RAW 264.7 macrophages, non-purified iron-rich SWCNT were more effective in generating hydroxyl radicals than purified SWCNT [34].

Toxic Effects to Viruses

There is a need to have more study on the effect of ZnO to virus, because there is also a lack of enough information in this field. nZVI has been shown to be capable of removing viruses (e.g., ØX174 and MS-2) from water by inactivating them and/or irreversibly adsorbing the viruses to the iron [35]. Although toxicity to viruses is not usually a primary concern, the information could be indicative of how the nZVI will interact with other organisms. Traditionally used disinfectant chemicals, such as chlorine, have been shown to be more effective for killing bacteria than viruses [36]. Recently, the virostatic potential of micro-nano filopodia-like ZnO structures against herpes simplex virus-1 also have been investigated and showed the potential of ZnO [37].

Effect on protozoa

The toxic effects of Nanoparticles (NPs) of ZnO and CuO to particle-ingesting model organism protozoa *Tetrahymena thermophila* were evaluated. Nano- ZnO was remarkably more toxic than nano- CuO (EC₅₀ values ~5 mg metal/l versus 128 mg metal/l). Toxic effect of CuO depended on particle size: nano- CuO was about 10–20 times more toxic than bulk CuO. However, differently from CuO particles, bulk and nanosized ZnO as well as Zn²⁺ were of similar toxicity. Thus, the toxic effect of both, CuO and ZnO (nano)particles to protozoa was caused by their solubilised fraction [38].

Toxic Effects to Fish

Recently, due to ecological changes and degradation of their natural spawning ground in most water body, the number and variation of fish have been decreased sharply. The scientist have consideration attention in biological study and inducing artificial spawning to prevent diminish of some valuable and endangered fish species [39-41].

Nanoparticles (NPs) including ZnO have a potential environmental danger. For organisms living in the aquatic environment, there is uncertainty on exposure because of a lack of data regarding the effect of nanoparticles in behavior, physiology and bioactivity of organism in nanomaterials in the water. There are several sample of the effect of nanoparticles and its effect on fishes. Dietary Fe has previously been seen to cause lipid peroxidation in the liver and heart of African catfish [42]. An increase in intracellular reactive oxygen species (ROS) was observed in zebrafish embryos exposed to nano-ZnO and implemented in some toxic effects [43].

Effects on early life stages of fish are emerging with reports of nanometals crossing the chorion (e.g., Ag-NPs), and suggestions that the nano-forms of some metals such as ZnO NPs may be more toxic to embryos or juveniles, than the equivalent metal salt. [11].

There is study also on the oral administration of TiO NPs in mice [44], and studies on the absorption of fine ZnO and TiO₂ particles across porcine skin [45]. These product applications of TiO₂ suggest these materials are likely to be in effluents, or released directly into the environment during use, and the known toxic effects in mammalian models raises concerns about other vertebrates including fish [46]. Furthermore, a bulk TiO₂ control may also be uninformative in a dietary study because of the background of natural titania already in the animal feed ingredients. This type of problem is well known for studies on dietary iron where the metal is so abundant in the earth's crust and in all the feed ingredients (e.g., fish meal) that it is technically impossible to make an iron-free basal diet; e.g., Carri-quiriborde et al. [47].

In experiment with medaka fish (*Oryzias latipes*) and their embryos the effects of nZVI were examined. Both the exposed embryos and medaka adults were exposed to different doses of nZVI (0.5, 5, and 50 µg/mL) in water to determine if observed effects were dose-dependent. A significant decrease of SOD and glutathione (GSH) activity was observed in liver and brain samples taken from the adults, but as the exposure time increased, the adults appeared to recover from the exposure by adjusting the levels of antioxidant enzymes [48].

The adults were also examined for possible histopathological and morphological changes. The gill and intestine samples showed considerable change but the liver and brain samples did not show significant change. At exposures of 5 and 50 µg/mL of nZVI, gill samples were observed with swollen epithelium cells, missing scales, black particles deposited on the surface, and few tacticpillar cells. Pilot remediation tests have previously used concentrations of approximately 4.5 to 10g/L of nZVI slurry (i.e., 4,500 to 10,000 µg/mL) [49].

In experiment by Baker et al., [42], in order to determine the effect of increased iron intake on growth and lipid peroxidation criteria in fish, African catfish (*Clarias gariepinus*) juveniles of mean weight 32.25 g were fed a ration of 2% body-weight per day, for 5 weeks on fishmeal-based diets containing either 663.5 ± 56.4 or 6354.4 ± 70.3 mg iron per kg dry diet (supplied as FeSO₄·7H₂O). Ingestion of the higher dietary iron ration resulted in suppressed growth in catfish, implying that the metal was supplied at toxic levels, though tissue concentrations of the metal were unaffected by dietary regime and haematocrit values were not significantly different between treatments. In experiment by Dalzell his colleague, the 96-h LC50 on brown trout *Salmo trutta* of a commercial iron (III) sulphate liquor, used for treating reservoirs to reduce algal growth, was 28 mg total Fe l⁻¹ (0.05 mg soluble Fe l⁻¹). The 96-h LC50 for analar grade iron (III) sulphate was 47 mg total Fe l⁻¹ (0.24 mg soluble Fe l⁻¹). Lethal and sublethal exposure to both grades of iron resulted in accumulation on the gill, which appears to be the main target for iron toxicity. Greater iron accumulation occurred during exposure to commercial iron sulphate liquor. Iron did not accumulate in plasma of fish exposed to iron compared to controls. Respiratory disruption due to physical clogging of the gills is suggested as a possible mechanism for iron toxicity [10].

In integrative biological and physicochemical studies on the uptake of unmodified commercial nanoscale metal oxides, zinc oxide (ZnO), cerium dioxide (CeO₂), and titanium dioxide (TiO₂), from the water and diet to determine their potential ecotoxicological impacts on fish as a function of concentration were reported by Johnston et al., [50]. Significant uptake of nanomaterials was found only for cerium in the liver of zebrafish exposed via the water and ionic titanium in the gut of trout exposed via the diet. For the aqueous exposures undertaken, formation of large NP aggregates (up to 3 µm) occurred and it is likely that this resulted in limited bioavailability of the unmodified metal oxide NPs in fish.

Effect on Water treatment

Different studies have been initiated focusing on safety issues of manufactured nanomaterials to minimize or eliminate their toxicity and ecotoxicity, even before they are used in the industry [51, 52, 53].

Water pollution is one of the largest environment problems in several countries. It mainly arises from wastewater released from household, industrial and agricultural processes that may contain high hydrocarbon solvents, heavy metals, pesticides, dyes and so on. Therefore treatment of wastewater before release into the environment is required [54]. The investigation into the effects on the aquatic environment from nanomaterial exposure is of high interest, particularly since the water cycle ultimately receives runoff and wastewater from domestic and industrial sources. In addition, there has also been increased development of water remediation techniques based on the use of nano- materials such as zero-valent iron NPs for wastewater treatment [55]. There are many works proposing that the degradation mechanism comprises of heterogeneous reactions. The reactions occur when the reactant molecules reach the iron solid surface. They then associate with the surface at sites that may be either reactive or non-reactive. Competition can also occur between the reactant solute of interest and other solutes for the available sites [56]. Chemical treatments of wastewater, surface water, and seawater involve the removal or the conversion of contaminants either by the addition of chemicals or through other chemical reactions. Flocculation is one of the most commonly used chemical treatments of water. In another study Flocculation is suggested and are believed it can be applied to remove organic matter from contaminated water, which may cause trihalomethane formation during disinfection in waste or drinking water treatment plants. Aluminum sulfate, iron salt, and polyaluminum chloride are mainly used as coagulants [57]. The flocculation processes using these salts produce a large amount of sludge that is disposed either into a landfill and/or dumped into the ocean at this time.

Removal of Heavy Metals by nano-particles

There are several techniques to eliminate the toxicity and pollution of water before drinking. Nano filtration membranes (NF membranes) are used in water treatment for drinking water production or waste water treatment [58].

NF membranes have been shown to remove turbidity, microorganisms and inorganic ions such as Ca and Na. They are used for softening of groundwater (reduction in water hardness), for removal of dissolved organic matter and trace pollutants from surface water, for wastewater treatment (removal of organic and inorganic pollutants and organic carbon) and for pretreatment in seawater desalination. Carbon nano tubes have been arranged to form a hollow monolithic cylindrical membrane [59], which was efficient for the removal of bacteria or hydrocarbons and that can easily be regenerated by ultra sanitations or autoclaving. Zero-valent iron also can be used to remove wastewater pollutants such as halogenated hydrocarbon compounds, heavy metals, dyes, pesticides, and herbicides. Zero-valent iron has been widely studied for removal of heavy metals such as chromium Arsenic [60]. The degradation mechanisms are based on transformation from toxic to non-toxic forms or adsorption on the iron surface depending on the type of heavy metals. The removal of chromium by zero-valent iron is based on transformation from toxic to non-toxic forms. Hexavalent chromium (Cr(VI)), which is a strong oxidant, a potential carcinogen and more mobile in soils and aquifers, is transformed to trivalent chromium (Cr(III)), which is less hazardous and less water soluble and associated with solids (Lee T.,2003). The reduction rate of Cr(VI) by Fe(0) produces ferric ion (Fe(III)) and chromium ion (Cr(III)) [61].

CONCLUSION

Nanotechnology has been shown to be an important of high technologies that can be used in a width range of human activities. It is used in agriculture, industry and medicine therapy. The development of nanotechnologies is the case of impact nano material in environment. Deposit of nanomaterials into the aquatic environment causes serious effect on environment organism either in fish or other living animals. Nanoparticle ZnO that recently are used frequently also may deposit in natural environment and via the fish causes hazard in human. Therefore it is suggested using of this nanoparticle such as others should be limited in aquatic organism.

REFERENCES

- [1]. zin A., Arsenault A.C. and L. Cademartiri 2009. *Nanochemistry: A Chemical Approach to Nanomaterials* (RSC Publishing, Cambridge,).
- [2]. Khlebtsov N.G. and L.A. Dykman 2010. "Optical Properties and Biomedical Applications of Plasmonic Nano particles," *J. Quant. Spectrosc. Radiat. Transfer*, 111, 1–35
- [3]. Picot D.R. and S. B. Ross 2002. *Murphy, Polymer Gels and Networks*, Ed. by Y. Osada Y. and A. R. Khokhlov (Marcel Dekker, New York).
- [4]. Oberdorster G., Oberdorster E. and J. Oberdorster 2005. Nanotoxicology: an emerging discipline evolving from studies of ultrafine particles. *Environ Health Perspect* 113 (7):823
- [5]. Dowling A.P. 2004. Development of nanotechnologies. *Mater Today* 7: 30–35.
- [6]. Shvedova, A.A., Castranova, V., Kisin, E.R., Schwegler-Berry, D., Murray, A.R., Gandelsman, V.Z., Maynard, A., Baron, P., 2003. Exposure to carbon nanotube material: assessment of nanotube cytotoxicity using human keratinocyte cells. *J. Toxicol. Environ. Health*.66: 1909–1926.
- [7]. D'Autréaux B. and M.B. Toledano 2007. ROS as signalling molecules: mechanisms that generate specificity in ROS homeostasis. *Nat. Rev. Mol. Cell Biol.* 8:813-824.
- [8]. Lacinova, L., Kvapil P. and M. Cernik 2011. A field comparison of two reductive dechlorination (NZVI and lactate) methods. *Environ. Technol.* DOI: 10.1080/ 09593330.2011.592225.
- [9]. Bury N.R., Walker P.A. and C.N. Glover 2003. Nutritive metal uptake in teleost fish. *J Exp Biol.*, 206: 11–23.
- [10]. Dalzell D.J.B. and N.A.A. MacFarlane 1999. The toxicity of iron to brown trout and effects on the gills: a comparison of two grades of iron sulphate. *J Fish Biol.*,55:301–315.
- [11]. Shaw B.J. and R.D. Handy 2011. Physiological effects of nanoparticles on fish: A comparison of nanometals versus metal ions. [Environment International 37: 1083–1097](#)
- [12]. Kirschling T.L., Gregory K.B., Minkley E.G., Lowry G.V. and R.D. Tilton. 2010. Impact of nanoscale zero valent iron on geochemistry and microbial populations in trichloroethylene contaminated aquifer materials. *Environ. Sci. Technol.*, 44:3474-3480.
- [13]. Ghauch A., Tuqan A. and H.A. Assi 2009. Antibiotic removal from water: Elimination of amoxicillin and ampicillin by microscale and nanoscale iron particles. *Environ. Pollut.*, 157:1626-1635.

- [14]. Zhang W.X. 2003. Nanoscale iron particles for environmental remediation: An overview. *J. Nanopart. Res.*, 5:323-332.
- [15]. Lead J.R. and K.J. Wilkinson 2006. Aquatic colloids and nanoparticles: current knowledge and future trends. *Environ Chem.*, 3:159-171
- [16]. Bourrinet P., Bengel H.H., Bonnemain B., Dencausse A., Idee J.-M., Jacobs P.M. and J.M. Lewis 2006. Preclinical safety and pharmacokinetic profile of ferumoxtran-10, an ultrasmall superparamagnetic iron oxide magnetic resonance contrast agent. *Invest. Radiol.* 41: 313-324.
- [17]. Goodman C.M., McCusker C.D., Yilmaz T. and V.M. Rotello 2004. Toxicity of gold nanoparticles functionalized with cationic and anionic side chains. *Bioconjug. Chem.* 15: 897-900
- [18]. Heinlaan M, Ivask A, Blinova I, Dubourguier H.C. and A. Kahru 2008. *Chemosphere* 71:1308-1316.
- [19]. Brayner R., Ferrari-Iliou R., Brivois N. et al. 2006. Toxicological impact studies based on *Escherichia coli* bacteria in ultrafine ZnO nanoparticles colloidal medium. *Nano Lett.*, 6:866-870.
- [20]. Auffan M.I., Achouak W., Rose J.r., Roncato M.-A., Chanéac C. et al. 2008. Relation between the Redox state of iron-based nanoparticles and their cytotoxicity toward *Escherichia coli*. *Environ. Sci. Technol.* 42:6730-6735.
- [21]. Li, Z.Q., Greden, K., Alvarez, P.J.J., Gregory K.B. and G.V. Lowry 2010. Adsorbed polymer and NOM limits adhesion and toxicity of nano scale zerovalent iron to *E. coli*. *Environ. Sci. Technol.* 44:3462-3467.
- [22]. Xiu, Z.M., Jin Z.H., Li T.L., Mahendra S., Lowry G.V. and P.J.J. Alvarez 2010. Effects of nano-scale zero-valent iron particles on a mixed culture dechlorinating trichloroethylene. *Bioresour. Technol.* 101:1141-1146.
- [23]. Lin D. and B. Xing 2007. Phytotoxicity of nanoparticles: Inhibition of seed germination and root growth. *Environ Pollut.*, 150(2):243-250.
- [24]. Franklin N.M., Rogers N.J., Apte S.C. et al. 2007. Comparative Toxicity of Nanoparticulate ZnO, Bulk ZnO, and ZnCl₂ to a Freshwater Microalga (*Pseudokirchneriella subcapitata*): The Importance of Particle Solubility. *Environ. Sci. Technol.*, 41(24): 8484-8490.
- [25]. Estevez M.S., Malanga G. and S. Puntarulo 2001. Iron-dependent oxidative stress in *Chlorella vulgaris*. *Plant Sci.*, 161:9-17.
- [26]. Kobayashi M., Kakizono T. and S. Nagai 1993. Enhanced carotenoid biosynthesis by oxidative stress in acetate-induced cyst cells of green unicellular alga, *Haematoococcus pluvialis*. *Appl. Environ. Microb.*, 59: 867-873.
- [27]. Li Y., Sommerfeld M., Chen F. and Q. Hu 2008. Consumption of oxygen by astaxanthin biosynthesis: A protective mechanism against oxidative stress in *Haematoococcus pluvialis* (Chlorophyceae). *J. Plant Physiol.*, 165:1783-1797.
- [28]. Diao M. and M. Yao 2009. Use of zero-valent iron nanoparticles in inactivating microbes. *Water Res.*, 43:5243-5251.
- [29]. Navarro E., Baun A., Behra R., Hartmann N.B., Filser, J., Miao A.-J., Quigg A., Santschi P.H. and L. Sigg 2008. Environmental behavior and ecotoxicity of engineered nanoparticles to algae, plants, and fungi. *Ecotoxicology*. 17:372-386.
- [30]. Smith S.E., Facelli E., Pope S. and F.A. Smith 2010. Plant performance in stressful environments: interpreting new and established knowledge of the roles of arbuscular mycorrhizas. *Plant Soil.* 326:3-20.
- [31]. Zhu X., Zhu L., Chen Y. and S. Tian 2009a. Acute Toxicities of Six Manufactured Nanomaterial Suspensions to *Daphnia Magna*, *J. Nanopart. Res.*, 11: 67-75.
- [32]. Zhu X.S., Wang J.X., Zhang X.Z., Chang Y. and Y.S. Chen 2010. Trophic transfer of TiO₂ nanoparticles from *Daphnia* to zebrafish in a simplified freshwater food chain. *Chemosphere* 79:928-33.
- [33]. Adams L, Lyon D.Y. and P.J.J. Alvarez 2006. Comparative ecotoxicity of nanoscale TiO₂, SiO₂, and ZnO water suspensions. *Water Res* 40(19):3527-3532
- [34]. Kagan V.E., Tyurina Y.Y., Tyurin V.A., Konduru N.V. et al. 2006. Direct and indirect effects of single walled carbon nanotubes on RAW 264.7 macrophages: role of iron. *Toxicol Lett.* 165(1):88-100.
- [35]. You Y., Han J., Chiu P.C. and Y. Jin 2005. Removal and inactivation of waterborne viruses using zerovalent iron. *Environ Sci Technol.* 39:9263-9269.
- [36]. Keane E. 2009. Fate, Transport, and Toxicity of Nanoscale Zero-Valent Iron (nZVI) Used During Superfund Remediation U.S. Environmental Protection Agency. Washington, DC www.epa.gov.

- [37]. Mishraa Y.K., Adelunga R., Röhlb C., Shuklac D., Sporse F. and V. Tiwarif 2011. Virostatic potential of micro–nano filopodia-like ZnO structures against herpes simplex virus-1. *Antiviral Research*, **92(2)**: 305–312
- [38]. Mortimer M., Kasemets K. and A. Kahru 2010. Toxicity of ZnO and Cu Onanoparticles tociiliated protozoa *Tetrahymena thermophila* *Toxicology*. **269(2–3)**: 182–189.
- [39]. Yousefian M., Gezel, H.G. and M. Hedayatifard 2008a. Induction of ovulation in endemic *Chalcarburnus chalcoides*, living in the Caspian Sea, using LRH-Aa. Combined with metoclopramide. *African Journal of Biotechnology*, **7 (22)**: 4199-4201
- [40]. Yousefian M., Hosseinzadeh-Sahafi H., Golshahi H., Laloei F., Tagavi M., Taheri A. and Y. Seidanloo 2011. Genetic parameters estimation of growth in *Salmo trutta caspius* as a function of body weight and Length. *Iranian Journal of Fisheries Sciences*, **11(1)** 214- 222.
- [41]. Yousefian M. and H.Mosavi 2008b. Spawning of south Caspian kutum (*Rutilus frisii kutum*) in most migratory river of south Caspian Sea. *Asian Journal of Animal and Veterinary Advances*, **3(6)**: 437-442.
- [42]. Baker R.T.M., Martin P. and S.J. Davis 1997. Ingestion of sub-lethal levels of iron sulphate by African catfish affects growth and tissue lipid peroxidation. *Aquat Toxicol.*, **40**: 51–61.
- [43]. Zhu X., Wang J., Zhang X., Chang Y., Chen Y. 2009b. The impact of ZnO nanoparticle aggregates on the embryonic development of zebrafish (*Danio rerio*). *Nanotechnology*. **20**: 195103. doi:10.1088/0957-4484/20/19/195103.
- [44]. Wang J.X., Zhou G.Q., Chen C.Y., Yu H.W., Wang T.C. et al. 2007. Acute toxicity and biodistribution of different sized titanium dioxide particles in mice after oral administration. *Toxicol Lett*, **168**:176–185
- [45]. Gamer A.O., Leibold E. and B. van Ravenzwaay 2006. The in vitro absorption of microfine zinc oxide and titanium dioxide through porcine skin. *Toxicol In Vitro*, **20**:301–307.
- [46]. Handy R.D., Henry T.B., Scown T.M., Johnston B.D. and C.R. Tyler 2008. Manufactured nanoparticles: their uptake and effects on fish—a mechanistic analysis. *Ecotoxicology*, **17**:396–409
- [47]. Carri-quiriborde P., Handy R.D. and S.J. Davies 2004. Physiological modulation of iron metabolism in rainbow trout (*Oncorhynchus mykiss*) fed low and high iron diets. *J Exp Biol* **207**:75–86
- [48]. Li H., Zhou Q., Wu Y.F. J., Wang T. and G. Jiang 2009. Effects of waterborne nano-iron on medaka (*Oryziaslatipes*): Antioxidant enzymatic activity, lipid peroxidation and histopathology. *Ecotoxicol Environ Saf.*, **72(3)**:684-692.
- [49]. Gavaskar A., Tatar L. and W. Condit 2005. Cost and performance report nanoscale zero-valent iron technologies for source remediation. Naval Facilities Engineering Command (NAVFAC). Contract report: CR-05-007-ENV.
- [50]. Johnston B.D., Scown T.M., Moger J., et al. 2010. Bioavailability of Nanoscale Metal Oxides TiO₂, CeO₂, and ZnO to Fish, *Environ. Sci. Technol.*, **44(3)**: 1144–1151.
- [51]. Lam C.W., James J.T., McCluskey R. and R.L. Hunter 2004. Pulmonary toxicity of singlewall carbon nanotubes in mice 7 and 90 days after intratracheal instillation. *Toxicol. Sci.*, **77**: 126–134.
- [52]. Hoet P.H.M., Bruske-Hohfeld I. and O.V. Salata. 2004. Nanoparticles – known and unknown health risks, *J Nanobiotechnol* **2** DOI: 10.1186/1477-3155-2-12.
- [53]. Zhu S., Oberdorster E. and M.L. Haasch 2006. Toxicity of an engineered nanoparticle (fullerene, C-60) in two aquatic species, *Daphnia* and fathead minnow. *Mar Environ Res* **62**:S5–S9
- [54]. National Research Council. 1994 Alternatives for Ground Water Cleanup, Committee on Ground Water Cleanup Alternatives. National Academy Press, Washington, D.C.
- [55]. Vaseashta A., Vaclavikova M., Vaseashta S., Gallios G., Roy P and O. Pummakarnchana 2007. *Sci Technol Adv Mat.*, **8**:47–59
- [56]. Burris D.R., Campbell T.J. and V.S. Manoranjan 1995. Sorption of Trichloroethylene and Tetrachloethylene in a Batch Reactive Metallic Iron-water System, *Environmental Science and Technology*, **29**: 2850-2855.
- [57]. DeWolfe J., Dempsey B., Taylor M. and J.W. Potter 2003. Guidance manual for coagulant changeover. American Water Works Association Press, Denver
- [58]. Hilal N., Al-Zoubi H., Darwish N. A., Mohammad A.W. and M. Abu Arabi 2004. Desalination, **170**, 281.
- [59]. Srivastava A., Srivastava O. N., Talapatra S., Vajtai R. and P. M. Ajayan 2004. *Nat. Mater* **3**, 610.
- [60]. Nikolaidis N.P., Dobbs G.M. and Lackovic J.A. 2003 Arsenic Removal by Zero-valent Iron: Field, Laboratory and Modeling Studies, *Water Research*, **37**: 1417-1425.
- [61]. Junyapoon S. 2005. Use of zero-valent iron for waste water treatment. *Kmitl Sci. Tech. J.*, Vol. 5 No. 3.