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Review Paper

Environmental impact of engineered nanomaterials

Saima Akram Khan
Department of Chemistry, St. Xavier's College - Autonomous, Mumbai 400 001, India
saima.khan@xaviers.edu

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Abstract

Advancements in the field of nanotechnology, have led to a concomitant rise in the incorporation of nanomaterials in consumer products. Engineered nanomaterials today are already being used in diverse commercial products in the fields of energy, sensing, food technology, electronics, pharmaceuticals, cosmetics, and material applications and have an estimated global market value of €20 billion. This has given rise to concerns about the undesirable effects of this technology on the environment. This review presents an overview of published studies about likely impact of nanoparticles in the ecosystem, their ecotoxicology, threat to human health and the environment and lack of sufficient data in the Indian context.

Keywords: Engineered nanomaterials, toxicity.

Introduction

Nanoparticles have been around for millions of years but our increasing ability to manipulate matter at the nanoscale has brought nanotechnology research into focus globally[1,2]. Roco et al predicted a global increase in the number of people working in the field of nanotechnology to an estimated total of 6 million by 2020[3]. This rapid development in nanotechnology has created new opportunities for high performance applications and new product innovation. However, there is a growing concern that the handling and disposal of engineered nanomaterials, may result in new, undesirable impacts on health and the environment[4-6]. Governments worldwide have started implementing policies and regulations for evaluating the risks of nanomaterials on health and environment[7]. Several reviews have focussed on the problems and risks associated with engineered nanomaterials[6,8-10].

Engineered Nanoparticles

The term 'nanomaterial' includes a range of materials that show unique properties due to their small size[11]. As per the definition adopted by the European Union "engineered nanomaterial" is any intentionally manufactured material, containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50% or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm to 100 nm'.

Extensive research has been carried out on the toxicology and health implications of nanoparticles, a majority of which is related to the impact of fullerenes, carbon nanotubes, quantum dots and ZnO and titania nanoparticles[12-14]. But data on nanoparticle toxicity is largely heterogeneous and also conflicting[14,15]. Understanding and interpretation of results is complicated because different types of tests have been used to study toxicity[16].

Difficulties in evaluating their potential impact arise because interactions of nanomaterials with the environment may often give indistinct signals[17,18]. Although characterization of nanomaterials with high degree of resolution is now achievable and some of these techniques maybe used to detect ENPs in water and soil samples but identification and quantification of ENPs in the environment still pose a challenge[19,20]. Further difficulties in detection of nanoparticles arise due to their interaction with other contaminants, influencing their ecotoxicity. Chemical transformations of nanoparticles in the environment and within living systems change their properties and reactivity[21]. Complications in characterization of engineered nanoparticles in natural environments arise also due to the fact that many engineered nanoparticles have their natural counterparts with the same composition.

Several papers outline the physicochemical principles that govern particle behaviour in an ecotoxicological context and some techniques that may be used to trace and quantify ENPs in various biological and chemical matrices[22,23]. Roth et al, and White et al have used Hyperspectral imaging (HSI) to evaluate the interaction of optically active nanoparticles in biological media and cells[24,25].

Toxicity of Engineered Nanoparticles

Small size, large surface area and enhanced reactivity are some of the features that are responsible for the widespread applications of nanomaterials but these very features also increase the possibility for them to cross cell membranes and enter inside cell organelles unlike bulk materials of the same chemical composition[26,27]. Results of various in vivo and in vitro studies carried out to compare the behaviour of nanoparticles with their bulk counterparts point to their enhanced toxicity. Several studies focus on the absorption, incorporation and translocation of nanoparticles and its effects in organisms[28]. Metal nanoparticles, carbon-based nanomaterials and quantum dots are some of the most widely studied ENPs.

Formation of reactive oxygen species(ROS) is found to be an important route of nanoparticle toxicity[29]. Generation of free radicals and ROS such as hydroxyl radicals leads to oxidative stress[30-32].

Large surface area of NPs increases its inherent toxicity due to enhanced interaction of organisms with these surfaces[33-35].

Ecotoxicity of Engineered Nanoparticles

To assess the impact of nanomaterials both toxicity and ecotoxicity need to be taken into account. Whereas toxicity deals with the harmful effects of a compound after its uptake, ecotoxicity looks at absorption mechanisms, bioavailability and its dependence on environmental factors. Transformations brought about by factors like pH, temperature, and salinity can alter ecotoxicity.

There are concerns that pollution could alter the path of natural nano-scale processes. Interaction of nanoparticles with other species could lead to their being rendered less harmful or less easily absorbed by organisms. Engineered nanomaterials have a tendency for aggregation, and agglomeration which depends on shape, size and surface area of particles[36,21].

Even though ecotoxicity studies of engineered nanoparticles are insufficient, data available from several studies indicate that several engineered nanoparticles are toxic to organisms even in low concentrations. To assess the threat posed by ENPs to organisms, data regarding reactivity, transport, absorption mechanisms and persistency in the environment is required.

Ecotoxicity of Carbon based nanoparticles

One of the first engineered nanoparticles to be investigated for their ecotoxicity is C60 fullerenes. Oberdörster was one of the first to examine that C60 even in concentrations as low as 0.5 mg/l can cause oxidative damage in fish (large mouth bass; *Micropterus salmoides*)[37] Although several publications attributed the toxic products to a THF degradation product. Adverse health effects of C-60 have since been reviewed and debated. Oxidative, genotoxic, and cytotoxic responses have been attributed to C-60[38,39]. These effects vary according to the form and chemical modifications of fullerenes[40]. Although in another contradicting report Gharbi et al show C-60 to be a powerful anti oxidant. The study involved use of C(60) in acute carbon tetrachloride intoxication in rats pointing to the fact that in the absence of a polar organic solvent C(60) could help protect the livers of rats from free-radical damage[41].

Liu Y, et al highlight variations in CNT toxicity through alterations in factors such as size, shape, impurities, surface charge and agglomeration. They discuss how CNT toxicity proceeds through oxidative stress, DNA damage mutation and progression towards malignancy and how routes of exposure routes influence its behavior[42]. Several studies highlight the dependence of CNT toxicity on exposure conditions, type of carbon nanotubes, structural characteristics, surface properties, chemical composition dispersion state and concentration[43-45] although more studies would help to gain a more comprehensive interpretation of the toxicity of CNTs[38].

Ecotoxicity of Inorganic Nanoparticles

Inorganic ENPs mainly Ag°, titania, ceria, zinc oxide, and iron oxides present in various manufactured products are associated with biota. Bottero et al found a strong relationship between biological malfunctions and the physico-chemical characteristics of very small nanoparticles. Ag° and CeO_2 are found act even at very low concentrations. TiO_2 being photo-active induced toxicity through ROS production[46].

Cytotoxic effects of TiO_2, ZnO, and CeO_2, were compared by Xia et al to explain the relationship between physicochemical properties and cellular uptake and translocation. ZnO acts via formation of reactive oxygen species (ROS), inflammation, and apoptosis, CeO_2 nanoparticles did not cause inflammation or cytotoxicity on absorption by cells but suppressed the formation of reactive oxygen species whereas TiO_2 even though followed the same uptake mechanism as CeO_2 but did not exhibit either protective or harmful impact. This leads to the conclusion that metal oxide nanoparticles could induce varied biological responses ranging from cytoprotective to cytotoxic[47].

ZnO NPs which have widespread applications in electronics, clothing, paints, cosmetic products, catalysts as well as in biosensors and medical devices are shown to have cytotoxic and genotoxic potential[48,49]. Various studies showed that ZnO NPs were cytotoxic for human lung epithelial cells They are shown to upset glucose metabolism in such cells cause mitochondrial dysfunction, and induce apoptosis[50,51]. Han Z et al carried out in-vitro studies on mice injected with single doses of ZnO nanoparticles which were taken up by Leydig and Sertoli cells, causing cytotoxicity due to DNA damage brought about by increase in reactive oxygen species[52]. Johnson et al showed that the exposure to ZnO NPs led to autophagocytosis of immune cells, due to rise in the levels of the autophagosome protein LC3A reactive oxygen species (ROS) production[53]. Several others reported DNA damage in human epidermal cells, and apoptosis in pulmonary epithelial cell lines through ROS and oxidative stress even when exposure to ZnO NPs was very low[49,54,55].

Experimental studies with nanotitania (having applications in self cleaning glass, low cost solar cells and cosmetics) have shown genotoxicity in aquatic organisms[56,57] and documented lung injury and inflammation, toxicity via oxidative stress in human cells[58-60].

A study investigating the impact of short-term exposures on workers in TiO_2 manufacturing units, documented increased oxidative stress, DNA and protein damage, as well as lipid peroxidation in their exhaled breath condensate (EBC) in comparison to unexposed control groups[61].

Silver nanoparticles are another example of nanoparticles commercialized into various products[62] and a large amount of AgNPs enter into aquatic ecosystems[63-65], are bioaccumulated[66-68] and liberate Ag^+ and induce formation of ROS[69,70]. Through observation of gene expression pattern Kwok et al suggested that disruption of sodium regulation was responsible for toxicity of AgNPs. They found that dissolution of silver nanoparticles depends on particle size, but coating materials influence agglomeration and toxicity[71] whereas Guo et al reported that particle size plays an important role in the genotoxicity of AgNPs. Comparative study of genotoxicities of silver acetate and silver nitrate has been done, to see the effect of nanosilver vis a vis ionic silver[72].

QDs with applications in semiconductor devices, lasers, TV and computer displays and for drug delivery may also pose a threat to human health. The uptake, transport and toxicity of QD are determined by environmental factors as well as properties such as size, charge, outer coating of quantum dots, and their oxidative and photolytic stability[73,74].

Environmental Hazards and Risks

A lot of the data available from toxicity studies is based on experiments performed on organisms in laboratory settings but the same results are not always obtained when the experiment is carried out in actual environments[75]. Despite a huge number of publications on nanotoxicology, it is still unclear how significant the potential adverse impacts are, and whether the benefits from nanotechnological developments outweigh the risks involved. The current literature on ecotoxicity of nanomaterials lacks much of the information needed to evaluate potential hazards and quantify exposure with hazard[27]. Assessment of hazard requires evaluation of the form of nanomaterial in the environment, transport, transformation bioavailability and bioaccumulation. Gebel, et al suggest categorisation of nanoparticles based on exposure pathway and mode of action, to evaluate hazards[76]. A large number of ongoing studies utilize different models to evaluate toxicology of diverse NPs but there is often a gap between modeled values with actual measured values.

There is a need to study sets of ENPs to allow for quantification of characteristics such as physicochemical properties and biological response outcomes which would help to build dose-response relation data[77,78].

Regulations

A study[79] on nano titania reported the surface water concentrations of TiO_2 nano particles between 0.012–0.057 μgL^{-1} in Europe, 0.002– 0.010 μgL^{-1} in the U.S., and 0.016–0.085 μgL^{-1} in Switzerland, but such data is hardly available for Indian environments[80] even though, much higher concentrations of nanoparticles due to rapid industrialization and lack of proper regulations may be expected[81].

Some studies have focussed recently on the presence of nanoparticles in commercial products in India and their distribution and prevalence in the environment[62] and risk management.

A few organizations, such as Indian Institute of Toxicology Research (IITR) and National Institute of Pharmaceutical Education and Research (NIPER), CSIR etc. are involved with nanotechnology related risk research in India.

However, there are no nanotechnology specific regulations in India currently, though there is an entire range of regulations that can extend to nanotechnology applications[82,83]. India is making rapid and noteworthy progress in nanotechnology but research on toxicity is not in pace with the rate of introduction of new materials[84-86].

Conclusion

Nanotechnology is a field with immense potential and applications in all walks of life. In a context of uncertainty about the risks there is a need for research to monitor the environmental occurrence and hazards related to nanoparticles so that benefits from nanotechnology and nanoscience outweigh the risks associated with it.

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