

Nanoparticles for Environmental Clean-Up: An Overview

Dr. Abhay Singh

*Associate Professor, Department Of Chemistry,
K.L.P College, Rewari-123401, Haryana, India.*

1. INTRODUCTION

This review considers aspects of the movement of nanoparticles in their passage from the selected point of administration to their intended locus of action, with an emphasis on the effects of particle diffusion in the often confined and complex spaces of the body. Nanomaterial extractions from renewable resources are significantly advantageous over particle synthesis techniques because of low energy cost involvement, process scalability parameters and simpler instrument requirement. Diverse nanotechnologies are currently experimented both for extraction and in post shaping of functional biopolymer materials [1]. In different earlier occasions large quantities of surfactants or hazardous stabilizers were essential to keep the biopolymer nanoparticles dispersions stable in water for final application [2]

Nanoscience and nanotechnology offer new opportunities for making superior materials for use in industrial, health, and environmental applications [3-7]. Nanoparticles (NPs), the primary building blocks of many nanomaterials, are of particular interest in various studies, as the fate of NPs in aqueous environments will depend on their extraordinary properties and widespread range of applications in different scientific and industrial backgrounds. NPs (i.e., particles with structures ~1-100 nm in size) have a significant impact in many scientific fields, including chemistry, electronics, medicine, biology, and material sciences [8-17]. The physical, material, and chemical properties of NPs are directly related to their intrinsic composition, apparent size, and extrinsic surface structure [18-23], so the design, the synthesis, the characterization, and the applications of nanostructures are critical aspects of the emerging field of nanomaterials.

Currently, large quantities of engineered nanomaterials are being produced for diverse applications, and the trend is expected to increase in the future. This increases the probability that nanoparticles will enter the environment during their production, manufacture, use, or disposal. Despite excessive use, data are lacking on the bioaccumulation, toxicity, and biodegradation of nanoparticles in humans and environmentally relevant species. In addition, limited information is available

regarding the weathering potential of both coatings and covalent surface modifications. Therefore, no blanket statements about the toxicity of nanoparticles can be made at this time. Limited ecotoxicological data for nanomaterials preclude a systematic assessment of the impact of nanoparticles on ecosystems. The aim of this work is to discuss the status of public and environmental health strategies currently in use to control the possible adverse effects of nanoparticles in the absence of sufficient toxicity data. [24]

2. ROLE OF NANOTECHNOLOGY

The integration of nanotechnology and material science has facilitated to develop novel nano particle functional materials, suitable for various applications in all the fields and particularly in the bio-medical field for the benefit of human health and well being. The use of nanotechnology in various sectors of therapeutics has revolutionized the field of medicine where nano particles of varying dimensions are designed and used for diagnostics, therapeutics and as biomedical tools for research [25]. It is now possible to provide therapy at molecular level with the help of these tools, thus treating the disease as well as assisting in study of the pathogenesis of disease [26].

3. NATURAL SOURCE

Nano particles are not confined to technology; they are the building blocks of nature and are found in every flowering meadow. Nano particles are produced in many natural processes, including photochemical reactions, volcanic eruptions, forest fires, and simple erosion, and by plants and animals, e.g. shed skin and hair. With a diameter of one nanometer, C60 buckminsterfullerene occurs in nature, in the air after a forest fire. Small particles suspended in the atmosphere, often known as aerosols which affect the earth's energy balance by absorbing the radiation from the sun and scatter it back to space [27] are 90% of natural origin [28], and remaining 10% of the total is estimated to be by the activities of human [29]. The dust storms of the Sahara desert, which blow so much sand over the ocean consists of large amount of nanoscale quartz and silicon dioxide (SiO₂). Fast growing algae that emit dimethyl sulphide, which forms microscopic crystals in the air is no doubt also nano particles. When they reach high altitudes, water droplets condense on them and clouds are formed: nano particles thus act as rain makers.

4. EFFECTS OF NANOPARTICLES IN THE ENVIRONMENT

The increasing use of engineered nanoparticles (NP) in industrial and household applications will very likely lead to the release of such materials into the environment. Assessing the risks of these NP in the environment requires an understanding of their mobility, reactivity, ecotoxicity and persistency. This review presents an overview of the classes of NP relevant to the environment and summarizes their formation, emission, occurrence and fate in the environment. The engineered NP is thereby

compared to natural products such as soot and organic colloids. To date only few quantitative analytical techniques for measuring NP in natural systems are available, which results in a serious lack of information about their occurrence in the environment. Results from ecotoxicological studies show that certain NP has effects on organisms under environmental conditions, though mostly at elevated concentrations. The next step towards an assessment of the risks of NP in the environment should therefore be to estimate the exposure to the different NP. It is also important to notice that most NP in technical applications are functionalized and therefore studies using pristine NP may not be relevant for assessing the behavior of the NP actually used

4.1. Silver nanoparticles and their heteroaggregation in aqueous environments

The rising application of silver nanoparticles (AgNPs) and subsequent release into aquatic systems have generated public concerns over their potential risk and harm to aquatic organisms and human health. Effective and practical analytical methods for AgNPs are urgently needed for their risk assessment. In this study we established an innovative approach to detect trace levels of AgNPs in environmental water through integrating a filtration technique into surface-enhanced Raman spectroscopy (SERS) and compared it with previously established centrifuge-based method. The purpose of filtration was to trap and enrich salt-aggregated AgNPs from water samples onto the filter membrane, through which indicator was then passed and completed with AgNPs. The enhanced SERS signals of indicator could reflect the presence and quantity of AgNPs in the samples. The most favorable benefit of filtration is being able to process large volume samples, which is more practical for water samples, and greatly improves the sensitivity of AgNP detection. In this study, we tested 20 mL AgNPs-containing samples and the filter based method is able to detect AgNPs as low as 5 mg/L, which are 20 folds lower than the centrifuge based method. In addition, the speed and precision of the detection were greatly improved. This approach was used to detect trace levels of AgNPs in real environmental water successfully. Meanwhile, the heteroaggregation of AgNPs with minerals in water was reliably monitored by the new method. Overall, a combination of the filtration-SERS approach provides a rapid, simple, and sensitive way to detect AgNPs and analyze their environmental behavior.

4.2. Environmental applications of Pd nanoparticles

One of the most widely applied catalysts in chemistry, and the currently applied production methods of Pd nanoparticles are not always sustainable, biogenic Pd nanoparticles (bio-Pd) can be considered as very promising and readily applicable for full-scale environmental purposes. Dehalogenation of organic contaminants is one of the most straightforward environmental applications for bio-Pd, since these compounds are ubiquitous in almost all environmental compartments and dehalogenation reactions are very efficiently catalyzed by Pd under ambient conditions. As other reviews describe the historical track of the development of bio-Pd in depth, this overview is focused on the newest findings and considerations in the field, and on how bio-Pd can become introduced into environmental market segments, given the current knowledge.

4.3. Effect of NNPs on environmental hydroxyl radical's concentration and ozone depletion in the atmosphere

The hydroxyl radical, which is one of the most reactive free radicals in the environment and plays an important role in the photochemical degradation of natural organic matter and organic pollutants in the environment. NNPs being very reactive immediately bind with hydroxyl radicals and ultimately result in the overall reduction of hydroxyl radicals [29,30]. As hydroxyl radicals are strong oxidants and thereby degrading many pollutants, its reduction is responsible for the increase in green house gases, which are ultimately responsible for ozone layer depletion and cause severe environmental damage [31]. Furthermore it increases the exposure to UV radiation [32], which leads to the increase in incidences of various types of skin cancer in humans

5. NATURAL OCCURRENCE OF NPS IN ENVIRONMENTAL MATRICES AND THEIR EFFECTS

NNPs can serve as a model for ENPs in the environment and naturally occurring mineral NPs. Their behavior can point out important mechanisms in which NPs can move through environments and affect various environmental systems [22]. Once NPs are released in the environment from either natural or man-made sources, very little is known about their environmental fate. Especially NNPs in the atmosphere have been studied in atmospheric sciences particulate matters and carbon NPs from unprocessed fuel [33] The regional haze, known as atmospheric brown clouds, contributes to glacial melting, reduces sunlight, and helps create extreme weather conditions that impact agricultural production. The pollution clouds also reduced the monsoon season in India [34,35].

6. EFFECTS ON ORGANISMS

6.1. Uptake and toxicity

A consistent body of evidence shows that nano-sized particles are taken up by a wide variety of mammalian cell types, are able to cross the cell membrane and become internalized uptake on NP is size-dependent). Aggregation and size-dependent sedimentation onto the cells or diffusion towards the cell were the main parameters determining uptake .The uptake occurs via endocytosis or by phagocytosis in specialized cells. One hypothesis is that the coating of the NP by protein in the growth medium results in conformational changes of the protein structure, which triggers the uptake into the cell by specialized structures, limiting uptake to NP below about 120 nm (Lynch et al., 2006). Within the cells NP are stored in certain locations (e.g. inside vesicles, mitochondria) and are able to exert a toxic response. The small particle size, a large surface area and the ability to generate reactive oxygen species play a major role in toxicity of NP (Nel et al., 2006).

6.2. Uptake under environmental conditions and ecotoxicity

Most toxicology studies have been carried out with mammalian cells, and the NP were exposed to a cell culture medium containing a mixture of proteins and other biological compounds. Results from such in vitro studies can therefore not be directly transferred to environmental conditions where uptake of NP into the aquatic biota is a major concern. Potential uptake routes include direct ingestion or entry across epithelial boundaries such as gills or body wall. At the cellular level prokaryotes like bacteria may be largely protected against the uptake of many types of NP since they do not have mechanisms for transport of colloidal particles across the cell wall. However, for eukaryotes, e.g. protists and metazoans, the situation is different since they have processes for the cellular internalization of nanoscale or microscale particles, namely endocytosis and phagocytosis (Moore, 2006). The uptake of different NP has indeed been observed. CNT were taken up by a unicellular protozoan and were localized with the mitochondria of the cells. Latex NP were taken up by eggs of the fish *Oryzias latipes* and adult fish accumulated the NP in gills and intestine but particles were also detected in brain, testis, liver and blood. Another study reported that C60 adsorption onto the gram-negative *E. coli* was 10 times higher than on gram-positive *Bacillus subtilis*. Also inorganic NP are taken up by cells. Nano-sized ZnO, for example, was internalized by bacteria. Also nano-sized CeO₂ particles were adsorbed onto the cell wall of *E. coli*, but the microscopic methods were not sensitive enough to discern whether internalization had taken place. Ecotoxicological studies show that NP is also toxic to aquatic organisms, both unicellular and animals. CNT induced a dose-dependent growth inhibition in a protozoan and were found to be a respiratory toxicant in rainbow trout.

6.5 Environmental risk assessment of NP

Environmental exposure varies on the basis of conditions such as the way in which materials are handled in the workplace, how nanomaterials partition to various phases (e.g., water and air), the mobility of nanomaterials in each of these phases, their persistence, and the magnitude of the sources. A lot of research is currently devoted to these topics. This basic information about the behavior and toxicity is needed, but is not sufficient to allow for a realistic risk assessment of NP in the environment. What is also needed is an evaluation of the expected quantities and concentrations of NP in environmental systems. To date nothing is known about this issue, neither from an analytical point of view (e.g. actual measurements of NP in the environment) nor with respect to theoretical or modeling studies. Only few products containing NP are actually on the market, but this is expected to change rapidly in the next years as more and more nano-products are sold. It is therefore not only necessary to get an overview on current exposure, but also more important to anticipate future scenarios on the use of nano-products and exposure to released NP.

7. CONCLUSION AND FUTURE PERSPECTIVE

In this review, we explained the applications of AgNPs as adsorbents of several organic, gaseous and trace metal species in sample-pretreatment and separation

processes. The demands of chemical analysis in modern biology, environmental science, chemistry, medicine, and industry need very high sample throughput and parallel analytical strategies. While the increasing role of AgNPs in separation and preconcentration science is evident, in future, there will need to be greater control over their size and composition. After being utilized for sample pretreatment, AgNPs are difficult to recycle and might cause environment problems, so practical considerations for recycling AgNPs have been addressed. The current interest in the analytical applications of AgNPs is largely related to their high molar absorptivity, their intrinsic capacity to respond to a diversity of chemical environments, physical stimuli leading to a change in their optical properties and numerous sorption sites present on their extensive surface.

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