Nanoparticles from biowastes and microbes: Focus on role in water purification

and food preservation

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Abstract

Biowasts are eco-friendly to produce typical nanoparticles with well-defined chemical composition, size, and morphology. This paper highlights the recent developments of the produce nanoparticles from biowastes e.g. eggs and shrimp peels etc.... Bio-processing of nanoparticles from such resources with microbes such as bacteria, fungi and yeasts are being increasingly explored to meet the twin objectives of resource recycling and pollution mitigation. This review focuses on all the available information on the preparation methodologies of bio-nanoparticles, and highlighted the inherent advantages and disadvantages involved in each method. The second objective was to appear how microorganisms could be used for bio-extracting bionanoparticles. Recently, increasing public concern about microbial pathogens has been driving many investigations for anti-microbial modification of food and water. This review is also concerned with the application of nanoparticles in water and food stuff areas for enhanced filtrating of water contaminated by microbial pathogenic and industrial activities of food systems.

Highlights

- Review focuses on extraction of nanobarticles from biowastes.
- Bio-processing of certain nanoparticles from peel eggs and shrimps is explained.

- Morphology and characterization of nanoparticles from biowastes is highlighted for recovering eco-friendly material.
- Bio-recovery of nanoparticles using bacteria, fungi and yeasts is also included with briefly.
- Methodology/mechanism of nanoparticles in water purification and against foodborne pathogens is discussed.

Keywords: Biowastes; Nanoparticles; Microbes; Bio-extraction; Water, Food

Introduction

Biowaste refers to any organic waste such as cow dung ash, corn cob ash, mango stone ash, lemon peel, pomegranates peel, orange peel, eggs and shrimp peel as well as the organic fraction of municipal solid wastes and animal manure. Biowaste is often interpreted as being the organic biodegradable fraction of the municipal waste stream, including garden waste, food waste and other biodegradable materials such as paper cardboard, some textiles and wood. The rapid expansion of poultry production has caused an increased production of poultry biowaste, i.e. chicken manure (Axtell 1999). Improper use of chicken manure can result in pollution of air, soil and groundwater (Yetilmezsoy &Sakar 2008). Food waste is a growing problem in many parts of the world, but discarded fruit peel, in the case of pomegranates, lemon could be put to good use in the burgeoning field of nanotechnology according to (Ahmad & Sharma 2012, Nisha et al. 2014). Environmental concern about the management of these materials is increasing at the same time that legislation is becoming more restrictive.

Plants, garden waste, remnants of food industries, fruit seeds, carbohydrates, bacteria, actinomycetes, fungi, yeasts, and viruses have used for the biosynthesis of gold, silver, gold–silver alloy, selenium, tellurium, platinum, palladium, silica, titania, zirconia, quantum dots, magnetite and uraninite nanoparticles (Narayanan & Sakthivel 2010). Microbial route for the synthesis of nanoparticles has one the most exciting process as several factors such as microbial cultivation methods on organic and/or inorganic wastes and the extraction techniques can be optimized for the fast synthesis of monodisperse nanoparticles. It has been, therefore, of increasing interest to develop efficient green synthesis of gold nanoparticles. In recent years, there is lot of interest shown in the environmentally benign synthesis of nanoparticles that do not use any toxic chemicals or extreme conditions in the synthesis process. Many biological systems such as that of fungi (Jain et al 2011, Mohammadian et al. 2007), algae (Singaravelu et al. 2007), bacteria (Reddy et al. 2010), actinomycetes (Otari et al. 2014), and plants (Mohanpuria et al. 2008, Choi, et al. 2011, Gan et al., 2012, Vijayakumara et al. 2013) have been studied for biosynthesis of gold and silver nanoparticles.

Production of metal nanoparticles (NPs) by physical and chemical methods are too harsh and non-ecofriendly. Also such nano metals have limited shelf life. Metallic nanoparticles are traditionally synthesized by wet chemical techniques, where the chemicals used are quite often toxic and flammable (Nisha et al. 2014). In addition most of these physical and chemical methods need extreme conditions like temperature, pressure etc. The most widespread and common synthesis of gold nanoparticles is the chemical reduction of an ionic gold in aqueous phase by a chemical reducing agent such as NaBH₄, citrate, and ascorbate. But such reducing agents may be associated with environmental toxicity or biological hazards. Thus, nanobiotechnology is the branch of biotechnology which deals with synthesis and fabrication of nanoparticles by biological systems and their applications especially in biological systems. Nanoparticles possess at least one dimension in the size range of 1 to 100 nm. A nanometer is one billionth (10^{-9}) of a meter, roughly the width of three or four atoms. The principal properties of nanoparticles include size, shape and sub-surface of the substance. Nanoparticles can be classified as organic (for e.g. carbon nanoparticles) or inorganic (for e.g. magnetic and noble metal nanoparticles). This recent concept has proved to be a promising technology enabling the study of immensely efficient biological systems at the molecular level. The field of nanotechnology has gained attention in the recent past owing to a broad spectrum of applications in diagnostics, therapeutics, medicine, delivery system, agriculture, consumer goods, and cosmetics. Biological approaches using microorganisms and plant extracts for synthesis of metal nanoparticles have been suggested as valuable alternatives to traditional methods (Rassaei et al. 2008, Krumov et al. 2009).

Biological methods for synthesis of nanoparticles and their role in biotransformation process on formation of different bio-products, such as bioethanol, biohydrogen, biodiesel, enzymes and bioplastics is reported by Mohapatra, et al. (2011) because there is an increasing commercial demand for bio-nanoparticles due to their wide applicability in various areas and the other bio-products. The nanoparticles are going to prove revolutionary in the field of biotransformation by improving the efficiency and yield and often widening the application range (Mohapatra et al. 2011). Additionally, the possibility to recover H₂ from waste organic streams in biorefineries using photocatalytic approaches is an attractive option to enhance process sustainability and produce valuable energy products. With respect to the overall photoreforming to obtain H₂ and CO₂, the photo-dehydrogenation of bioethanol leads to the co-production of a valuable chemical (acetaldehyde) together with H₂ (Ampelli et al. 2013).

The metal nanoparticles obtained after bioleaching of waste can find a range of applications especially in the field of medicine, food and water. These applications include drug delivery, gene therapy, antimicrobials, medical prosthetics and tissue engineering. Thus, it is possible to 'marry' the two diverse fields as 'waste to nano' for biomedical sciences, thereby providing an active area of research in nanotechnology (Majumder 2013).

Biological and chemical contaminants present in water have threatened its drinking quality. Water treatment for drinking purposes is gaining attraction in the developing

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world due to increasing trend in water borne infectious diseases. These diseases are caused by microorganisms such as bacteria, viruses, protozoan etc. Nanotechnology is applying to disinfect these infectious microorganisms present in water because these microorganisms can multiply very rapidly in the body causing health and environmental concerns. The utilization of nanoparticles to remove these biological infectious microorganisms from water and food systems is an efficient and promising technique used to improve the water drinking quality. This review focuses on 1) extraction of nanobarticles from biowastes and microorganisms 2) recovering eco-friendly material and 3) role of nanoparticles in water purification and against foodborne in food systems.

Nanoparticles from biowastes

Green chemistry started for the search of benign methods for the development nanoparticles and searching antibacterial, antioxidant, and antitumor activity of natural products. Biosynthetic processes of nanoparticles have received much attention as a viable alternative for the development of metal nanoparticles where by products of factories and plant extract is used for the synthesis of nanoparticles without any chemical ingredients (Shankar et al. 2003, Narayanan & Sakthivel 2008, Vijayakumara et al. 2013). Recently weeds, popularly known as 'enemies of the farmer', have also been used successfully for the synthesis of gold, copper and silver nanoparticles.

Silver nanoparticles (AgNPs)

The use of environmentally benign and renewable plant material offers enormous benefits of eco-friendliness biosynthesis of silver nanoparticles (AgNPs) using lemon or pomegranate peel extract as the reducing agent. The biosynthesis of AgNPs using lemon peel extract is very simple and economic. The extract of lemon peel was prepared and mixed with 1mM AgNO₃ solution for the effective synthesize of AgNPs. The bioreduction of Ag+ ion in solution was monitored using UV-visible spectrometer, Fourier-Transform IR spectroscopy (FTIRS) and X-ray diffraction (EDAX) analysis. The AgNPs produced from lemon peels showed good activity against the isolated dermatophytes. The use of lemon peels for the effective synthesize of AgNPs are found to develop drug resistant towards broad-spectrum antibiotics (Nisha, et al. 2014). Pomegranate peel extract was challenged with AgNO3 solution for the production of AgNPs. The reaction process was simple for the formation of highly stable silver nanoparticles at room temperature by using the biowaste of the fruit. The morphology and crystalline phase of the NPs was determined from UV-Vis spectroscopy, transmission electron microscopy (TEM), selected area electron diffraction (SAED), Xray diffraction (XRD) spectra and FTIRS. TEM studies showed that the silver nanoparticles obtained were of sizes 5 ± 1.5 nm. Presumably biosynthetic products or reduced cofactors play an important role in the reduction of respective salts to nanoparticles (Ahmad & Sharma 2012). Additionally, preparation of chitosan nanoparticles include emulsion cross-linking, emulsion-droplet coalescence,

coacervation/precipitation, ionotropic gelation. reverse micelles. template polymerization, and molecular self-assembly. All these methods have their own advantages as well as drawbacks, in relation to the properties of the nanoparticles. However, careful preparation of chitosan nanoparticles could provide a higher affinity for negatively charged biological membranes and site-specific targeting in vivo, enabling their application as encapsulating materials of drugs, enzymes, and DNA, used in controlled release systems and as coatings of wound dressings to accelerate healing (Perera & Rajapakse 2014). Bovine femur bone hydroxyapatite (HA) containing silver nanoparticles was synthesized by thermal decomposition method and subsequent reduction of silver nitrate with N, N-dimethylformamide (DMF) in the presence of poly (vinylacetate) (PVAc). The structural, morphological, and chemical properties of the HA-Ag nanoparticles were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), field-emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS). TEM images showed that the Ag nanoparticles with size ranging from 8 to 20 nm and were arranged at the periphery of HA crystals (Fig. 1). Bactericidal activity of HA-Ag with different concentration of Ag nanoparticles immobilized on the surface of HA was investigated against Gram-positive Staphylococcus aureus (non-MRSA), Methicillin resistant S. aureus (MRSA) and Gram-negative Escherichia coli by the disc diffusion susceptibility test. The HA-Ag nanoparticles showed that broad spectrum activity

against non-MRSA, MRSA, and E. coli bacterial strains (Nirmala et al. 2011). Natural HA bioceramics has been extracted by normal calcination of biowastes (Barakat et al., 2009) and extraction of HA from biowaste is economically and environmentally preferable, compared to the other procedures (Chen et al. 2008). The utilization of the reductive potency of a common byproduct of food processing industry i.e. orange peel is reported here to prepare biopolymertemplated "green" silver nanoparticles. Aqueous extract of orange peel at basic pH was exploited to prepare starch supported nanoparticles under ambient conditions. The compositional abundance of pectins, flavonoids, ascorbic acid, sugars, carotenoids and myriad other flavones may be envisaged for the effective reductive potential of orange peel to generate silver nanoparticles. The nanoparticles were distributed within a narrow size spectrum of (312 nm) with characteristic Bragg's reflection planes offcc structure, and surface plasmon resonance peak at 404 nm. Anti-lipid peroxidation assay using goat liver homogenate and free radical scavenging "green" silver nanoparticles test established the anti-oxidant potency. Their synergy with rifampicin against Bacillus subtilis MTCC 736 and cytocompatibility with the human leukemic monocytic cell line, THP-1 were also investigated (Konwarh et al. 2011). Biosynthesis of silver AgNPs from seaweed extracts is currently under exploitation. Seaweed extracts are cost effective and eco-friendly and thus can be an economic and efficient alternative for large-scale synthesis of nanoparticles. The synthesis of AgNPs from silver precursor, silver nitrate using aqueous extract of seaweed Gracilaria corticata. The organic compounds present in the filtrate of G. corticata were mainly responsible for reduction of silver ions to AgNPs. The filtrate when added to 1 mM aqueous silver nitrate solution at 121°C changed to dark brown colour solution within ten minutes, which confirms the bioreduction. These extremely stable AgNPs were characterised by UV-Vis spectrophotometer, FTIR, XRD, TEM, and EDAX analysis. The nanoparticles exhibited maximum absorbance at 424 nm in the UV spectrum. The presence of proteins was identified by FTIR. TEM micrograph revealed the formation of polydispersed and spherical shaped nanoparticles with the size range of 10-50 nm and the presence of elemental silver were confirmed by EDAX analysis. These nanoparticles showed cytotoxic activity against Hep2 cells (Devi and Bhimba, 2013). Lantana camara, a weed commonly found in Maharashtra was also screened for leaching copper. The characteristics of the copper nanoparticles obtained were studied using X-ray diffraction analysis, energy-dispersive spectroscopy, scanning electron microscopy, Fourier Tranform Infrared analysis, Transmission electron Thermogravimetric analysis and Cyclic Voltammetry. microscopy, Copper nanoparticles were found to be effective against hospital strain Escherichia coli 2065 (Majumder 2012). Green synthesis of nanoparticles from other several plants and their used in biological application has been reported by several authors (Mohanpuria et al. 2008, Choi et al. 2011, Gan et al. 2012, Vijayakumara et al. 2013).

Gold nanoparticles (AuNPs)

Peel extract of pomegranate was challenged with chloroauric acid (HAuCl₄) solution for the production of gold nanoparticles (AuNPs). The reaction process was simple for the formation of highly stable gold nanoparticles at room temperature by using the biowaste of the fruit. The morphology and crystalline phase of the NPs were determined from UV-Vis spectroscopy, TEM, SAED and XRD spectra. TEM studies showed that the average gold nanoparticles were found to be 10 ± 1.5 nm (Ahmad et al. 2012). A facile green biosynthesis method has been successfully developed to prepare gold nanoparticles (AuNPs) of various core sizes (25+/-7 nm) using a natural biomaterial, eggshell membrane (ESM) at ambient conditions. In situ synthesis of AuNPsimmobilized ESM is conducted in a simple manner by immersing ESM in a pH 6.0 aqueous solution of HAuCl4 without adding any reductant. The formation of AuNPs on ESM protein fibers is attributed to the reduction of Au(III) ions to Au(0) by the aldehyde moieties of the natural ESM fibers. Energy dispersive X-ray spectroscopy, scanning electron microscopy, X-ray photoelectron spectroscopy, and X-ray powder diffraction unambiguously identify the presence of AuNPs on ESM. This works by Zheng et al. (2010) a very simple, non-toxic, convenient, and green route to synthesize AuNPs on ESM which is potentially useful in the biosensing field. The synthesis of AuNps from gold precursor using palm oil without adding external surfactant, capping agent or template has been studied by Gan et al. (2012). Silica powder at nanoscale was obtained by heat treatment of Vietnamese rice husk following the sol-gel method. The

rice husk ash (RHA) is synthesized using rice husk which was thermally treated at optimal condition at 600°C for 4 h. The silica from RHA was extracted using sodium hydroxide solution to produce a sodium silicate solution and then precipitated by adding H_2SO_4 at pH = 4 in the mixture of water/butanol with cationic presence. In order to identify the optimal condition for producing the homogenous silica nanoparticles, the effects of surfactant surface coverage, aging temperature, and aging time were investigated. By analysis of X-ray diffraction, scanning electron microscopy, and transmission electron microscopy, the silica product obtained was amorphous and the uniformity of the nanosized sample was observed at an average size of 3 nm, and the BET result showed that the highest specific surface of the sample was about 340 m²/g. The results obtained in the mentioned method prove that the rice husk from agricultural wastes can be used for the production of silica nanoparticles (Le, et al., 2013). Large amount of silica recovered from waste rice husk silica, hence the silica materials derived from waste product can be the low cost and used for potential application such as low-k dielectric material development. Gold doping on ceria-mixed silica derived from rice husk is carried out by in situ method (Au/Ce-silica-A) and deposition-co precipitation method (Au/Ce-silica-B). Au/Ce-silica-A and Au/Ce-silica-B shown the low-k dielectric constant compared to bulk ceria-silica (Shanmugan et al. 2013).

Nanocomposite fillers

Biowastes of rice husk and wheat straw are value-engineered to carbonaceous structures in a single-step process under ambient conditions. By controlling the laser fluence, structures with a variety of different morphologies from nanostructures to microstructures lead to influences the chemical composition of the synthesized structures. This sustainable approach presents an important step towards synthesizing 3-D micro/nanofibrous compounds from biowaste materials. These structures, assynthesized or as nanocomposite fillers, can have practical uses in electronic, sensing, biological, and environmental applications (Tavangar et al. 2013). Other study presented a laser-based approach to synthesize carbonaceous micro/nanofibrous structures from rice husks and wheat straws. This research is the first time that synthesizing 3-D micro/ nanofibrous structures generated from rice husks and wheat straws using femtosecond laser. The morphological analyses by SEM confirmed that fabricated structures were composed of approximately uniform 3-D structure at micro and nano sizes. Also, by altering the laser pulse energy and the number of laser pulses, different structures from micro- to nanoarchitectures with different porosities and features could be achieved. The EDAX analyses confirmed that laser irradiation affected the chemical composition as well; part of the organic matter is believed to be burned away owing to the laser irradiation. This approach suggests a promising step towards engineering green 3-D platforms from sustainable materials. The as-engineered carbonaceous materials would have very broad practical applications in a variety of areas, such as environmental, catalytic, electronic, sensing, and biological applications. They can also be utilized to form biodegradable nanocomposites with other materials, e.g., polymers (Tavangar et al. 2013).

Nanoparticles from microorganisms

The use of natural eco-friendly sources such as microorganisms for the production of nanomaterials is a promising approach, owing to the feasibility and cost-effectiveness of the process. Bacteria, actinomycetes and fungi have been known for ages for their potential to leach out metals from their surrounding over the last couple of decades. The biological agents in the form of algae and microbes have emerged as an efficient candidate for the synthesis of nanoparticles. These biogenic nanoparticles are cost efficient, simpler to synthesize, and focus toward a greener approach. But the exact mechanism of synthesis of biogenic nanoparticles needs to be worked out (Méndez-Vilas 2011). Synthesis of nanoparticles may be intracellular or extracellular of which the later is more preferred as it makes the downstream processing less laborious and also is effective in cost-cutting of the entire process during industrial applications. The biosynthesis of AgNPs was studied from bacteria such as Bacillus subtilis (Reddy et al. 2010), actinomycetes i.e. Rhodococcus sp. (Otari et al. 2014), fungi e. g. Aspergillus flavus, Fusarium oxysporum (Jain et al 2011, Mohammadian et al. 2007) and from marine alga, Sargassum wightii Greville for gold nanoparticles (Singaravelu et al. 2007). Howevere, the intracellular accumulation of gold nanoparticles with a dimension

of 5–15 nm by an alkalotolerant actinomycete, *Rhodococcus* sp., has been demonstrated by Ahmad et al. (2003). *Fusarium oxysporum* and *Pseudomonas* sp. were able to leach copper (84-130 nm) from integrated circuits present on electronic boards (e-waste) under ambient conditions. The characteristics of the copper nanoparticles obtained were studied using X-ray diffraction analysis, energy-dispersive spectroscopy, scanning electron microscopy, Fourier Tranform Infrared analysis, Transmission electron microscopy, Thermogravimetric analysis and Cyclic Voltammetry. Copper nanoparticles were found to be effective against hospital strain *Escherichia coli* 2065 (Majumder 2012).

Although the market of nanoparticles (NPs) is rapidly expanding, the environmental and health impact of manufactured NPs and nanomaterials is still poorly understood and predictable. The ecological impact of metallic and metal oxide NPs span from the surface atoms of NPs, to unicellular organisms, such as bacteria, and organism levels have been studied by Thié et al. (2012). On multicellular organisms, the authors focused on biomarkers reporting on stress, central nervous system endpoints and antioxidative balance assessment. On bacteria, which are key players in NPs transfer, they study not only the impact of NPs on cells, at the microbial community, cell and molecular level, but also the effect of cells on NPs (Thié et al. 2012). A novel approach for the green synthesis of silver nanoparticles (AgNPs) from aqueous solution of AgNO₃ using culture supernatant of phenol degraded broth has been reported by Otari et

al. (2014). The synthesis by phenol degraded *Rhodococcus* sp. was observed within 10 h, and AgNPs showed characteristic surface plasmon resonance around 410 nm. Spherical nanoparticles of size less than 30 nm were observed in transmission electron microscopy. X-ray diffraction pattern corresponding to111, 200, 220, and 311 revealed the crystalline nature of the as-formed nanoparticles (Fig. 2). It was found that the colloidal solution of AgNP suspensions exhibited excellent stability over a wide range of ionic strength, pH, and temperature. The effect of pH and ionic strength indicated that stabilization is due to electrostatic repulsion arising from the negative charge of the conjugate proteins. The AgNPs showed highly potent antimicrobial activity against Gram-positive, Gram-negative, and fungal microorganisms. The as-prepared AgNPs showed excellent catalytic activity in reduction of 4-nitrophenol to 4-aminophenol by NaBH₄. By manufacturing magnetic alginate beads, the reusability of the AgNPs for the catalytic reaction has been demonstrated.

The active and inactive cells/biomass (AB and IB) and their corresponding cell-free extracts (ACE and ICE) of *Aspergillus oryzae* var. *viridis* were found to be suitable agents for the synthesis of gold nanoparticles from gold chloride solution (Binupriya et al. 2010) and showed that *A. oryzae* var. *viridis* is a suitable candidate for the synthesis of gold nanoparticles. The formation of gold nanoparticles (Au NPs) was visually confirmed by the change in the color of reaction medium from colorless to purple. The Au NPs synthesized were monitored via UV–vis spectrophotometer and characterized.

The SPR (Surface Plasmon Resonance) showed the formation of Au NPs with respect to time, pH and initial biomaterial concentration. The peak area of UV-vis spectrum showed that the IB and ICE were found to synthesize more nanoparticles compared to their counterparts, which is believed to be due to presence of more organics in the autoclaved cells due to cell-rupture. High organic content in ICE was confirmed through TOC analysis. The TEM images of formed Au NPs showed that the particles were aggregated and entrapped insome regions possibly an organic matrix of fungal origin. The TEM micrographs of gold nanoparticles nanoparticles formed in cell-free extracts showed polydiversity in shape and size (Fig. 3). The particles formed were of different sizes as well as shapes. Particles of very small size of 10 nm as well of large triangular nanoplates of nearly 400nm were formed in ACE. High pH favored more number of spherical particles, whereas acidic pH did not favor the synthesis of Au NPs. The presence of zero valent gold nanoparticles was confirmed by EDX and XRD measurements. Other interesting result was the formation of high amount of Au NPs in autoclaved cells and extracts which indicate the role of organics other than enzymes in the reduction reaction. The autoclaved fungal-mediated green chemistry approach towards the synthesis of nanoparticles has many advantages such as ease with which the process can be scaled up, economic viability, simple downstream processing and easy handling of biomass. Compared to bacterial fermentations, in which the process technology involves the use of sophisticated equipment for getting clear filtrates from

the colloidal broths, fungal broths can be easily filtered by filter press or similar simple equipment, thus saving considerable investment costs for equipment. The capacity of fungi to produce high amounts of biomass than bacteria make them preferred candidates for nanoparticle synthesis studies.

Seaweeds constitute one of the commercially important marine living renewable resources. Seaweeds such as green *Caulerpa peltata*, red *Hypnea Valencia* and brown *Sargassum myriocystum* were used for synthesis of Zinc oxide nanoparticles. Seaweed *S. myriocystum* were able to synthesize zinc oxide nanoparticles. It was confirmed through the, initial colour change of the reaction mixture and UV visible spectrophotometer. The extracellular biosynthesized clear zinc oxide nanoparticles size 36 nm (Fig. 4) through characterization technique such as DLS, AFM, SEM –EDX, TEM, XRD and FTIR. The biosynthesized ZnO nanoparticles are effective antibacterial agents against Gram-positive than the Gram-negative bacteria. Based on the FTIR results, fucoidan water soluble pigments present in *S. myriocystum* leaf extract is responsible for reduction and stabilization of zinc oxide nanoparticles (Nagarajan & Kuppusamy 2013).

Application of nanoparticles in food systems

Among various metals, silver has been known since ancient times as an effective antimicrobial agent for the treatment of diseases and food preservation (Jain et al. 2008). Silver nano materials exhibit broad spectrum biocidal activity toward bacteria, fungi, viruses, and algae. This motivates its use in food applications. However, there is mounting evidence that silver nanoparticles exhibit an array of cytotoxic and genotoxic effects in higher organisms. This raises concern about possible impacts to higher organisms including humans. Although significant progress has been made to elucidate the mechanisms of silver nano material toxicity, further research is required to fully understand the processes involved and to safely exploit the tremendous antimicrobial properties of silver without jeopardizing human health, critical infrastructure, and the environment. Future in vivo, in vitro and environmental studies should consider more systematically the various effects of aquatic chemistry on nano-scaled silver fate, transport, and toxicity (Méndez-Vilas 2011). Although, there is a need to develop and implement more economical delivery approaches for multiple-hurdle antimicrobial interventions that can be applied to food matrices such as retail meats. Recently, potential opportunities have emerged to use nanoscience and nanoengineering principles to develop antimicrobial carriers for controlling the major foodborne pathogens such as Salmonella in meat and food preservation systems (Ricke & Hanning 2013). Several studies explore the potential of nanoparticle-based composite systems for practical and economical antimicrobial interventions to inhibit and decontaminate such pathogens on cooked ready-to-eat (RTE) poultry and red-meat products. The opportunities for specific systems such as chitosan-nanoparticle-based nanocomposite systems containing ε -polylysine peptide dispersed in organic acids and the potential health hazards that arise from the use of nanoparticles (Ricke & Hanning 2013). The methods of preparation of chitosan nanoparticles are significantly responsible for their bioactivities and behavioral characteristics in different systems and applications. Chitosan nanoparticles-based films are used in the food industry to control microorganisms in food and to enhance shelf life while strengthening the mechanical properties and stability of the food-packing materials. Although the chitosan nanoparticles appear to be safe in some of their applications, knowledge on the risks imposed in these food and pharmaceutical applications needs to be strengthened further (Perera & Rajapakse 2014).

Application of nanoparticles in water systems

In the area of water purification, nanotechnology offers the possibility of an efficient removal of pollutants and germs. Today nanoparticles, nanomembrane and nanopowder used for detection and removal of chemical and biological substances include metals (e.g. cadmium, copper, lead, mercury, nickel, and zinc), nutrients (e.g. phosphate, ammonia, nitrate and nitrite), cyanide, organics, algae (e.g. cyanobacterial toxins), viruses, bacteria, parasites and antibiotics. If the amount of nano-scaled silver entering sewage becomes higher than the tolerable levels for microbial communities in wastewater treatment plants, critical environmental infrastructure might be impacted (Méndez-Vilas 2011). Silver nanoparticles have been known as an effective antimicrobial agent and water purification (Jain et al. 2008). The comparison of some

nanoparticles, such as metallic and non- metallic oxide nanoparticles, especially Titanium Dioxide, Nanoscale Zero-Valent Iron and Carbon Nanotubes to remove organic impurities from the water has been studied by Ghauri et al. (2012). Biogenic Pd nanoparticles produced by Desulfovibrio vulgaris have been reported to efficiently catalyze the reduction of chromate (Mabbett et al. 2002), the degradation of perchlorate and nitrate by NPs produced by Shewanella oneidensis (De Windt et al. 2006), and the dehalogenation of chlorinated aromatic compounds by NPs produced by sulphatereducing bacteria (Baxter-Plant et al. 2003), trichloroethylene (Hennebel et al. 2009a), trichloroethylene (Hennebel et al. 2009b) and chlorophenols (Baxter-Plant et al. 2003). So, a new biological inspired method to produce nanopalladium is the precipitation of Pd on a bacterium, i.e., bio-Pd. This bio-Pd can be applied as catalyst in dehalogenation reactions. However, large amounts of hydrogen are required as electron donor in these reactions resulting in considerable costs (Boon & Verstraete 2011). This research demonstrates how bacteria, cultivated under fermentative conditions, can be used to reductively precipitate bio-Pd catalysts and generate the electron donor hydrogen. In these reduction and dehalogenation reactions, the Pd nanoparticles were activated by adding an external electron donor such as hydrogen or formate. Hydrogen was consistently identified as the most reactive among possible electron donors, but its use was found to be prohibitively expensive and presented significant safety and supply issues (Hennebel et al. 2009b).

Several reactor types were constructed to limit the hydrogen supply (Hennebel et al. 2010) or to produce hydrogen in a sustainable way (Yong et al. 2003, Hennebel et al. 2011). Humphries et al. (2007) used hydrogen produced by E. coli during the fermentation of sugar waste streams. In another recent study, Pd(0) nanoparticle formation by C. pasteurianum BC1 was coupled with the microbial generation of hydrogen to reductively immobilize aqueous chromate using biohydrogen as the electron donor (Chidambaram et al. 2010). In this way, one could avoid the costs coupled to hydrogen supply. The catalytic activities of Pd(0) nanoparticles produced by different strains of bacteria (bio-Pd) cultivated under fermentative conditions were compared in terms of their ability to dehalogenate the recalcitrant aqueous pollutants diatrizoate and trichloroethylene. While all of the fermentative bio-Pd preparations followed first order kinetics in the dehalogenation of diatrizoate, the catalytic activity differed systematically according to hydrogen production and starting Pd(II) concentration in solution. Batch reactors with nanoparticles formed by Citrobacter braakii showed the highest diatrizoate dehalogenation activity with first order constants of 0.45 ± 0.02 h⁻¹ and 5.58 ± 0.6 h⁻¹ in batches with initial concentrations of 10 and 50 mg L^{-1} Pd, respectively. Nanoparticles on C. braakii, used in a membrane bioreactor treating influent containing 20 mg L^{-1} diatrizoate, were capable of dehalogenating 22 mg diatrizoate mg⁻¹ Pd over a period of 19 days before bio-Pd catalytic activity was exhausted. This study demonstrate the possibility to use the combination of Pd(II),

acarbon source and bacteria under fermentative conditions for the abatement of environmental halogenated contaminants (Hennebel et al. 2011).

Tiwari et al. (2008) evaluated four classes of nanoscale materials that are being applied as functional materials for water purification e.g. metal-containing nanoparticles, carbonaceous nanomaterials, zeolites and dendrimers. Carbon nanotubes and nanofibers also show some positive result. Nanomaterials reveal good result than other techniques used in water treatment because of its high surface area (surface/volume ratio). It is suggested that these may be used in future at large scale water purification. It is also found that the coliform bacteria treated with ultrasonic irradiation for short time period before Ag-nanoparticle treatment at low concentration, enhanced antibacterial effect. In future, combination of both may be the best option for treatment of wastewater. The Co_xCu_{1-x}TiO₃ nanoparticles were used for removal of congo red (CR) from aqueous solutions. The effect of parameters such as contact time, pH and temperature on the adsorption of CR was investigated. Tow common kinetic models, pseudo-first-order and pseudo-second-order were employed to describe the adsorption kinetics. The adsorption of CR followed pseudo-first-order kinetic model. Thermodynamic results revealed that the adsorption of CR onto Co_xCu_{1-x}TiO₃ particles is endothermic and spontaneously process. The nanoparticles of Co_xCu_{1-x}TiO₃ can be conveniently regenerated by chemical and physical methods after adsorption. Two common isotherm models, the Langmuir and Freundlich were used to investigate the interaction of CR onto Co_xCu₁-

xTiO₃ nanoparticles. The equilibrium adsorption of CuTiO₃ was best described by the Langmuir isotherm model. The reused sorbent can be employ after 5cycle. The results showed that the adsorption capacity of Ilmenite type nanoparticles for CR is as followed: CoTiO3<Co{0.2}Cu_{0.8}TiO₃< Co_{0.5}Cu_{0.5}TiO₃< Co_{0.8} Cu_{0.2}TiO₃<CuTiO₃ (Hashemian& Foroghimoqhadam 2014). Magnetic MnFe₂O₄/chitosan nanocomposites (MCNCs) were prepared by a simple method. The as-prepared sample was characterized by various technologies. The MnFe₂O₄ nanoparticles were coated by chitosan without phase change, and the as-prepared **MCNCs** displayed superparamagnetic properties with a high saturation magnetization (39.5 emu g^{-1}). The as-prepared MCNCs were used to remove Cr(VI) from low concentration solutions (0.6-1.0 mg L-1). And it was found that the MCNCs showed a high Cr(VI) removal capacity of 35.2 mg g⁻¹. The effects of various parameters, such as pH, temperature, agitation time, and initial concentration on the adsorption performance were investigated. The experimental data were well described by the pseudo-second-order kinetics and Freundlich isotherm model. Taking advantages of the high adsorption capacity and quick magnetic separation from treated water, the MCNCs can be regarded as an efficient magnetic adsorbent for Cr(VI) removal from aqueous solution (Xiao, et al., 2013). Chitosan–MAA nanoparticles (CS–MAA) with an average size of 10–70 nm had ability to remove Cd(II), Ni(II) and Pb(II) from aqueous solution and were conducted as function of the pH, adsorbent dose and initial metal ions concentration.

The morphology and the composition of the biosorbent were characterized by using SEM images, NMR spectroscopy, and Zetasizer analyzer and FT-IR spectra. The presence of amine and carboxylic groups in the CS–MAA nanoparticle composition provided binding sites for the metal ions. The Langmuir adsorption and Freundlich models were used for analyzing the efficiency of adsorption of Cd(II), Pb(II) and Ni(II) ions onto CS–MAA nanoparticles. For CS–MAA nanoparticles and for the three metal ions studied, the value of the adsorption capacity increased in the following order: Pb(II) > Cd(II) > Ni(II). The aforementioned results suggest that the nanoparticles, developed as a natural biopolymer based biodegradable packaging material, can be used selectively for the elimination of heavy metal pollution from wastewater. Therefore, the CS–MAA nanoparticles could be successfully applied as adsorbent for the recovery of Ni(II), Cd(II) and Pb(II) ions from water and wastewater (Heidari, et al. 2013).

Consumer products such as clothing and medical products are increasingly integrating AgNPs into base materials to serve as an antimicrobial agent. Thus, it is critical to assess the effects of AgNPs on wastewater microorganisms essential to biological nutrient removal. Pulse and continuous additions of 0.2 and 2 ppm gum arabic and citrate coated AgNPs as well as Ag as AgNO₃ were fed into sequencing batch reactors (SBRs) inoculated with nitrifying sludge. Treatment efficiency (chemical oxygen demand (COD) and ammonia removal, Ag dissolution measurements, and 16S rRNA bacterial community analyses (terminal restriction fragment length polymorphism, T-

RFLP) were performed to evaluate the response of the SBRs to Ag addition. Results suggest that the AgNPs may have been precipitating in the SBRs. While COD and ammonia removal decreased by as much as 30% or greater directly after spikes, SBRs were able to recover within 24 h hydraulic retention times (HRTs) and resume removal near 95%. T-RFLP results indicate Ag spiked SBRs were similar in a 16S rRNA bacterial community. The results shown in this study indicate that wastewater treatment could be impacted by Ag and AgNPs in the short term but the amount of treatment disruption will depend on the magnitude of influent Ag (Christina et al. 2014).

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Fig. 1 SEM images of HA-Ag nanoparticles with various Ag concentrations of a 0%, b 1%, c 3%, and d 5% (cited from Nirmala, et al., 2011).



Fig. 2 a UV–Vis spectroscopy of AgNPs, b XRD of AgNPs, c TEM image of AgNPs (inset, SAED pattern), d fluorescence spectroscopy of AgNPs from phenol degrading *Rhodococcus* sp. (cited from Otari, et al., 2014).



Fig. 3. TEM images of the gold nanoparticles synthesized by *Aspergillus oryzae* var. *viridis* (A) ICE, (B) IB, (C) ACE and (D) AB (bar scale: 0.2_{7} m for A–C; 100nm for D) (cited from Binupriya, et al., 2010).



Fig. 4 TEM results of biosynthesized zinc oxide nanoparticles (cited from Nagarajan and Kuppusamy, 2013).