



NANOBIOTECHNOLOGY AS A PROSPECTIVE APPROACH FOR SAFE ENVIRONMENTAL REMEDIATION – A REVIEW

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ABSTRACT

Nanotechnology is an emerging field that covers a wide range of applications. Different types of nanomaterials are used in different sectors like biology, medicine, agriculture, pharmacy etc. The challenging task of the 21st Century is to clean up the contaminants of the environment by ecofriendly, green and sustainable and economically adoptable technologies. The need for such technologies is more pronounced in developing nations as clean up processes cost heavily and therefore are ignored but the 'development wheel' is kept going. This trend should be interrupted through innovative and progressive methodologies which otherwise would be detrimental for the very existence of life. Remediation of contaminated water/soil/gases using nanoparticles is one of the several potential applications with considerable benefits. The review focuses on different types of biomaterials and their adsorptive capacities when used on a nano scale. Majority of the biomaterials (plants, animals and microbes) that have been tested for environmental clean up have yielded very good results. The biopolymers like feathers and egg shells generated in huge quantities from poultry industry are found to be of significant use in environmental remediation.

KEYWORDS: Nanoparticles, Bioremediation, Biopolymers, Pollutants, Effluents, Metals, Microbes



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1. INTRODUCTION

Nanotechnology is a multidisciplinary field that applies both the scientific and engineering principles to manipulate materials and molecules to nanoscale that is 1-100nm size. Nanotechnology, a modern science has its history dating to as back as the 9th century. Mesopotamian artisans used gold and silver nanoparticles to generate a glittering effect to pots. In 1857, Michael Faraday in his famous Paper "Experimental relations of gold (and other metals) to light"¹ first described the scientific properties of nanoparticles. In 1959, Richard Feynman gave a first talk on nanoparticles describing molecular machines built with atomic Precision. This was entitled "There's plenty of space at the bottom"². During 1950's and 1960's the world turned its focus towards the use of nanoparticles in the field of drug delivery. One of the pioneers in this field was Professor Peter Paul Speiser, first investigated polyacrylic beads for oral administration, followed by microcapsules. In the late 1960's Speiser developed the first nanoparticles for drug delivery purposes and vaccines. This was followed by much advancement in developing systems for drug delivery across the blood brain barrier. In Japan, Sugibayashi et al. (1977), prepared modified albumin nanoparticles by binding 5-fluorouracil to the albumin nanoparticles, and studied denaturation temperature dependent differences in drug release as well as the distribution of the particles in the body of mice after intravenous injection through tail vein³. The nano- revolution conceptually started in the early 1980's with the first paper on nanotechnology being published in 1981 by K. Eric Drexler of Space Systems Laboratory, Massachusetts Institute of Technology. This was entitled "An approach to the development of general capabilities for molecular manipulation". Currently nanotechnology, has reached a stage where it is considered as the future to all technologies with the invention of techniques like TEM (Transmission electron microscopy), AFM (Atomic force microscopy), DLS (Dynamic light scattering) etc. The reason behind this is the unique properties of nanoparticles. Wide range of physical phenomena become more pronounced as the

size of the system decreases. With the shift of the system from macro to micro level certain phenomena may not come into consideration but may be prodigious at the nano scale. For example, increased surface area to volume ratio alters the mechanical, thermal and catalytic properties of the material by effecting the dominance of the behavior of atoms on the surface over that of those in the interior of the particle. The electronic and optical properties and the chemical reactivity of small clusters is completely different from the better known property of each component in the bulk or at extended surfaces. Some of the size dependant properties of nanoparticles are quantum confinement in semiconductors, surface plasmon resonance in some metallic nanoparticles and paramagnetism in magnetic nanoparticles. Surface plasmon resonance refers to the collective oscillations of the conduction electrons in resonance with the light field. The surface plasmon mode arises from the electron confinement in the nanoparticle. The surface plasmon resonance frequency depends not only on the metal, but also on the shape and size of the nanoparticle and the dielectric properties of the surrounding medium⁴. For example, noble metals, especially gold and silver nanoparticles exhibit unique and tunable optical properties on account of their surface plasmon resonance. Superparamagnetism is a form of magnetism that is a special characteristic of ferromagnetic nanoparticles. In such superparamagnetic nanoparticles, magnetization can randomly change direction under the influence of temperature. Superparamagnetism occurs when a material is composed of very small particles with a size range of 1- 10nm. In the presence of an external magnetic field, the material behaves in a manner similar to paramagnetism with an exception that the magnetic moment of the entire material tends to align with the external magnetic field. Quantum confinement occurs when one or more dimensions of the nanoparticles are made very small so that it approaches the size of an exciton in the bulk material called the Bohr exciton radius. The idea behind confinement is to trap electrons and holes

within a small area (which may be smaller than 30nm). Quantum confinement is important as it leads to new electronic properties. Scientists at the Washington University have studied the electronic and optical changes in the material when it is 10nm or less and have related it to the property of quantum confinement. Some of the examples of special properties that nanoparticles exhibit when compared to the bulk are the lack of malleability and ductility of copper nanoparticles lesser than 50nm. Zinc oxide nanoparticles are known to have superior UV blocking properties compared to the bulk. Bionanotechnology has emerged as integration among biotechnology and nanotechnology for developing biological synthesis and environmental benign techniques for synthesis of nanomaterials. At present the whole world is facing with the environmental pollution and its related problems. With increasing environmental awareness and stringent government policies, it has become necessary to develop advanced technologies like nanotechnology to clean up contaminants using low-cost methods and materials. When compared to the conventional methods these nanoparticles are more safe, effective and specific to environmental remediation. Due to different kinds of design, synthesis, characterization techniques that are used by different researchers for the environmental remediation applications, the findings are summarized in the tables (1-5) appended.

2. CLASSIFICATION OF NANOPARTICLES

Nanoparticles can be broadly classified into two groups – organic (Carbon) and inorganic nanoparticles (Non-carbon). Organic nanoparticles include carbon nanoparticles (fullerenes), inorganic nanoparticles include magnetic nanoparticles, noble metal nanoparticles (like gold and silver) and semiconductor nanoparticles (like titanium dioxide and zinc oxide). Inorganic nanoparticles are of special interest as they provide superior material properties with functional versatility and are therefore potential tools for medical imaging as well as for treating diseases and used in cellular delivery due to their versatile features like

wide availability, rich functionality, good biocompatibility, capability of targeted drug delivery and controlled release of drugs⁵. Inorganic nanoparticles exhibit intrinsic optical properties which may enhance the transparency of polymer- particle composites. Both organic and inorganic nanoparticles are widely employed in environmental remediation (Tables 1- 3).

2.1 CARBON BASED NANOPARTICLES

Carbon as a non-metal element can be found in every living organism and in millions of various compounds. Based on the structure, electronic, mechanical, optical and chemical characters, carbon nanoparticles are classified into various dimension dependent categories ranging from zero dimensional (fullerene, carbon-encapsulated metal nanoparticles, nanodiamond, and onion-like carbons) to one dimensional (carbon nanofibers and carbon nanotubes) and two dimensional (graphene and carbon nanowalls) depending on their nanoscale range (< 100nm) in different spatial directions.

2.1.1 ZERO-DIMENSIONAL CARBON NANOMATERIALS (0-DCNS)

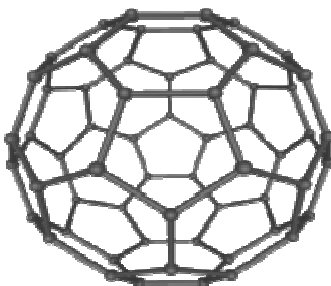
a. Fullerene

Fullerenes are large spherical, ellipsoid or cylindrical carbon caged molecules forming polyhedral structures consisting of pentagons and hexagons (Fig. 1). These are inert and indefinitely modifiable⁶. The suffix "ene" indicates that each C atom is covalently bonded to three others (instead of the maximum of four). The cylindrical fullerenes are known as buckytubes or nanotubes. A fullerene nanotube has about 20 times high tensile strength than that of a high strength steel alloy and a density half that of aluminium. The first synthesised and most commonly used fullerene is C₆₀; the other types of fullerene are C₇₀, C₇₆ and C₈₄ (the subscripts indicates the number of carbon atoms found in the structure). Fullerenes vary in size from 0.7-1.5 nm in diameter and can withstand high temperatures⁷. Fullerene is able to fit inside the hydrophobic cavity of HIV proteases, inhibiting the access of substrates to the catalytic site of enzyme⁸. It can be used as a free radical scavenger and antioxidant⁹.

Fullerene C_{60} targets the cancer cells and then be triggered by light radiation, minimizes the damage to the surrounding tissue¹⁰. Oral administration of these nanoparticles

increased the lifespan of rats by nearly 100% without any toxic effects¹¹. The detailed applications of fullerene in environmental remediation are appended in Table1.

Figure 1
Fullerene C_{60} (en.wikipedia.org/wiki/fullerene)

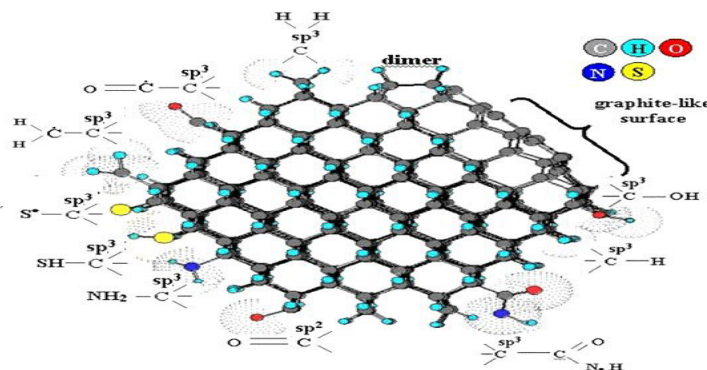


b. Nanodiamond

Diamond, spherical and truncated octahedron diamond with predominant sp^3 - bonded carbon (Fig. 2) is one of the hardest materials known to date and regarded as the king of all gemstones because of its scientific qualities in hardness, chemical corrosiveness, thermal expansion and conductivity, electrical insulation, and biocompatibility. Nanodiamond (ND) is a cubic structural diamond, with structure and properties as that of a diamond

and is 5nm in diameter on average. Nanodiamond contains a variety of diamond-based materials at nanoscale (the length scale of approximately 1–100 nm) including pure-phase diamond films, diamond particles, and their structural assemblies¹². Nanodiamonds have a wide range of applications in electrochemical coatings, polymer compositions, antifriction coatings, polishing, lubricants, biosensors, imaging probes, implant coatings and drug carriers¹³⁻¹⁸.

Figure 2
Nanodiamond (itc-inc.org)

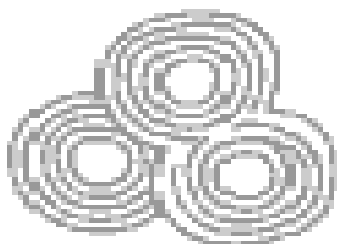


c. Onion-Like Carbons (OLCs)

The onion-like carbons (OLCs) are polyhedral nanoparticles with well aligned concentric rings and show a high degree of symmetry. Carbon onions are quasi- spherical nanoparticles, possess a hollow core encased with three to eight closed graphitic shell

structures (Fig. 3). The outer diameters are in the range of 20–100 nm. They can serve as nanocapsules for drug delivery systems. The external graphite acts as a template for the attachment of desirable functional groups and protects the substances present inside.

Figure 3
Onion-like carbons (research.ncl.ac.uk/nanoscale/research/olc.html)



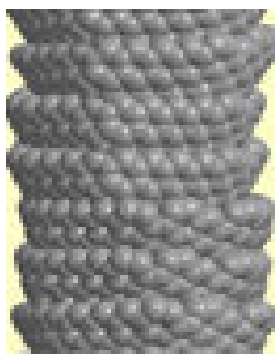
2.1.2 ONE-DIMENSIONAL CARBON NANOMATERIALS (1-DCNS)

a. Carbon Nanofibers

These are cylindrical or conical, filamentous carbon nanostructures from a quasi-one-dimensional (1D) filament¹⁹ (Fig. 4). Their diameter ranges from a few to hundred nanometers, where as lengths range from less than a micrometer to millimeters. The

morphological structure is often divided into plate CNFs, ribbon-like CNFs, herringbone CNFs²⁰. These are used for electrode materials²¹, as anodes for rechargeable lithium-ion batteries²². The detailed applications of carbon nanofibers in environmental remediation are appended in Table1.

Figure 4
Carbon nanofiber (halo.wikia.com)

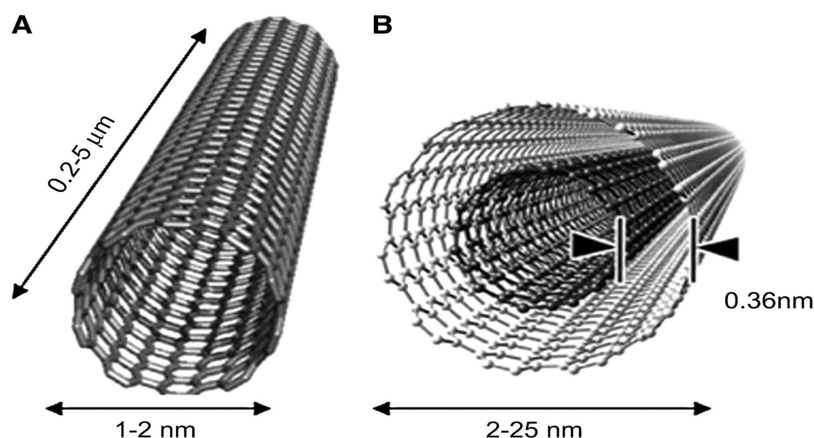


b. Carbon Nanotubes

These are the strongest material discovered till date. Carbon nanotubes are the most important members of the hollow 1-D nanosystem. They are tubular structures with nanometer diameter and large length ratio. The nanotubes consist of three different types of carbon nanotubes. viz, single wall nanotubes (SWNTs) made of single layers of graphene with a diameter of the order of 1.4 nm, multiwall nanotubes (MWNTs) made of 4–24 concentric cylinders of graphene layers with adjacent shells separation of 0.34 nm and a diameter of 10–20 nm and fishbone

nanotubes in which the graphene layers are not parallel to the growing axis (Fig. 5). These are widely used in nanotechnology, electronics, optics, material science and architecture. Due to amazing structural features these are used in industrials such as clothes, sports' equipment like stronger and lighter tennis rackets, bikes and various kinds of balls etc. Due to high tensile strength fiber these are applied in the build of bridges, ultrahigh-speed flywheels¹². The detailed applications of carbon nanotubes in environmental remediation are appended in Table1.

Figure 5
A. SWNTs B. MWNTs (jnm.snmjournals.org)



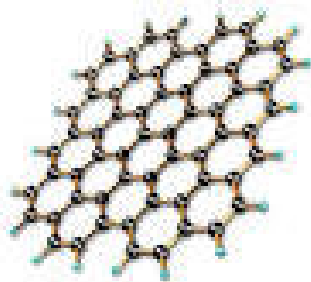
2.1.3 TWO-DIMENSIONAL CARBON NANOMATERIALS (2-DCNS)

a. Graphene

It is the basic building block of (0-D) fullerenes, (1-D) carbon nanotubes, and (3-D) graphite. Graphene is arranged densely in a two dimensional hexagonal honeycomb crystal lattice (Fig. 6). The three strong σ bonds provide mechanical stability of the carbon sheet and the π orbitals are responsible for the electron conduction. It is one of the strongest materials in nature—roughly 200 times the strength of steel. It is very thin and flexible in nature. Graphene is a

high electron mobility material with low resistivity at room temperature. Due to its high mobility these are applied in transistors which need to switch extremely fast¹². Because of its low resistivity these are applied in mechanical fields, electrical conducting and transparent films which are necessarily applicable in the fields of electronics such as producing touch screens and photovoltaic cells^{23, 24}. Ultracapacitors prepared from graphene, store larger amount of renewable energy from solar, wind or wave energy than the existing technologies.

Figure 6
Graphene (realclearworld.com)

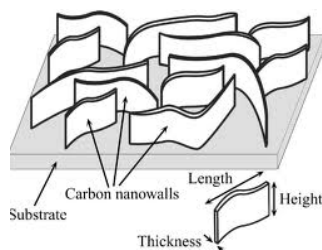


b. Carbon Nanowalls

These are also referred to as “carbon nanoflakes”. Carbon nanowalls (CNWs) consist of vertically aligned graphene sheets standing on the substrates, form two-dimensional wall structure with large surface

areas and sharp edges (Fig. 7). The thickness of CNWs ranges from a few nm to a few tens nm. CNWs can also be used as a template for loading other nanomaterials and the resulting hybrid nanostructures are used as photocatalysts²⁵.

Figure 7
Carbon nanowalls (Chemie.uni.hamburg.de)



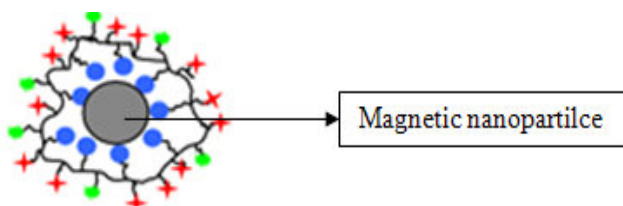
2.2 NON - CARBON BASED NANOPARTICLES

a. Magnetic Nanoparticles

Nanoparticles that can be manipulated by the application of magnetic field are called magnetic nanoparticles. The magnetic elements such as iron, nickel and cobalt and their chemical compounds are commonly used. Magnetic nanoparticles are available in the past four decades in different compositions, sizes and stabilisers. The magnetic nanoparticles attain magnetic property due to central iron oxides typically Fe_2O_3 and Fe_3O_4 ^{26, 27}. The central core is surrounded by a silicon coat or a layer of polymer such as dextran or polyacrylamide (Fig. 8). As the particle size is reduced to nano range, it increases the magnetic behavior. These nanoparticles lose magnetic

property when removed from the magnetic field. Many different ferrite nanoparticles were synthesised by the thermal decomposition of organometallic precursors followed by oxidation or by low-temperature reactions inside reverse micelles. Magnetic nanoparticles can be made to interact with biological entity. These particles are used as in vitro biosensing agents to detect cellular biomarkers²⁸. By conjugation of Fe_3O_4 nanoparticles and porphyrin, a biomodal imaging nanoprobe is obtained which can act as a multifunctional nanomedicine that combines photodynamic therapy anti-cancer treatment and noninvasive MRI imaging²⁹. The detailed applications of magnetic nanoparticles in environmental remediation are appended in Table 2.

Figure 8
Polymer coated magnetic nanoparticle

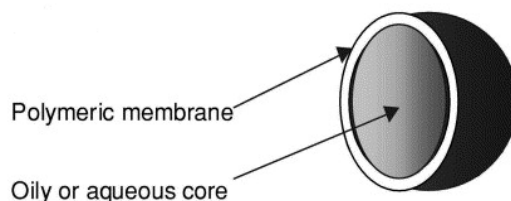


b. Nanocapsule

A 'Nanocapsule' is a nanoparticle that consists of a shell and a 'space', in which desired substances may be placed (Fig. 9). For example, polyelectrolyte (PE) capsules prepared by means of the layer-by-layer technique with tailored properties, fulfill the requirements for nano-organized systems in a satisfactory manner. With these shells, material can be delivered to predefined organs. Nanocapsules are prepared using

molecules called phospholipids, which are hydrophobic (water-repellant) on one end and hydrophilic (water-loving) on the other. When such molecules are placed in an aqueous environment, they can spontaneously form capsules in which the hydrophobic portions are inside, protecting them from contact with water. In particular these nanocapsules are used for the delivery of fragile biological substances.

Figure 9
Nanocapsule

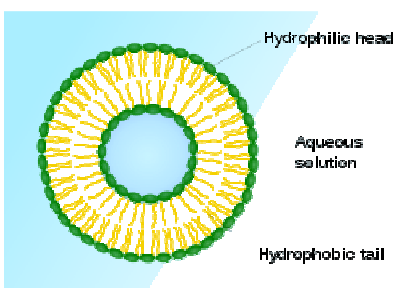


c. Liposomes

Liposomes are artificially constructed spherical cells of phospholipid bilayers. The bilayers are stabilised with charged nanoparticles (carboxyl-modified polystyrene) which can act as vehicles for drug delivery and are also biodegradable (Fig. 10). These nanoparticle-stabilized liposomes are interesting from several functional perspectives. Firstly, they comprise a novel colloidal-sized sensor. Antigens and other proteins can be placed on these nanoparticle stabilized liposomes because they do not allow for fusion with one another, thus can be concentrated to high volume fractions and functionality with a high surface to volume ratio. Secondly as each liposome is impermeable the elementary reactions can be performed with in the liposomes. Thirdly their rheology, diffusion and potential crystallization help in the study of the structure and

dynamics of colloidal-sized objects at very high volume fractions in which particle-particle interactions are more and when the particle contour is more raspberry than spherical³⁰. These liposomal particles can be used to detoxify drugs as they are hollow with a trans-membrane pH gradient where the vesicles act as sinks and scavenge the drug and prevent its toxic effect³¹. Another interesting feature of liposomes is their ability to target cancer cells. Naturally this ability is known as “Enhanced Permeability and retention effect”. Liposomes of size less than 200 nm can easily enter the tumor sites from the blood, and they can also be used as outer shells of some microbubble contrast agents, used in contrast-enhanced ultrasound³². These nanoparticles are used in medicine for drug and small molecule delivery. These are effectively used for encapsulation of cosmetics and for environmental remediation.

Figure 10
Liposome (en.wikipedia.org)



d. Dendrimers

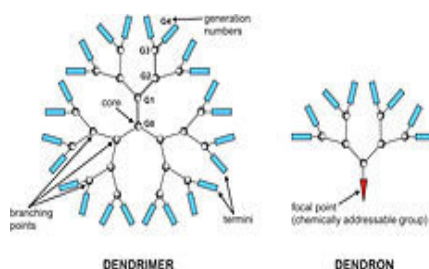
Dendrimers are a relatively new class of biodegradable macromolecules which are synthetic³³, hyper branched, symmetric, nanospherical³⁴ (Fig. 11). The dendritic molecules can be divided into two classes: One is low-molecular weight species which

includes dendrimers and dendrons and the other is high-molecular weight species which includes dendronized polymers, hyperbranched polymers, and the polymer brush. The dendronised polymers are cylindrical structures that possess a linear polymeric backbone and dendritic side chains.

These can provide new unique properties that can be used in the emerging field of nanotechnology. Dendrimers consist of multiple branches, and are designed to provide a versatile choice of external functional groups in order to reduce cytotoxicity and enhanced transepithelial transport, can interact with coupling molecules such as natural-based polymers³⁵, fluorescent probes³⁶, and an inner hydrophobic core where other molecules can be trapped³⁷. The dendrimers can be synthesised by different methods, their polymer size ranges in several nanometers (typically in the order of ~10–20 nm)³⁸. Polyamidoamine dendrimers have the properties like water soluble, transfective, low polydispersity, well defined surface functions, devoid of immunogenesity. Moreover, it has also been found³⁹ that high generation dendrimers (G7) with amine capping-groups cause haemolysis and changes in red cell morphology, and in general are overall cytotoxic. To avoid the cytotoxic effects of high-generation dendrimers, a dendrimer core is grafted to natural-based and biocompatible polymers (linear polymer chains) to obtain copolymers of new architectures (different surface properties). With tuned nanoparticle size (sizes larger than 10nm)³³ more such versatile macromolecules could be synthesised by surface engineering. A poly (amidoamine) (PAMAM) dendrimer core grafted to carboxymethylchitosan (CMCht) chains forms dexamethasone-loaded CMCht/PAMAM nanoparticles. These

nanodevices show properties like higher loading capacity, and allow the bulk incorporation of bioactive molecules of higher molecular weight and of different chemistry, while maintaining high internalization and transfection efficiency. The dexamethasone-loaded CMCht/PAMAM are also used in intracellular controlled delivery of biological agents, to modulate stem cell behaviour⁴⁰. Dendrimers can also act as biosensors, for example multifunctional Au nanoparticles. Bifunctional hydroxyl/thiol functionalized fourth generation polyamidoamine dendrimer (G4-PAMAM) – encapsulated Au nanoparticles were immobilized on a mixed self-assembled monolayer - modified gold surface⁴¹. Some of the dendrimer thiol groups are converted into hydrazide functionalities which provide an activated surface to immobilize the receptor for immunoaffinity reactions. These biosensors can be used for analyzing the insulin of 0.5pM with high stability and sensitivity. Poly (propylene imine) dendrimers are used as pH sensors⁴². Dendrimers can act as vehicles for drug delivery³⁷, DNA (transfection)⁴³, imaging agents³⁸, and tissue engineering scaffolding⁴⁴. Cadmium-sulfide/polypropylenimine tetrahexacontaamine dendrimer composites are used to detect fluorescence signal quenching⁴⁵, and poly propylenamine first and second generation dendrimers are used for metal cation photodetection⁴⁶. The detailed applications of dendrimers in environmental remediation are appended in Table1.

Figure 11
Dendrimer & Dendron (en.wikipedia.org/wiki/dendrimer)



e. Yolk/Shell Nanoparticles (YSNS)

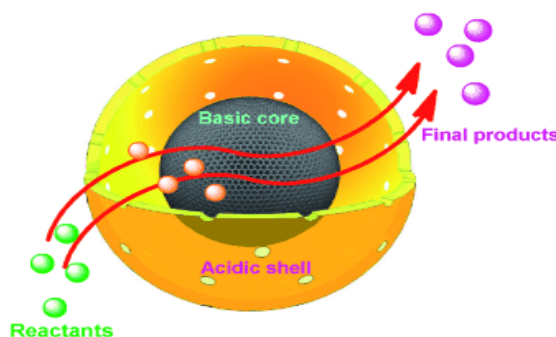
Yolk/shell nanoparticles (YSNs) consist of a nanoparticle core surrounded by a hollow shell and are named after an egg with a shell, interstitial space and the core - the yolk (Fig.

12). Yolk-shell structures have been prepared with various types of movable cores, such as gold, SiO₂, and magnetic Fe₃O₄. The vesicle template, formed of a fluorocarbon surfactant, is built up around the core⁴⁷. To prevent the

nanoparticles from sintering and losing their activity while still providing the reactants free access to the metal surface, gold nanoparticles are encased inside hollow titania nanospheres⁴⁸. Yolk/shell nanoparticles are one of the important nanomaterials for a wide variety of applications such as catalysis, delivery, lithium-ion batteries and biosensors due to their tailorability and functionality in both the cores and hollow shells⁴⁹. Due to its tiny size they provide a large surface area. These nanostructures reduce drug risks, by breathable pores the drug enters into the cell and do not flow. YSNs structures are used as

anode materials - used to put electricity into a cell - for lithium-ion batteries. These can provide a high-efficiency, high power, and high level of reliability. FePt@CoS₂ yolk-shell nanocrystals are used in the treatment of cancer (HeLa cell lines) because of their controlled drug release⁵⁰. Multifunctional Ag@Fe₂O₃ yolk-shell nanoparticles are used for simultaneous rapid detection and capture of bacteria and safe detoxification treatments - these are prepared by combining silver and iron oxide nanoparticles by the Kirkendall effect⁵¹.

Figure 12
Yolk/shell nanoparticles (online library. Wiley.com)



f. Bionanoparticles

The biogenic method of nanoparticles production is simple, eco-friendly and is of great interest due to possible application in catalysis, medicine and nano-optoelectronics. Biologically fabricated nanostructures offer substantially different properties like good adhesion, tribologically good properties (like lubrication - due to this it is able to interact with surfaces), optical and electrical properties. It is possible to get the nanoparticles from simple microbes and bacteria up to more evolved plants⁵². For the synthesis of metal and metal sulphide nanoparticles, fungi are the most efficient biological agents. *Verticillium sp.* and *Fusarium oxysporum* are used for the synthesis of metal nanoparticles, as they can reduce the metal ions extracellularly. An extracellular enzyme, hydrogenase in the *F. oxysporum* shows excellent redox properties and it can act as an electron shuttle in metal reduction. The electron shuttle or other reducing agents (e.g. hydroquinones) released by microorganisms are capable of reducing

ions to nanoparticles. When challenged with silver nitrate in aqueous medium the fungal members *Aspergillus flavus*, *Aspergillus fumigatus* and Phanerochaete *Chrysosporium*⁵³ produce stable silver nanoparticles. Diatoms (brown algae), are unicellular photosynthesizing eukaryotic algae which produce controlled natural nanostructures. They have a silica exoskeleton named Frustules that consists of well organized SiO₂ nanoparticles (size 50-100 nm). The nanoparticles silicic acid is a precursor of silica in aqueous environment. The first isolated silicic acid transporter (SIT) was from diatom species *Cylindrotheca fusiformis*. Germanium is also incorporated into diatom cells. *Stauroneis sp.*, a freshwater diatom can be used to fabricate Silicon-Germanium nanoparticles. Silica from bioreactor cultured *Nitzschia frustulum* cells possess blue photo-luminescence. The luminescence intensity and wavelength are dependent on the change in frustule's nanostructure as the cell culture moved from the exponential to the stationary phase of

growth⁵⁴. *Pleurotus sajor* an Oyster can be used for the synthesis of silver nanoparticles⁵⁵. CdS and PbS nanoparticles can be synthesised successfully using yeast. NanoscalePbS (intracellularly) can be synthesised by exposing *Torulopsis* species to aqueous Pb²⁺ ions⁵⁶. *Schizosacharomyces pombe* yeast cells can be used to get the CdS Quantum dots. Recently, high quantity of extracellular silver nanoparticles are obtained by using silver tolerant yeast strain MKY3⁵⁶. Using sun-dried peel of *Citrus sinensis*, gold and silver nanoparticles can be synthesised in aqueous medium. Different shapes and morphologies (nanotriangles, nanoprisms, octahedral) of gold particles are synthesised using plant parts, such as tamarind leaves extract⁵², *Pelargonium graveolens* (geranium) leaves extract and its endophytic fungus *Colletotrichum sp*⁵⁷, *Hibiscus rosa - sinensis*⁵⁸, coriander leaf extract⁵⁹, *Magnolia kobus* and *Dyopiros kaki* leaf extracts⁶⁰, Phyllanthium⁶¹, Aloe vera extract, mushroom extract and even honey. Detailed lists of bionanoparticles are presented in tables - 4 & 5. Biologically synthesized metal (Ex: silver) nanoparticles could have many applications such as spectrally selective coating for solar energy absorption and intercalation material for electrical batteries⁶² as optical receivers, catalysts, biolabelling etc... Nanoparticles could be successfully used in cancer diagnosis and treatment.

2.3 EFFICIENCY OF BIOMATERIALS

Nanoparticles have been widely used in engineering applications. Due to the high cost and environmental hazard of the petroleum and mineral derived products, a growing effort has emerged in the recent years on research and development and application of biomaterials obtained from agricultural waste, industrial by products or natural materials. Egg shells are one of the natural, inexpensive and abundant biosorbent used for the removal of heavy metals, dyes and as a template to synthesise metal nanoparticles. Eggshell membranes have potential use for clinical, nutraceutical and nanotechnology applications⁶³. An egg shell contains 94% CaCO₃ with small amounts of MgCO₃, calcium phosphate and other organic materials such

as type X collagen, sulfated polysaccharides, and other proteins⁶⁴. In addition to these it contains many surface functional groups, including amines, amides and carboxylic groups⁶⁵. The egg shell's powders of 75-212 µm particle size are used for removal of zinc up to 86.50%⁶⁶. NaceraYeddou et al. (2009) studied the adsorption isotherms using eggshells for the removal of iron⁶⁷. From eggshells and eggshell membrane, nanosized calcium phosphate (Ca₃(PO₄)₂) particles were prepared that showed potential use in drug delivery systems⁶³ and nanowires for electronic devices⁶³. With the above valuable information from the literature, an attempt was made to prepare a nanoadsorbent of eggshells which is a new technology. The eggshells were subjected to cleaning and size reduction by various methods: the most commonly used methods being mechanochemical, sonochemical and ballmill techniques. The nanoscale level eggshell material had increased the surface area, so that more metals are adsorbed. In our study of bioremediation these eggshells at nanoscale were used as adsorbents to remove copper and lead. The removal efficiencies of lead and copper were 94.0555% and 92.055% respectively.

2.4 ENVIRONMENTAL APPLICATIONS

Nanotechnology has started in 9th century and it has spread its wide applications in various fields. A few of the applications of nanomaterials to biology/ medicine /agriculture are fluorescent biological labels, drug and gene delivery, bio-detection of pathogens, biosciences, detection of proteins, probing of DNA structure, tissue engineering, tumour destruction via heating (hyperthermia), separation and purification of biological molecules and cells, MRI contrast enhancement, pharmacokinetic studies, antimicrobials, and anti insect molecules. Using bionanoparticles is an innovative way to attain a clean and green environment. Nanoparticles that are used in environmental cleanup are focused in this review and are classified into three categories: they are carbon nanoparticles, metal nanoparticles (include both magnetic and non magnetic) and bionanoparticles. Different kinds of carbon

nanotubes are excellent sorbents for adsorption of inorganic⁶⁸⁻⁷³ and organic compounds⁷⁴⁻⁷⁸. The carbon nanoparticles are excellent antimicrobial agents for the removal of pathogenic microorganisms^{84, 85}.

Dendrimers are exploited for the recovery of valuable metal ions¹⁰¹. Carbon nanoparticles and their detailed applications are represented in detail in Table 1.

Table 1
Different carbon nanoparticles and their environmental applications

S. No.	Carbon nanoparticles	Application	References
1	Carbon nanotubes	Adsorbents for inorganic compounds like Cr ³⁺ , Zn ²⁺ , Cu, Ag, Co, Mn, nickel, Pb(II) and rare earth metals	Rao et al., 2007 (68); Liang et al., 2004(69); Ding et al., 2006 (70); Stafiej et al., 2007 (71); Lu et al., 2008 (72); Tian et al., 2010 (73).
		Adsorbents for organic compounds like dioxin, PAH, DDT, dyes, pesticides, herbicides, phenolic compounds	Sohn et al., 2006 (74); Gotovac et al., 2006(75); Biesaga et al., 2006 (76); Zhou et al., 2006 (77); Lin et al., 2008 (78).
		Detection of pollutants such as ammonia (NH ₃) and sulfur dioxide (SO ₂)	Nguyen et al., 2007 (79); Moon et al., 2008(80).
		Used for harvesting solar energy, enhance photoconductivity upon illumination.	Kamat et al., 2007(81); Scarselli et al., 2009 (82); Liu et al., 2009 (83).
		Used to remove pathogenic microorganisms such as bacteria, protozoa	Srivastava et al., 2004 (84); Mostafavi et al., 2009 (85).
2	Multi walled carbon nanotubes	Sorbents for organic compounds like NOM (natural organic matters), benzene and its aromatic compounds, humic acids, nicotine and tar onto the cigarette filters, arcidine orange, EtBr, eosin blue, orange G, methyl blue, acridine orange, and acid fuchsin	Lu et al., 2007 (86); Li et al., 2004(87); Jin et al., 2007 (88); Wang et al., 2009 (89); Chen et al., 2006 (90); Fugetsu et al., 2004(91); Shili et al., 2010 (92).
		Separation and preconcentration of heavy metals, adsorption of Pb(II)	Wang et al., 2011(93); Xu et al., 2008 (94).
		Removal of bacteria	Srivastava et al., 2004 (84)
3	Single walled carbon nanotubes	Hydrogen storage	Liu et al., 1999 (95).
		Acts as sensors for gaseous molecules such as NO ₂ and NH ₃	Kong et al., 2000 (96).
		Removal of bacterial and viral pathogens from water	Brady-Estevéz et al., 2008 (97).
4	Self-Assembled Monolayers on Mesoporous Supports (SAMMS)	Adsorption of silver, cadmium, lead, thallium, mercury, cesium	Mattigod et al., 1999 (98); Chen et al., 1999 (99); Lin et al., 2001 (100).
5	Dendrimer	Removal of Co(II), Cu(II), Hg(II), Ni(II), Pb(II) and Zn(II)	Rether et al., 2003 (101).
6	Fullerenes	Used as a sorbent for PAC(Poly cyclic aromatic compounds)	Cheng et al., 2004 (102).
7	Fullerene	Deactivation of pathogen	Lyon et al., 2008 (103).
8	Nanoclays	Removal of Dyes and phosphorus	Yang et al., 2005(104); Yuan et al., 2007 (105).
9	Nanofibers	As nanocomposite materials for water treatment membranes, catalysis, hydrogen storage	Lee et al., 2005 (106).
10	Nanoporous carbon xerogels	sorbent for Organic contaminants like acetylene	Molchanov et al., 2008 (107).
11	Nanowires	Decompose humic acid	Zhang et al., 2008 (108).

Different kinds of magnetic nanoparticles are used in environmental applications. Nanozerovalent iron particles are one of the magnetic nanoparticles and are able to transform, remove organic, inorganic

pollutants and dyes. Iron nanocomposites are able to remove the azo dye orange II. The detailed applications of different magnetic metal nanoparticles are represented in Table 2.

Table 2
Different magnetic metal nanoparticles and their environmental applications

S. No.	Magnetic metal nanoparticles	Application	References
12	Nano Zero- valent iron	Removal of arsenic, Ni	Biterna et al., 2007 (109); Li et al., 2006 (110).
		Removal of nitrate, RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine), perchlorate, alachlor, pretilalachlor and catalysis of Chlorinated ethenes	Choe et al., 2000 (111); Singh et al., 1999 (112); Wanaratna et al., 2006 (113); Moore et al., 2003(114); Kim et al., 2006 (115)
		Degrades chlorinated hydrocarbons, lindane, atrazine, pentachlorophenol, 4,4'- dinitrostilbene-2,2'-disulfonic acid.	Lowry et al., 2004 (116); Liu et al., 2005 (117); Song et al., 2005 (118); Fan et al., 2007 (119); Joo et al., 2008 (120).
13	Nanoscale iron particles	Used in transformation and detoxification of chlorinated organic solvents, organochlorine, pesticides and polychlorinated biphenyls (PCBs).	Zhang et al., 2003 (121); Yean et al., 2005 (122).
14	Magnetic chitosan nano-adsorbent	Removal of Co	Chang et al., 2006 (123).
15	Magnetic alginate microcapsules	Removal of Ni	Ngomsik et al., 2006 (124).
16	ZVI, iron-nickel, and iron-palladium nanowires	Remediation of chlorinated organics	Yoo et al., 2007 (125).

Non-magnetic nanoparticles like that of nanosilver particles have different number of applications: these are used in immunoassays¹³⁰, sensors for histidine¹²⁶, ammonia¹²⁷, detection of herbicides¹²⁹. Nano silver acts as antimicrobial agent & even kills antibiotic-resistant strains¹³². Titanium dioxide is used for degradation of inorganic¹⁴⁰, organic pollutants and dyes¹³³⁻¹³⁹. Titanium dioxide

kills animals by attaching to the chitinous exoskeleton of the juvenile animals¹⁴². Magnesium oxide (MgO) nanoparticles act as biocides against Gram positive & negative bacteria¹⁴⁶. An alumina nanofiber removes 99.9999% of bacteria, viruses and protozoan cysts from water¹⁴⁹. The detailed applications of various non-magnetic metal nanoparticles are represented in Table 3.

Table 3
Different non - magnetic metal nanoparticles and their environmental applications

S. No.	Non magnetic metal nanoparticles	Application	References
17	Nanosilver	Colorimetric sensors for Histidine, ammonia, determination of fibrinogens in human plasma	Xiong et al., 2008 (126); Dubas et al., 2008a (127); ZhiLiang et al., 2007 (128).
		Detection of herbicides, DNA/RNA, Used in immunoassays	Dubas et al., 2008b (129); Aslan et al., 2005 (130).
		Anti-inflammatory activity	Nadworny et al., 2010 (131).
		Antimicrobial agent	Yin et al., 2011(132).
18	Titanium dioxide	Concentration and degradation of contaminants. Removal of atrazine organochlorine pesticides, Methyl orange, phenanthrene.	Seitz et al., 2011(133); Zhanqi et al., 2007 (134); Chen et al., 2003 (135); Peng et al., 2005(136); Li et al., 2006 (137); Yang et al., 2009 (138); Konstantinou et al., 2003(139).
		Removal of inorganic pollutants arsenate	Zhang et al., 2009 (140).
		Simultaneous water purification coupled with H ₂ generation	Choi et al., 2010 (141).
		Kills animals by attaching to the chitinous exoskeleton of the juvenile animals	Dabrunz et al., 2011(142).
19	Zinc oxide	Adsorption of organic contaminants, degradation of organic dyes, methyl orange, rhodamine B.	Yang et al., 2009 (138); Ullah et al., 2008 (143); Wang et al., 2007(144); Huan et al., 2007 (145).
20	Magnesium oxide (MgO) nanoparticles	Biocides against Gram positive & negative bacteria	Stoimenov et al., 2002 (146).
21	Nanocontact sensor	Used for monitoring heavy metals in drinking water.	Forzani et al., 2005 (147).
22	Silicate (ETS-10) & aluminum - substituted ETAS-10	Removal of heavy metals like Pb ²⁺ and Cd ²⁺	Choi et al., 2006 (148).
23	Alumina nanofibres	Removes 99.9999% of bacteria, viruses and protozoan cysts from water	Smith et al., 2006 (149).
24	Regenerable gold nanowires	Used as sensors for mercury	Keebaugh et al., 2007 (150).
25	Nanoscale zeolitic imidazole frameworks (ZIFs) & metal organic frameworks(MOFs)	Able to capture CO ₂	Banerjee et al., 2008 (151); Phan et al., 2010 (152); Deng et al., 2010 (153).
26	CuO Nanoparticles	Adsorption of As(III) and As(V)	Martinson et al., 2009 (154).

2.5 Bionanoparticles

Bionanoparticles are naturally produced entities that are of nanometer dimension. The commonly used metals in the synthesis of nanoparticles are Silver, Aluminum, Gold, Zinc, Carbon, Titanium, Palladium, Iron, Copper etc. However, these metals are used individually and in combination in the synthesis of bio-nanomaterial. The biosynthesis of nanoparticles employs use of biological agents like bacteria, fungi, actinomycetes, yeast, algae and plants^{155, 156}.

In case of plants as biological agents, extracts of plant parts like leaves, bark, seeds, latex and pulp are used. The advantage of using biological agents is faster reduction of metal ions at ambient temperature and pressure conditions. Most of these show antimicrobial activity & inhibit the growth of pathogenic microbes. The different bionanoparticles synthesized using silver, gold, silver-gold, and other metals are listed in Tables 4 & 5.

Table 4
Bionanoparticles synthesized using silver with microbes and botanicals

S. No.	Organism	References
Bacteria		
27	<i>Pseudomonas stutzeri</i> AG259, <i>Lactobacillus</i> strains, <i>Klebsiella pneumonia</i> , <i>Bacillus licheniformis</i> , <i>Corynebacterium sp.</i> , <i>Corynebacterium sp.</i> , <i>Geobacter sulfurreducens</i> , <i>Bacillus subtilis</i> , <i>Escherichia coli</i> , <i>Staphylococcus aureus</i> , <i>Lactic acid bacteria</i> , <i>Brevibacterium casei</i> , <i>Streptomyces rochei</i>	Tanja et al.,1999 (157); Nair et al., 2002 (158); Ahmad et al., 2007 (159); Kalimuthu et al., 2008 (160); Zhang et al., 2005 (161); Law et al., 2008 (162); Saifuddin et al., 2009 (163); Gurunathan et al., 2009 (164); Nanda et al., 2009 (165); Sintubin et al., 2009 (166); Kalishwaralal et al., 2010 (167); Selvakumar et al., 2012 (168).
Fungi		
28	<i>Fusarium oxysporum</i> , <i>Aspergillus fumigates</i> , <i>Aspergillus niger</i> , <i>Phanerochaete chrysosporium</i> , <i>Aspergillus flavus</i> , <i>Cladosporium cladosporioides</i> , <i>Fusarium semitectum</i> , <i>Trichoderma viride</i> , <i>Pencillium fellutanum</i> , <i>Aspergillus clavatus</i>	Bhainsa et al., 2006 (53); Ahmad et al., 2003 (169); Gade et al., 2008 (170); Vigneshwaran et al., 2006 (171); Shivaraj et al., 2013 (172); Balaji et al., 2009 (173); Basavaraja et al., 2008 (174); Fayaz et al., 2010 (175); Kathiresan et al., 2009 (176); Verma et al., 2010 (177).
Algae		
29	<i>Navicula atomus</i> , <i>Diadesmis gallica</i> , <i>Sargassum wightii</i> , <i>Fucus vesiculosus</i> , <i>Turbinaria conoides</i>	Asmathunisha et al., 2013 (178); Shanmugam et al., 2012 (179).
Plants		
30	<i>Azadirachta indica</i> , <i>Cinnamomum camphora</i> , <i>Phyllanthus amarus</i> , <i>Carica papaya</i> , <i>Pelarogonium graveolens</i> , <i>Aloe vera</i> , <i>Eclipta</i> , <i>Jatropha curcas</i> , <i>Cynnamon zeylanicum</i> , <i>Murraya koenigii</i> , <i>Coriandrum sativum</i> , <i>Gliricidia sepium</i> , <i>Amaranthus polygonoides</i> , <i>Syzygium cumini</i>	Kasthuri et al., 2009 (61); Shankar et al., 2004 (180); Huang et al., 2008 (181); Mude et al., 2009 (182); Shankar et al., 2003 (183); Zhang et al., 2010 (184); Jha et al., 2009 (185); Bar et al., 2009a (186); Sathishkumar et al.,2009 (187); Philip et al., 2011a (188); Philip et al., 2011b (189); Sathyavathi et al., 2010 (190); Rajesh et al., 2009 (191); Jannathul firdhouse et al., 2013 (192); Ramprasad et al., 2012 (193).

Table 5
Bionanoparticles synthesized using Silver, Gold, copper, platinum and lanthanide with botanicals

S. No.	Botanicals	References
31	<i>Eucalyptus camaldulensis</i> , <i>Medicago sativa</i> , <i>Chilopsis linearis</i> , <i>Tamarindus indica</i> , <i>Tagetes erecta</i> , <i>Helianthus annuus</i>	Ankamwar et al., 2005(52); Haratifar et al., 2009 (194); Singh et al., 2006 (195); Armendariz et al., 2004 (196); Krishnamurthy et al., 2012 (197); Liny et al., 2012 (198).
32	<i>Black tea</i> , <i>Aloe vera</i> , <i>Cinnamomum camphora</i> , <i>Lycopersicon esculentum</i>	Begum et al., 2009(199) ; Chandran et al., 2006 (200); Huang et al., 2007 (201); Asmathunisha et al., 2013 (202).
33	<i>Aloe vera</i> , <i>Diopyros kaki</i> , <i>Brassica juncea</i>	Maensiria et al., 2008 (203); Song et al., 2010 (204); Haverkamp et al., 2007 (205).

2.5.1 BIONANOPARTICLES WITH ANIMAL POLYMERS

In our recent study, the eggshells at nanoscale were used as adsorbents to remove copper and lead from synthetic waste water. We carried out experiments with small quantities of egg shell nanoparticles and could

achieve higher percentages of metal removal (Pb:94.055%, Cu:92.055%) as compared to non-nanoparticles (Table 6). The preparation of eggshells at nano level uses the green technology: it does not involve the use of any of the chemicals; just the size was reduced. In the same way the other animal polymers like

chick and duck feathers were used adsorbents for the remediation of lead and the percentage removal was 70.73 and 58.8% respectively²⁰⁶.

To increase the efficiency of biosorption, an attempt is being made to bring these feathers also to nanoscale level.

Table 6
Percentage removal of toxic metals by various non- nanoparticles

S. No.	Non-nanoparticle	% removal	Reference
34	Chick feather	70.73	Ratna kumari et al.,2011 (206)
35	Duck feather	58.8	Ratna kumari et al.,2011 (206)
36	<i>Adenanthera pavonina</i>	93.72	Srinivasa rao et al.,2013 (207)
37	Carbonate hydroxyapatite	93.7	Zheng et al.,2007 (208)
38	Gum kondagogu	93.7	VTP Vinod et al.,2011 (209)
39	<i>Saccaromyces cerevisiae</i>	54.98	Salem M Hamza et al.,2010 (210)

2.6 CONCLUSION

Traditional techniques like chemical precipitation, coagulation, ion exchange are still in vogue for remediation of heavy metals from contaminated environments. But these techniques have some limitations & require high capital investments. So, to overcome these disadvantages, currently more attention is paid towards non conventional alternative techniques like biosorption. Till date different kinds of biosorbents like bacteria, fungi, algae, plant, animal polymers etc. are in use for removal of heavy metals. If a sorbent is a waste or low cost material, the sorption efficiency can be improved by increasing the concentration of the sorbent. Eggshells, a waste material produced in huge quantities from poultry and food industries, are being

explored as a sorbent for sorption of heavy metals. Due to the tolerance and bioaccumulation ability of metals, the egg shells at nanoscale level showed an enhanced percentage of removal of lead and copper and this sorbent could be used in scale-up process to remediate effluent water. This is suggestive of the fact that biosorption rates could be effectively increased by just size reduction of the biosorbent material. Thus eggshells at nanoscale level are excellent, eco-friendly, animal biopolymers and a viable choice for remediation of toxic metals. Also, nanocomposites could be designed with the eggshells and eggshell membranes for enhanced efficiency and manufacture of filter devices for use in effluent treatment plants.

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