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Waste to health: Bioleaching of nanoparticles from e-waste and their medical applications
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KEYWORDS: e-waste, metal nanoparticles, microbial leaching, weed extract, biomedical sciences

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ABSTRACT *World today is run by the electronic gadgets which have become in despensable, but they are a bane to the environment once they turn into electronic waste or 'e-waste'. Due to frequent upgradation of gadgets, enormous accumulation of e-waste and its recycling for extraction of essential metals via traditional means are a matter of real concern especially in developing countries, due to release of hazardous materials in nature. Similarly production of metal nanoparticles by physical and chemical methods are too harsh and non-ecofriendly. Also such nano metals have limite shelf life. The economy of the e-waste recycling industry depends on the recovery of precious metals such as copper, gold and silver. Therefore e-waste can be recycled and metal nanoparticle can be produced in eco-friendly manner. 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. Recently weeds, popularly known as 'enemies of the farmer', have also been used successfully for the synthesis of gold, copper and silver nanoparticles. The use of natural eco-friendly sources such as microorganisms and weed extracts for the production of nanomaterials is a promising approach, owing to the feasibility and cost-effectiveness of the process. The metal nanoparticles obtained after bioleaching of e-waste can find a range of applications especially in the field of medicine. These applications include drug delivery, gene therapy, antimicrobials, medical prosthetics and tissue engineering. Thus, it is possible to 'marry' the two diverse fields as 'e-waste to nano' for biomedical sciences, thereby providing an active area of research in nanotechnology.*

1. Introduction
The idea of nanotechnology was introduced by the physicist Michael Faraday in 1857. It was in 1974 at Tokyo when a Science University professor Norio Taniguchi coined the term 'nanotechnology'. The nano-revolution conceptually started in the early 1980s when the first work on nanotechnology was published by Eric Drexler in 1981(Drexler, 1981).

Nanotechnology deals with development of structures by physical / chemical methods which posses 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).

Nanobiotechnology is the branch of biotechnology which deals with synthesis and fabrication of nanoparticles by biological systems and their applications especially in biological systems. 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.

Electronic waste popularly known as 'e-waste' broadly comprises of waste from electronic appliances such as computers, mobile phones, digital music recorders, refrigerators, washing machines and televisions. Today a huge quantity of e-waste is generated because of the purchasing power of the consumers; which has resulted in a massive influx of advanced models, leading to the disposal of the old and obsolete ones. In general, any electronic good is a complicated assembly of hundreds of materials, a lot of which are highly toxic. These include halogenated derivatives, heavy metals, plastics and its additives. In reality, 90-92% of the e-waste components can be recycled / reused but it is rarely brought into practice.

Industrialized nations export their e-waste to countries such as India, China and Pakistan, even though these developing countries are not adequately equipped to deal with the burden of such waste. The cost of recycling of a single computer in the United States is US $ 20 while that in India is only US $ 2. Thus, an amount of US $ 18 can be saved if the computer is exported to India (Elcina, 2009). According to United Nations Environment Program, it is estimated that 20 to 50 tonnes of e-waste is being generated per year worldwide (UNEP, 2011).

The Central Pollution Control Board, India had carried out a survey during 2005, which estimated 0.1347 million metric tonnes of e-waste was generated in the country in the year 2005. Considering the growth rate, the mass of e-waste generated will reach nearly 0.7 million metric tonnes by 2015 and 2 million metric tonnes by 2025 (Figure 1) (Chatterjee, 2011).

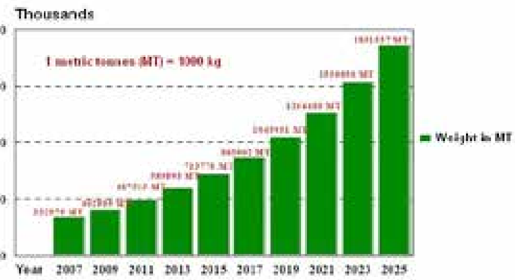

Figure 1: Projected data for e-waste growth in India (Chatterjee, 2011)

An integrated circuit (also known as microcircuit, microchip, silicon chip or chip) is a miniaturized electronic circuit. This circuit mainly consists of semiconductor devices in addition to other components, manufactured on a thin surface of a semiconductor. The electronic circuits in computers, cathode ray tubes, capacitors and transistors comprise of many materials which have been listed in Table 1.

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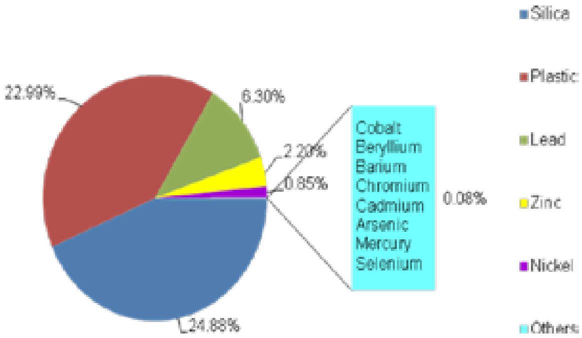

Figure 2: Distribution of hazardous metals in an Integrated Circuit

Disposal and recycling of this new kind of waste is posing a serious threat to both developed and developing countries. Silica and plastics form the major component of the integrated circuits followed by iron and aluminium. Heavy metals such as copper, lead, mercury etc are also present in batteries, cathode ray tubes, printed wiring boards, wires and conductors. Figure 2 denotes the distribution and the percentage of all hazardous components present in E-waste. Many of these materials are harmful not only to humans but also to the ecosystem as a whole. These hazards can be categorized into health and environmental hazards as shown in Figure 3.

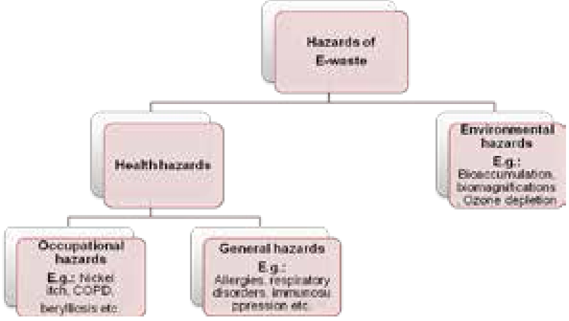

Figure 3: Hazards of e-waste

Health hazards due to commercial methods of recycling can be further classified as occupational and general based on duration of exposure to the component. Individuals who are constantly exposed to such hazardous materials, especially labourers suffer from chronic disorders. The emission of these contaminants pollutes the environment affecting masses, resulting in a number of health problems. These pollutants are also responsible for environmental issues such as depletion of the ozone layer and biomagnification. They are also known to have drastic effects on economically significant crops and animals thus disrupting the food chain. Table 1 gives all the health and environmental effects of the hazardous metals found in e-waste.

Table 1: Hazardous components of e-waste with their health and environmental effects (SVTC, 2000)

Sr. No.	Component	Content (% of total weight)	Health hazards		Environmental hazards	Reference
			Occupational	General		
1.	Silica	24.8803	Chronic respiratory effects, Lung cancer, Bronchitis, renal diseases, Immunological disorders, autoimmune diseases, Chronic obstructive pulmonary disease (COPD) and emphysema	Irritation and inflammation of skin, eyes, lungs and mucous membranes, silicosis	-	(Lenntech: Silicon)
2.	Plastic	22.9907	Induction of skin and lung cancers	Respiratory problems	Depletion of the ozone layer, release of toxic fumes and dioxin, threat to marine ecosystem	(EMPA, c2000)
3.	Lead	6.2988	Damage to kidneys and nerve connections, blood and brain disorders	Vomiting, diarrhea, convulsions, skin damage, headache, gastric ulcers, coma or even death	Bioaccumulation in soil, plants and animals, Affect aquatic life	(Pinto, 2008; Blake, 2010)
4.	Zinc	2.2046	Metal fever	Cytotoxicity, ischemia and trauma, stomach cramps, skin irritations, vomiting, nausea, allergies and anaemia	threat to cattle, affect soil fertility, contamination of groundwater	(Plum and Haase 2011, Lenntech: Zinc)
5.	Nickel	0.8503	'Nickel itch'	Skin-allergy, cancer, Sickness and dizziness, Lung embolism, Respiratory failure, Birth defects, Asthma and chronic bronchitis, Heart disorders	damage plants, diminish the growth rates of algae	(Pant et al., 2012)
6.	Cobalt	0.0157	asthma and pneumonia	Vomiting and nausea, vision problems, heart problems, thyroid damage	-	(Lenntech: Cobalt)
7.	Beryllium	0.0157	Chronic Beryllium Disease- berylliosis	Skin diseases- wart-like bumps, lung cancer, allergic reactions, weakness, tiredness, breathing problems, pneumonia	-	(Wellman)
8.	Barium	0.0315	Increased blood pressures, heart rhythm changes, stomach irritation, muscle weakness, changes in nerve reflexes, swelling of brains and liver, kidney and heart damage	brain swelling, muscle weakness, damage to the heart, liver and spleen	Bioaccumulation	(EMPA, c2000)
9.	Chromium	0.0063	Ulcerations, dermatitis, and allergic skin reactions, ulceration and perforation of the mucous membranes of the nasal septum, irritation of the pharynx and larynx, asthmatic bronchitis, bronchospasms and edema, gastro-intestinal bleeding, shock, coma and may even prove fatal.	Chemical burns (caused while chromium electroplating), asthmatic bronchitis, skin rashes, upset stomachs and ulcers, respiratory problems, weakened immune systems, kidney and liver damage, alteration of genetic material, lung cancer	Affect the gills of fish, low immunity, birth defects and infertility in animals	(Lin et al., 2009; Pellerin and Booker, 2000)

10.	Cadmium	0.0094	lung cancer and kidney damage, pulmonary emphysema and bone disease (osteomalacia and osteoporosis), Itai Itai disease.	flu-like symptoms of weakness, fever, headache, chills, sweating and muscular pain, Shortness of breath, lung edema, immune system is affected.	Accumulation in cattle and aquatic ecosystem, Cadmium poisoning in earthworms	(Han et al., 2009; Godt et al., 2006)
11.	Arsenic	0.0013	Irritation of the stomach and intestines, infertility and miscarriages with women, lung cancer, declined resistance to infections, heart disruptions and brain damage	Skin and lung irritation, decreased production of RBCs and WBCs	Alteration of genetic material of fish, Arsenic poisoning and death of birds consuming these fish	(Eisler, 1988; Woolson, 1975; EMPA, c2000; Saldivar and Soto, 2009)
12.	Mercury	0.0022	Mercury poisoning, affect human fertility, damage to genitourinary system, central and peripheral nervous system, tremors, leg cramps, irritability, paraesthesia, (a sensation of pricking in the skin), pink extremities and exfoliation of skin (Pink Disease)	Brain and liver damage, depression, and behavioral disturbances, Cough, dyspnoea, chest tightness, lethargy, restlessness, fever and signs of pneumonitis	Biomagnification in predatory fish, concentrates through the food chain	(Langford and Ferner, 1999)
13.	Selenium	0.0016	Selenosis, neurological damage, hair loss, sloughing of nails, swelling, rashes, neurological disorders such as numbness	Gastrointestinal disorders, fatigue, irritability, bronchial asthma, conjunctivitis, vomiting and diarrhoea	Biomagnification through the food chain in terrestrial and aquatic animals, reproductive failure and birth defects in animals	(Lenntech: Selenium; Vinceti et al., 2001; Lemly, 1997)

2. Problems in traditional methods of e-waste disposal and recycling

Improper recycling and disposal of e-waste can result in dangerous health and environmental hazards. Electronic waste contains not only hazardous but also precious and valuable metals such as gold and silver. The recommendation for electronic waste is to refurbish and reuse the devices. If not possible to reuse, the waste can be either recycled or disposed depending upon its components. The most common methods used for e-waste disposal include incineration, land filling and open air burning. Use of environment-friendly methods serves as a promising solution to minimize the hazards of e-waste disposal. Figure 4 explains the different methods which can be employed for managing electronic waste.

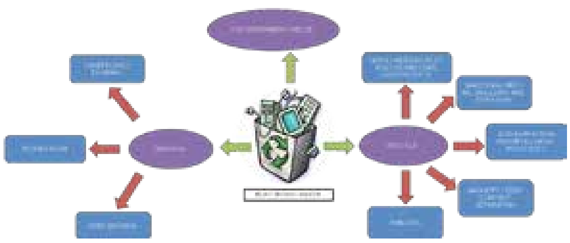

Figure 4: E-waste management

The old electronic devices dumped off can be refurbished i.e. the device can be restored to a workable condition and reused. The repaired and modified device can then be used for domestic purposes (Schluep, 2009).

Drawbacks of the conventional and primary disposal methods for e-waste: (Onwughara et al., 2010; Lundstedt, 2011; Tam, 2011)

- E-waste including printed circuit boards and plastic cases when incinerated becomes an issue of public health concern as both the toxic fumes (such as dioxins, furans etc. emitted when plastics with halogenated flame retardants are burned) and the toxic slag are released into the environment having a negative impact on health and environment.
- Methods such as land filling causes hazardous compounds (lead, cadmium, zinc, nickel etc.) to leak into the surrounding environments, including nearby surface and ground water reservoirs, and also evaporate to the atmosphere. Landfills are also prone to uncontrolled fires, which can release toxic fumes and thus making it an non-ecofriendly method of e-waste disposal.
- Open air burning of electronic waste causes contamination of air, food, ground water and drinking water.
- In addition to dioxins, a large amount of other pollutants are also emitted into the air, e.g. Poly Aromatic Hydrocarbons, various chlorinated and brominated compounds and several metals including tin, arsenic, lead, nickel, chromium, copper, antimony, zinc and cadmium.
- All the physical and chemical treatment prodesses require harsh conditions.

Table 2 gives the list of different components of e-waste recycled by different treatment methods and the related health hazards. These traditional methods have a number of hazardous effects on the environment and on human health. Also the overall cost of recycling has been a matter of concern as all the e-waste from the developed countries are now being transferred to developing countries such as India and China. The harsh conditions required for such physical and chemical treatment processes emphasizes the need for new eco-friendly techniques to recycle e-waste and obtain materials in usable and valuable form (Onwughara, 2010; Chatterjee and Kumar, 2009). The most acceptable replacement to the existing conventional processes can be 'biological treatment' of e-waste.

Table 2: Components of e-waste and their recycling methods

Sr. No.	Material to be recycled	Treatment	Reference
1.	Plastic	Shredding, melting, moulding, extrusion, pyrolysis, depolymerization, coke oven etc.	(Tam, 2011)
2.	Ferrous metals (Eg. iron and steel)	Magnetic separation, acid extraction, sid extraction, Son, AD, nano-Cuium exposure: [www.liardtech.comhredding, smelting hydrometallurgic processes etc.	(Schluep et al., 2009)
3.	Non-ferrous metal (Eg. copper, lead, tin, nickel)	Smelting, pyrometallurgic processes, optical sorting, density separation, eddy current separation or vibration separation	(Schluep et al., 2009)
4.	Glass (from Cathode Ray Tubes)	Smelting (to separate lead)	(Chatterjee and Kumar, 2009)
5.	Aluminium and others	Aluminium remelter/ refiner	(Schluep et al., 2009)
6.	Precious metals (Eg. gold, silver, palladium, copper etc.)	Pyrolysis, solvent extraction	(Chatterjee, 2012; Park and Fray, 2009)

3. Synthesis of nanoparticles

Synthesis and fabrication of nanoparticles can be carried out by one of the following approaches (indicated in Figure 5)-

1. Top-down approach

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2. Bottom-up approach

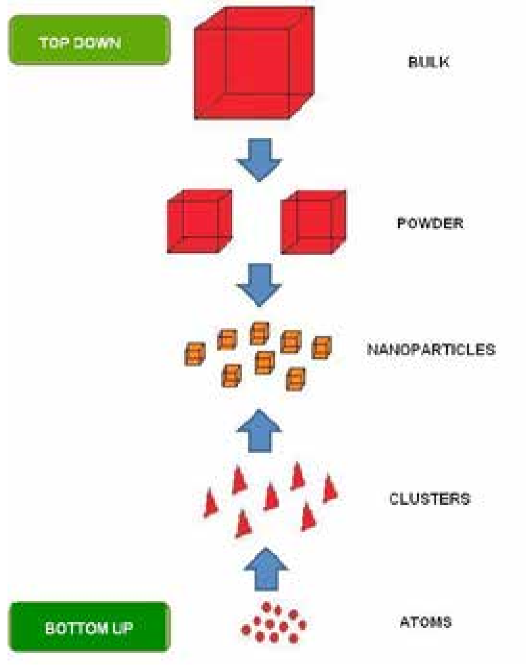

Figure 5: Approaches for synthesis of metal nanoparticles

As the name suggests, the top-down approach refers to the splitting up of a bulk material to finally obtain a nano-sized particle. For this purpose, various chemical, electrochemical and mechanical methods can be used (Singh et al., 2011). Since this approach involves cutting/slicing of a material to bring to a nano-size, sometimes the particles obtained are imperfect with respect to their crystal structure. Nevertheless, this process is widely used in the bulk synthesis of nanoparticles.

The bottom-up approach follows the exact reverse of the earlier method and works on the principle of molecular self-assembly. Using this approach, a nanoparticle is built up atom by atom, leading to molecules and clusters until the specific dimensions are obtained. This method is found to yield nanoparticles that are more homogenous in nature and perfectly structured. Due to its clear advantages, the bottom-up approach is far more popular in the synthesis of metal nanomaterials (Thakkar et al., 2010). Inspite of these advantages over top-down methods, the bottom –up methods do have a number of drawbacks.

Metal nanoparticles can be synthesized by a variety of bottom-up methods, which fall under 3 broad categories as described in Figure 6.

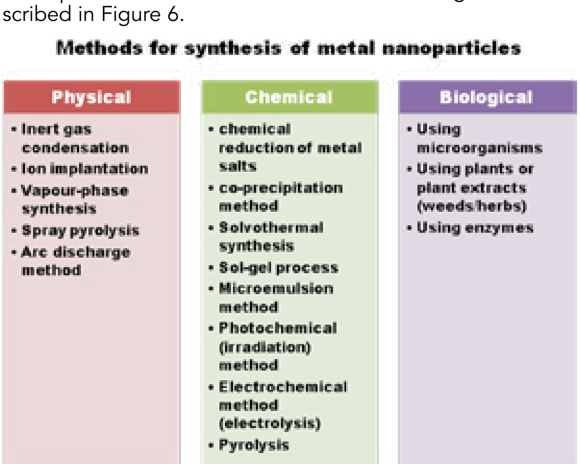

Figure 6: Methods of metal nanoparticles synthesis

3.1 Drawbacks of Physical methods: (Swihart, 2003; Kruis et al., 1998; Raab et al., 2011)

- Controlling the reaction conditions is highly significant in determination of the size and shape of nanos obtained.
- Nano metals having high melting points can only be synthesized by methods such as Arc discharge method.
- The most important disadvantage of physical methods of nanoparticles synthesis is that high quality pure source materials are required.
- Another problem of these usual methods is that the particle size distributions are relatively wide and not uniform.
- Scaling up such processes is difficult.
- Also the extremely short shelf life of the nanoparticles produced makes addition of a capping agent indispensable.
- The nanoparticles produce have very low thermal stability.

3.2 Drawbacks of Chemical methods: (Moshfegh et al, 2011; Vaidyanathan et al, 2009; Korbekandi and Iravani, 2012)

- Controlling the size and shape of the nanoparticles synthesized by these methods is difficult.
- Controlling the growth of crystals and its maintaining stabilization is a major issue of concern.
- Multiple purification steps required.
- Requires use of explosive solvents.
- High consumption for processes such as sonication or microfluidization.
- Requirement of high-priced equipments.
- Harmful effects of byproducts formed during the process.
- The nanoparticles produced by these methods have shorter shelf life.

3.3 Need for Biological Methods:

Considering all the above demerits of physical and chemical methods of nanoparticle synthesis there was a need felt to find new favourable techniques for the same. Biological methods for nanoparticle synthesis were then attempted and proved to be a boon to the field of nanotechnology. Biological systems involving bacteria, fungi, actinomycetes, algae, plants etc. were examined for their capacity to produce nanoparticles.

Advantages over Physical and chemical methods: (Korbekandi and Iravani, 2012; Jain et al., 2010; Natarajan et al., 2010; Kaler et al., 2010)

- Toxic, explosive materials are not required.
- Pure and expensive chemicals are not required.
- Controlling and maintaining the ideal process conditions is easier.
- Environmental friendly processes with no toxic byproducts.
- Nanoparticles produced have a longer shelf life and stability as natural capping takes place.
- Cost effective and single step methods which can be easily scaled up.
- Easy downstream processing and purification of nanoparticles produced.

Among the above mentioned merits of biological synthesis of nanoparticles, natural capping of the nanoparticles has been of great importance. This property of biosynthesis has solved the major problems of formation of nano aggregates and artificial capping as required by the other conventional methods. During the biological synthesis, the nanoparticles produced are immediately coated with a protein molecule making a natural cap and thus preventing formation of aggregates. Natural capping obtained in turn provide a longer shelf life and stability to the nanoparticles synthesized. The later section of the review details out the different microorganisms and weeds known for their property to synthesize metal nanoparticles. Thus considering the commendable advantages of biological methods of metal leaching from electronic waste by passing the harsh physico-chemical methods

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and using these biological systems to leach out the metals from e-waste in 'nano' form could be considered on a big way in near future.

4. Bioleaching of metals from e-waste and obtaining them in nano form

Bioleaching is the process of extracting metals from the waste using biological systems such as microorganisms and plants. Microorganisms (bacteria and fungi) are known to leach out the precious metals commonly present in electronic-waste such as gold, silver, palladium and others such as copper, zinc, nickel etc. Bacteria such as Chromobacterium violaceum and Pseudomonas sp.(Pradhan and Kumar, 2012), Sulfobacillus thermosulfidooxidans (Ilyas et al., 2007), Acidiphilium acidophilum (ATCC 27807) (Hudec et al., 2009) are observed to bioleach metals copper, nickel, gold, silver etc. from e-waste. Also fungi such as Aspergillus niger, Penicillium simplicissimum (Brandl et al., 2001), Aspergillus fumigatus, Aspergillus flavus (Jena et al., 2012) produce organic acids to leach out metals copper, lead, nickel, strontium and aluminium from printed circuit boards. However the form of metal derivatives leached out of the waste by these organisms are found in the soluble form with not much relevant applications. Thus, bioleaching of metals from e-waste in pure and desirable form is required.

4.1 Microbial leaching of metals in nano form

Microorganisms (bacteria, fungi, actinomycetes, algae) and plants extracts are known for production of nanoparticles of many metals such as copper, gold, silver, zinc, nickel, palladium, lead etc. Table 4 denotes the different micoorganisms synthesizing nanoparticles of metals which are generally present in e-waste.

Table 3: Biosynthesis of metal nanoparticles using microorganisms

Metal	Organism	Size of metal nano obtained	Reference
Gold (Au)	Bacteria:		
	Pseudomonas aeruginosa	15-30 nm	(Husseiny et al., 2007)
	Stenotrophomonas maltophilia	~40 nm	(Nangia et al., 2009)
	Plectonema boryanum	20-200 nm	(Lengke et al., 2007)
	Rhodopseudomonas capsulata	10-20 nm	(He et al., 2008)
	Fungi:		
	Verticillium luteoalbum	10-100 nm	(Gericke and Pinches, 2006)
	Trichothecium sp.	10-25 nm	(Ahmad et al., 2005)
	Actinomycetes:		
	Rhodococcus sp.	5-15 nm	(Ahmad et al., 2003)
	Yeast:		
	Yarrowia lipolytica	15 nm	(Agnihotri et al., 2009)
	Algae:		
	Calothrix pulvinata	~5.5 nm	(Brayner et al., 2007)
	Anabaena flos-aquae	~12.5 nm	(Brayner et al., 2007)
	Leptolyngbya foveolarum	~6.5 nm	(Brayner et al., 2007)
	Laminaria japonica	15-20 nm	(Ghodake and Lee, 2011)
Silver (Ag)	Bacteria:		
	Klebsiella pneumonia	50-100 nm	(Minaeian et al., 2008)
	Escherichia coli	40-60 nm	(Minaeian et al., 2008; Natarajan et al., 2010)
	Enterobacter cloacae	50-100 nm	(Minaeian et al., 2008)
	Bacillus sp.	5-15 nm	(Pugazhenthiran et al. 2009)
	Shewanella oneidensis	9-12.5 nm	(Suresh et al., 2011)
	Pseudomonas sp. ram bt – 1	20-100 nm	(Rammohan et al., 2011)
	Bacillus amyloliquefaciens	14.6 nm	(Joerger et al., 2001)
	Fungi:		
	Aspergillus fumigatus	5-25 nm	(Bhainsa et al., 2006)
	Penicillium sp.		(Sadowski et al., 2008)
	Coriolus versicolor	32.5 nm	(Sanghi and Verma, 2009)
	Alternaria alternate	5-50 nm	(Gajbhiye et al., 2009)
	Trichoderma reesei	8-10 nm	(Vahabi et al., 2011)
	Penicillium purpurogenum NPMF	7 nm	(Nayak et al., 2011)
	Aspergillus flavus		(Moharrer et al., 2012)
	Algae:		
	Calothrix pulvinata	~15.5 nm	(Brayner et al., 2007)
	Anabaena flos-aquae	~40 nm	(Brayner et al., 2007)
Selenium (Se)	Bacteria:		
	Klebsiella pneumoniae	245 nm	(Fesharaki et al., 2009)
	Pseudomonas alcaliphila	50-500 nm	(Zhang et al., 2011)
	Bacillus cereus	150-200 nm	(Dhanjal and Cameotra, 2010)
Copper (Cu)	Bacteria:		
	Pseudomonas stutzeri	50-150 nm	(Varshney et al., 2011)
	Morganella sp.	3-10 nm	(Ramanathan et al., 2011)
	Pseudomonas sp.	84-130 nm	(Majumder, 2012)
	Fungi:		
	Fusarium oxysporum	93-115 nm	(Majumder, 2012)
	Actinomycetes:		
	Streptomyces sp.	100-150 nm	(Usha et al., 2010)
Palladium (Pd)	Bacteria:		
	Clostridium pasterianum	1-15 nm	(Chitambaram et al., 2010)
	Shewanella oneidensis	10-50 nm	(Windt et al., 2006)
	Desulfovibrio desulfuricans	50 nm	(Lloyd et al 1998)
Titanium (Ti)	Bacteria:		
	Lactobacillus sp.	40-60 nm	(Prasad et al., 2007)
	Fungi:		
	Fusarium oxysporum	6-13 nm	(Bansal et al., 2005)

Mercury (Hg)	Bacteria: Enterobacter sp.	2-5 nm	(Sinha et al., 2011)
Manganese (Mn)	Bacteria: Bacillus sp.	4.6 nm	(Sinha et al., 2011)
Silica (SiO_2)	Fungi: Fusarium oxysporum	5-15 nm	(Bansal et al., 2005)
Cadmium Sulphide (CdS)	Bacteria: Escherichia coli	2-5 nm	(Rozamond et al., 2004)
	Yeast: Candida glabrata Schizosaccharomyces pombe	200 nm 200 nm	(Dameron et al., 1989) (Dameron et al., 1989)
Lead (Pb) / Lead sulfide (PbS)	Bacteria: Rhodobacter sphaeroides Bacillus megaterium	10.5 ± 0.15 nm 10-20nm	(Bai et al., 2008) (Prakash et al., 2010)
	Fungi: Aspergillus sps.	5-20 nm	(Pavani et al., 2012)

Microorganisms are considered as potential mini biofactories which can be considered for the synthesis of nanoparticles like gold and silver. Gold being the most precious metal after platinum, is known to be potentially obtained in pure nano form by bacteria such as Pseudomonas aeruginosa (Husseiny et al., 2007), Stenotrophomonas maltophilia (Nangia et al., 2009) etc., fungi such as Verticillium luteoalbum (Gericke and Pinches, 2006) and Trichothecium sp. (Ahmad et al., 2005) and actinomycetes such as Rhodococcus (Ahmad et al., 2003). Also yeast such as Yarrowia (Agnihotri et al., 2009) is reported to produce gold nanoparticles. Algae Calothrix and Anabaena sp. (Brayner et al., 2007) can produce gold and silver nanoparticles with an average size range of 5 to 40 nm. Gold nanoparticles synthesised by these organisms have found to be having a number applications. Common bacteria such as Klebsiella pneumoniae, Escherichia coli, Pseudomonas (Minaeian et al., 2008; Pugazhenthiran et al., 2009) and many more are known to produce extracellular spherical silver nanoparticles of diameter ranging from 50 to 100 nm. Species of Aspergillus, Penicillium and Trichoderma can also synthesise silver nanoparticles of very small size (Sadowski et al., 2008; Vahabi et al., 2011; Nayak et al., 2011; Moharrer et al., 2012). Pseudomonas sp. has the potential to synthesis selenium and copper nanoparticles which could have a number of biomedical applications (Zhanga et al., 2011; Varshney et al., 2011). Hazardous metals such as titanium, cadmium, mercury, manganese, selenium and the most precious palladium have also been obtained in nano form using common bacteria and fungi, some of which are specified in the Table 4 (Chidambaram et al., 2010; Windt et al., 2006; Lloyd et al., 1998; Prasad et al., 2007; Bansal et al., 2005; Sinha et al., 2011; Sweeney et al., 2004; Dameron et al., 1989). Expanding this capability of commonly available microorganisms to produce a variety of metal nanoparticles has a wide scope in the area of nanobiotechnology.

Many species of bacteria and most Archaea possess a crystalline layer as the outermost component of their cell envelopes known as the S-layer. These S-layers are made up of proteins or glycoproteins and have a pore size ranging from 2 to 6 nm (Pum and Sleytr, 1999). Organisms of the Bacillaceae family possess long O-glycosidically linked glycans as their S-layer (Messner et al., 2008). S-layers serve as templates for the synthesis of inorganic nanocrystals within a broad diameter range of 3–15 nm. Nanoparticles with lattice symmetries such as oblique, square or hexagonal can be easily synthesised using these S-layer templates (Pum and Sleytr, 1999). Exploring this potential of the S-layers of bacteria, 'tailor-made' nanoparticles of a uniform size and shape can be obtained artificially (Puranik et al., 2008). This method of bio-engineered nanoparticles synthesis can prove to be beneficial in many aspects of nanoparticles synthesis and applications.

4.2 Synthesis of metal nanoparticles using weed extracts

Weeds are notorious for infiltrating farmlands, affecting the quality of soil and its flora. These undesirable plants start competing with the economically significant crops growing in the same field for space, water, minerals etc., thereby depriving the latter of adequate nutrition. These wild species are therefore popularly known as 'enemies of the farmer'. One way of making productive use of these noxious weeds is using them for synthesis of nanoparticles. Table 5 gives an account of weeds successfully used for the biosynthesis of metal nanoparticles in the recent years.

Table 4: Biosynthesis of metal nanoparticles using weed extracts

Metal	Weed	Size of metal nano obtained	Reference
Gold	Sargassum wightii	8-12 nm	(Singaravelu et al., 2007)
Silver	Parthenium hysterophorus L	50 nm	(Parashar et al., 2009)
	Eclipta	2-6 nm	(Jha et al., 2009)
	Ipomoea aquatica, Enhydra fluctuans, Ludwigia adscendens	100-400 nm	(Roy and Barik, 2010)
	Euphorbia hirta	40-50 nm	(Elumalai et al., 2010)
	Argemone mexicana	10-50 nm	(Singh et al., 2010)
	Gelidiella acerosa	20 nm	(Marimuthu et al., 2011)
	Desmodium triflorum	5-20 nm	(Ahmad et al., 2011)
	Lantana camara	40 nm	(Thirumurugan et al., 2011)
	Morinda pubescens	15-20 nm	(Jancy and Inbathamizh, 2012)
Copper	Lantana camara	20 nm.	(Majumder, 2012)

Precious metals have successfully been obtained in their nano size using biological synthetic approaches, wherein weed extracts serve as the reducing as well as capping agents. The brown sea weed Sargassum has been used successfully in the process of biosynthesis of gold nanoparticles. Bioreduction of the metal salt precursor by the weed extract resulted in formation of crystalline gold nanoparticles at the end of the process (Singaravelu et al., 2007).

Weeds have widely been used in the synthesis of silver nanoparticles during the recent years. Examples of weeds used for this productive purpose are Parthenium (commonly known as Congress weed) (Parashar et al., 2009) , Euphorbia hirta (Elumalai et al., 2010), Gelidiella acerosa (Marimuthu et al., 2011) and Morinda pubescens (Jancy et al., 2012), all of which are abundantly found in India. Others include Eclipta sp. (Jha et al., 2009), Argemone mexicana (Singh et al., 2010), Desmodium triflorum (Ahmad et al., 2011) and the well-known ornamental weed Lantana camara (Thirumurugan et al., 2011). The utilization of these wild species in nanotechnology-based processes has helped not only in designing a 'green approach' for synthesis of nanoparticles but also has

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eliminated the environmental concern regarding the disposal of such troublesome weeds.

The unusual properties of nanoparticles arise mainly due to shift in the size from centimeter to nanometer. During this transition, the electrons confine themselves to particles of smaller dimensions and having less electron delocalization length. This is called quantum confinement, which is responsible for tuning the absorption/emission properties of nanoparticles (Shen et al., 2008).

When the particles shift to the nanoscale, there is a complete change in their properties different and unique from the ones, which are observed when in the micrometer range. This is mainly due to the change in the absorption spectra and the increased surface area to volume ratio. These unique attributes are as the surface properties become more dominant than the bulk material properties. Table 5 lists metals with difference in their properties at nano and macro scale. These unique properties such as changed optical sensitivity, stability, conductivity, hardness, reactivity etc make nano metals more desirable and efficient over the macro and micro metals. (Thakur and Saikhedkar,

Table 5: Comparative account of metal particles at 'nano' and 'macro' scale

Sr. No.	Metal	Unique Properties	
		Nano scale	Micro and Macro scale
1.	Copper	Transparent	Opaque
2.	Platinum	Catalytic	Inert
3.	Aluminum	Combustible, flammable	Stable
4.	Gold	Liquid, red, catalytic	Solid, yellow, inert
5.	Silicon	Red, Exist in pure form, conductor	Usually found as silicon dioxide, insulator, gray

Zinc oxide nanoparticles are used for selective destruction of tumor cells and have a tremendous potential for drug delivery (Pissuwan et al., 2006). In today's world, some of the most commonly used nanoparticles include fumed silica, colloidal silica, copper oxide and alumina, besides zinc oxide (Dickerson et al., 2008).

5. Medical applications of metal nanoparticles

Metal nanoparticles such as gold, silver, copper, titanium and magnetite (generally present in electronic-waste) synthesized biologically have found many applications in the fields of diagnostics and therapy.

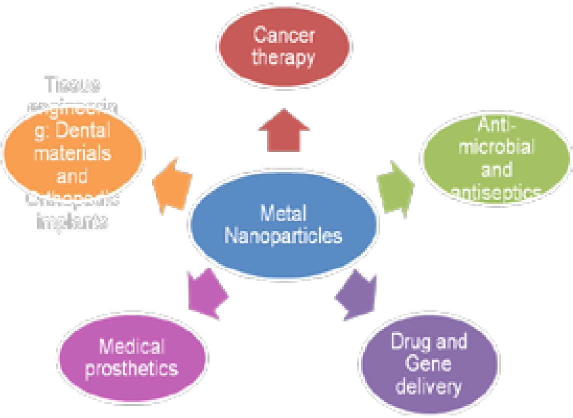

Figure 7: Medical applications of metal nanoparticles

5.1 Cancer therapy: Metal nanoparticles can be applied to amplify the biorecognition of anticancer drugs. For example, the specific interactions between anticancer drug Dacarbazine [5-(3, 3-dimethy-1-triazenyl) imidazole-4-carboxamide] and DNA or DNA bases can be facilitated by gold nanoparticles (Hadjipanayis et al., 2008). Gold nanoparticles have the ability to absorb light and produce a localized heating effect, thereby leading to irreversible thermal cellular destruction. This is the principle of hyperthermia therapy which is commonly used in oncological treatment (Sastry et al., 2003; Rasmussen et al., 2010). Iron-based nanoparticles have been found to enhance contrast in Magnetic Resonance Imaging and effectively generate local hyperthermia (Lines, 2008).

5.2 Anti-microbials and antiseptics: Silver nanoparticles are known to be potent anti-bacterial, anti-fungal, anti-viral, anti-angiogenic and anti-inflammatory agent. Antimicrobial activity of silver nanoparticles against Gram negative bacteria such as E. coli and Gram positive bacteria such as Staphylococcus aureus has been reported (Rai et al., 2009; Shahverdi et al., 2007). Hence, silver nanoparticles have found diverse medical applications as an antiseptic ranging from silver based dressings, silver coated medicinal devices such as surgical masks and implantable devices, nanogels and lotions etc (Furno et al., 2004). This incredible anti microbial property makes its applications vast in making bacteria free fomites. More and more anti bacterial door handles, toilet seats, dish washers, detergents and of refrigerators and washing machines with inner linings of silver nanoparticles are being produced (Wijnhoven ett al., 2009; Silver et al., 2006).

5.3 Drug and Gene delivery: Due to their small size and high surface to volume ratio, nanoparticles can prove to be effective drug carriers. In addition to being biocompatible, nanoparticles also help to increase the stability and shelf life of the active drug molecule. First example of in vitro magnetic nanoparticle-mediated gene delivery was in the year 2002. Non-viral gene delivery by the technique of magnetofection was demonstrated (Scherer et al., 2002; McBain et al., 2008).

5.4 Tissue engineering: Nowadays bone tissue is coated with nanoparticles in order to reduce the chances of rejection as well as to stimulate production of osteoblasts inside the host. Silver nanoparticles have already been used as dental restorative material and dental implants (Contreras et al., 2011). Titanium is a well-known bone repairing material widely used in orthopaedics and dentistry (Salata, 2004).

5.5 Medical prosthetics: Surfaces of medical prosthetics or devices such as artificial teeth, bone implants etc. can be coated with gold or silver nanoparticles, empowering its anti-microbial properties and making it more wear resistant. Also superparamagnetic iron oxide nanoparticles have known for their numerous anti-infection orthopedic applications. They are recognized to bring about prevention of biofilm formation on prosthetics (Taylor et al., 2009).

6. Future

The future prospects in the field of nanobiotechnology include-

- Exploring more and more microorganisms and noxious weeds for their potential to synthesize metal nanoparticles from e-waste
- Finding novel applications of nanomaterials in the field of medicine such as nano metal Intrauterine Contraceptive Devices

Studies regarding effects of metal nanoparticles on spermatozoa have been a largely unexplored area of research. The first world report in the year 2009 explained the spermicidal action of gold nanoparticles. According to the study, the gold nanoparticles penetrated into the sperm head and tails, affecting its mobility (Wiwanitkit et al., 2009). The traditional method of contraception using copper T (T220C IUD) shows many side effects such as bleeding and spotting, pelvic pain etc. Following the same mechanism of action as that of T220C IUD, nano-copper Intrauterine Contraceptive Devices showed high contraceptive efficacy with minimum side effects (Yu et al, 2008). In addition to gold and copper, metal oxides of zinc and titanium in the nano range have also been reported to exert a negative effect on human sperms (Gopalan et al., 2009). Unification of 'e-waste to nano' and biomedical sciences can give rise to notable breakthroughs in nanobiotechnology research.

7. Conclusion

The traditional methods of e-waste management have proved to be an environmental burden. Using microorganisms and weed extracts for the bioremediation of the hazardous e-waste and obtaining valuable metals from the same proves to be a remarkably economical and eco-friendly approach. These biosynthesised nanoparticles with natural protein caps are know for their commendable longer shelf life and stability as compare to those obtained by artificial capping. Obtaining these metals from e-waste in the pure nano form and exploring their diverse biomedical applications can go a long way in improving the quality of existing medical practices.

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