**Nanoparticles: A New Paradigm for Wastewater Treatment**

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**Introduction**

Water is the largest part of essential substances for all existence on earth and a source of evolution of human civilization. (1). Clean water is a vital element for all living organisms. In agriculture, the demand for and consumption of clean water has increased on a large scale. The consumption of fresh and clean water with a high range of pollutants in industry, household sectors, and other forms of consumption is about 70%, 22%, and 8%, respectively The main classes of pollutants are heavy metal ions and dyes. Water containing such pollutants should not be used for drinking purposes without purification. Once these heavy metal ions enter water, it is extremely difficult to completely treat it (2).Water is being polluted by various means of sources such as textile industry, dye house, factory, poultry etc. This polluted water brings more health hazards to the population and caused more social, economical problems (3). All over the world, about 780 million people do not have access to clean drinking water. Therefore, these pollutants need to be eliminated from contaminated water (2).

The removal of these pollutants through environmentally friendly and efficient methods is crucial. In the literature, numerous strategies have been used for wastewater treatment, such as solvent extraction, ultrafiltration, evaporation, and reverse osmosis. These techniques, however, remove impurities from water without making them harmless end products (2). The treatment of drinking water mostly consists of flocculation, filtration, disinfection processes, precipitation, adsorption, ion-exchange, electrodialysis membrane separation, and aerobic, anoxic or anaerobic oxidation methods (4, 5). However, wastewater treatment through these physicochemical methods often involve chemicals (such as chlorine compounds, ammonia, permanganate, alum, sodium hydroxide, hydrochloric acid, ozone, and ferric salts, coagulation and filtration aids, ion exchange resins and regenerants) and energetically and operationally intensive mechanical methods, and thus requires engineering expertise and infrastructure (5).

Nanotechnology is being explored as a promising technology, and has demonstrated remarkable accomplishments in various fields including wastewater treatment (5). Nanoparticles are considered as the fundamental component of nanotechnology. Nanoparticles are part of an emerging field of science that refers to the synthesis and development of numerous nanomaterials with size ranges of 1–100 nm (4). Some unique physical, chemical and biological properties are displayed by nanoparticles at nanoscale compared to their respective particles at higher scales. The reason behind this phenomena is a larger surface area of nanoparticles to the volume, increment in stability or reactivity during chemical process, enhancement in mechanical strength, etc. Due to these unique properties of nanoparticles they are considered for various applications (6). The highly efficient, modular, and multifunctional processes enabled by nanotechnology are envisaged to provide high performance, affordable water and wastewater treatment solutions that less relies on large infrastructures. Nanotechnology-enabled water and wastewater treatment promises to not only overcome major challenges faced by existing treatment technologies, but also to provide new treatment capabilities that could allow economic utilization of unconventional water sources to expand the water supply (7). The various methods of synthesis, applications of nanoparticles mainly depend on the field at which it is used (3). In contrast with conventional materials, the properties of nanoparticles, such as their magnetic, visual, and electrical properties, are significantly different compared to conventional materials. Characteristics such as high adsorption, catalytical activity, and reactivity are associated with nanomaterials (2). Nowadays, a new term is coined in the modern era, which is nothing but green nanotechnology. Green nanotechnology is aimed at bringing the cleaner eco system since the cleaner and healthier environment is the need of the hour. The main objective of green nanotechnology is to;

(i) Minimize environmental risks

(ii) Minimize various health hazards

(iii) Replace existing hazardous particle with nanoparticles which are of minimal unwanted effects (3).

1. **Classification**
   1. **Organic nanoparticles**

Generally, dendrimers, micelles, liposomes and ferritin, etc. are known as the organic nanoparticles or polymers. All these nanoparticles are biodegradable, non-toxic in nature. Some of these particles such as micelles and liposomes are also known as nanocapsules and it has been found that they are sensitive to thermal and electromagnetic radiation which includes heat and light. In drug delivery system, organic nanoparticles have been used widely because of their efficiency and can be easily injected on specific parts of the body which is also known as targeted drug delivery (6).

* + 1. **Dendrimers**
* **Reverse Osmosis(RO) membranes-** have pore sizes of 0.1-1.0 nm and thus are very effective at retaining dissolved inorganic and organic solutes with molar mass below 1000Da (8).
* **Nanofilter (NF) membranes-**  removing hardness (e.g., multivalent cations) and organic solutes with molar mass between 1000-3000Da (e.g., natural organic material) .However, high pressures are required to operate both RO and NF membranes (8).
* **Ultrafine (UF) membranes**- require lower pressure (200-700 kPa). Unfortunately, they are not very effective at removing dissolved organic and inorganic solute with molar mass below 3000Da (8).
  1. **Inorganic nanoparticles -** The direct delivery of drugs and biomolecules, however, is generally inefficient and suffering from problems such as enzymatic degradation of DNAs. In past decades, many carriers have been developed and investigated extensively which can be generally classified into four major groups: viral carriers, organic cationic compounds, recombinant proteins and inorganic nanoparticles (9). There is no presence of carbon in inorganic nanoparticles (6). Inorganic nanoparticles generally possess versatile properties suitable for cellular delivery, including wide availability, rich functionality, good biocompatibility, potential capability of targeted delivery (e.g. selectively destroying cancer cells but sparing normal tissues) and controlled release of carried drugs (9). Under inorganic nanoparticles, metal and metal oxide based nanoparticles have been categorized (6).
     1. **Metal based inorganic nanoparticles-** Synthesis of Nanoparticles from metals to nanometric sizes by destructive or constructive method are metal based nanoparticles. Nanoparticles are synthesized from almost all the metals. [6]. Among all the metals, aluminium (Al), cadmium (Cd), cobalt (Co), copper (Cu), gold (Au), iron (Fe), lead (Pb), silver (Ag) and zinc (Zn) are the most commonly used metals for synthesis of nanoparticles.. Widely used metal based nanoparticles for wastewater treatment have been mentioned below.
* **Silver (Ag) Nanoparticles:** Silver nanoparticle is one of the most important and widely used types of nanoparticles. Nanosilver has been used for more than 150 years in the form of colloidal silver, and has been registered as a biocidal material in the United States since 1954. Silver ions are also used into water purification systems in hospitals, community water systems, pools and spas. It is slowly replacing chlorine as the widespread element of choice for filtration. Silver nanoparticle has adverse effect on sludge, that impact the aerobic and anaerobic microorganisms. Silver ions and silver nanoparticles concentrations as low as 0.4 mg/L inhibited the growth of nitrifying bacteria. In addition, anaerobic microbial activity in biomass (i.e., sewage sludge) was inhibited at silver nanoparticles concentrations of 19 mg/L. the inhibitory effect of silver is due to its sorption to negatively charged bacterial cell walls, deactivating cellular enzymes, disrupting membrane permeability, and ultimately leading to cell lysis and death. That is why; nanomaterials are very much useful in the secondary treatment of waste water (3).
* **Gold (Au) Nanoparticles:** Gold nanoparticles are versatile materials that used for a wide range of applications with well characterized electronic and physical properties. This nanoparticle has been used to reduce the pollutants in the form of heavy metals, fertilizers, detergents, and pesticides. Gold metal has intriguing potential to deal with the water pollution problem, as recent research on several fronts is advancing the concept of nanoscale gold as the basis for cost-effective nanotechnology-based water treatment. In addition, their surface chemistry is easy to modify (3). Nanoparticles of gold coated with palladium are very effective catalysts for removing tri-chloroethane (TCE) from groundwater 2,200 times better than palladium alone (8). Au NPs can bind to water-soluble organomercury compounds, which suggests that they may be effective for the adsorptive removal of other heavy metal-containing organic compounds (10).
* **Iron (Fe) Nanoparticles:** Iron nanoparticles (FeNPs) for the treatment of water are being used since 1990s due to its specific properties viz. high specific surface area, unique adsorption phenomenon and wide distributions of reactive surface sites. Leaf extracts of *Mangifera indica, Murraya Koenigii, Azadiracta indica, Magnolia champaca*  can be used for synthesis of iron nanoaprticles and also can be used to check its potential for treatingdomestic waste water. Among all the synthesis mediated by plant for iron nanoparticles, *Azadiracta indica* showed 98.08% of phosphate, 84.32% of ammonia nitrogen and 82.35% of chemical oxygen demand removal (11).
  + 1. **Metal Oxide Based Inorganic Nanoparticles:** Metal oxide nanoparticles (MONPs) are made of purely metal precursors. These nanoparticles have unique opto-electrical features because of their well-known localized surface plasmon resonance characteristics. Metal oxide-based nanomaterials include manganese oxides, nanosized iron oxides, titanium oxides, cerium oxides, ZnOs, magnesium oxides, aluminum oxides, and zirconium oxides. For both antibacterial activities and the removal of dye from wastewater, MONP depends on a variety of factors such as morphology, size, and aggregation (2).
* **Zinc Oxides (ZnO):** ZnO is regarded as a good photocatalyst due to its high chemical stability and excellent photocatalytic activity when removing water pollutants (2). zinc oxide nanoparticles that were successfully synthesized starting from zinc acetate dihydrate and sodium hydroxide, through a simple co-precipitation method. . For the evaluation of the photocatalytic activity of ZnO nanoparticles, methyl orange was used as a model pollutant, and it proved that ZnO has great photocatalytic activity against the organic dye. The antibacterial activity of ZnO nanoparticles was tested against Gram-negative and Gram-positive strains and it was found that the most activity was experienced against Gram-positive bacteria (*S. aureus*). ZnO nanoparticles obtained through the co-precipitation method have great potential as an antibacterial and photocatalytic agent for further use in developing nanocomposite membranes for water purification. The safety and photocatalytic activity of ZnO have become important factors when referring to its antimicrobial activity and antimicrobial potential for water treatment (12).

Zinc stannate (ZTO) was grown directly on zinc oxide (ZnO) nanorods coated polyester fiber membranes and porous ceramic substrates by a mild hydrothermal method where the nanorods supplied zinc ions for the zinc stannate growth. 50% of methyl orange and ~ 95% methyl orange could be degraded within 1 hour and 3 hours of UV light irradiation respectively, by using the porous ceramic supported catalysts (C-ZnO/10ZTO), due to efficient charge separation. The formation of ZTO islands on ZnO nanorods led to an enhancement in photocatalytic activity in the exposed areas of electron rich ZnO nanorods (13).

* **Copper Oxides (CuO):** Copper oxide nanoparticles (CuO NPs) has been shown to be effective in adsorption and in variety of applications owing to their small size, high surface area, natural abundance of its starting material, low-cost production processing and non-toxic nature Conventional chemical processes like microwave heating technique and precipitation are the most popularly employed techniques for the synthesis of CuO NPs. CuO NPs is applicable as an adsorbent for the removal of dyes, heavy metals, pharmaceutical compounds and other ions from wastewater. The highest reported adsorption capacity for CuO NPs was 3152 mg/g for fluoride showing it can remove more than 3 times its weight fluoride from the aqueous phase (14).

CuO metal oxide has been proved to be an effective visible range active photocatalyst for photodegradation of contaminants without the addition of H2O2. Furthermore, physical parameters such as shape, size, structure, and composition which could influence CuO nanostructure can be controlled, and by controlling these parameters, the photocatalytic activities of CuO can be modified to achieve efficient degradation of contaminants (15).

* **Titanium dioxide (Tio2):** The aim of the study conducted by J.S. Sudarsan et. al. was to compare the efficiency of the wetland technique conventionally and with nanoparticles. In this study, TiO2 needed UV source for irradiation and showed very high efficiency in the treatment of heavy metals and there is no harm from the product during treatment. Since it does not contain Fe, it has no risk of oxidation. So, TiO2 is found to be most efficient in the removal of heavy metals from the effluents, as it has an efficiency of over 96% removal of Cr and Pb impurities from the polluted water (16).

According to S. Ghosha & A. P. Dasa, upon irradiation with light, the electron-hole pairs get generated in TiO2 NP have the ability to convert a wide range of organic compounds into harmless end products such as water, carbon dioxide and inorganic ions (17).

* **Iron Oxide (Fe2O3):**  Iron oxide magnetic NMs, possessing the capability to treat large volume of wastewater and being convenient for magnetic separation, are most promising materials for heavy metal treatment (18). In a study performed by Nassar et. al., it was found that the maximum adsorption capacity for Pb(II) ions was 36.0 mg g−1 by Fe3O4 nanoparticles, which was much higher than that of reported low cost adsorbents. In addition to this, Iron oxide NMs are currently being explored for organic contaminant adsorption, particularly for the efficient treatment of large-volume water samples and fast separation via employing a strong external magnetic field. According to Iram et.al., Fe3O4 hollow nanospheres were shown to be an effective sorbent for red dye with the maximum adsorption capacity of 90 mg g−1 (19).

The modified nanoparticles can achieve high efficiency. For example, a novel magnetic nanosorbent (MNP– NH2) has been developed by the covalent binding of 1,6-hexadiamine on the surface of Fe3O4 nanoparticles for the removal of Cu2+ ions from aqueous solution (20). The chemisorptions occurred between Cu2+ and NH2 groups on the surface of MNP–NH2 are responsible for the high efficiency of MNP- NH2.

1. **Green Synthesis of Nanoparticles**

The major reaction that takes place during the biosynthesis of nanoparticles is reduction/oxidation. The requirement of biosynthesis has increased as both the physical and chemical processes had a price. Frequent use of chemicals during the synthesis of nanoparticles results in the presence of some of the hazardous substance that get absorbed on the surface might have a negative impact on medical applications. These are not a problem with synthetic biomolecules using a strategy called “green synthesis of nanoparticles”(21). In comparison to physical and chemical methods, green synthesis is more environmentally friendly, economically advantageous, and easily scaled up for the production of large quantities of nanoparticles (NPs). Green synthesis also does not require the use of hazardous chemicals, high temperatures, or high energy inputs (22).

In this article, green synthesis of metal based inorganic nanoparticles: AgNPs, AuNPs and FeNPs has been discussed. Few bacteria and plant mediated green synthesis of nanoparticle has been described below.

**Bacteria mediated green synthesis of NPs:** Microbes have the ability to produce nanoparticles either intracellularly or extracellularly. The three main processes that comprise the intracellular mechanisms are stability, reduction, and trapping. They essentially rely on the metal ions being transported inside the microbial cell wall. In this approach, through electrostatic forces, the negatively charged cell wall and positively charged metal ions interact. The dangerous metals are then converted by internal cell wall enzymes to innocuous nanoparticles, which then pass through the cell wall. According to several investigations, metal NPs like silver and gold can be rapidly and easily biosynthesized inside of cells (49).

**Plant mediated green synthesis of NPs:** The biosynthesis of metallic and semiconductor nanoparticles using aqueous extracts of various plants has been recognized as a versatile and suitable alternative to chemical and physical methods of nanoparticle synthesis. Synthesis of metal nanoparticles using plant extracts is inexpensive and thus can be used as an economical and valuable alternative for large-scale production of nanoparticles. During the synthesis of nanaopaticles, it has been observed that plant extracts act as both reducing and stabilizing agents (34).

* 1. **Silver Nanoparticles**

For the green synthesis of silver nanoparticles, biological entities like bacteria, fungi, and yeast, as well as various plant biomasses and plant extracts, have been employed. These applications range from electronics and catalysis to biology, pharmaceuticals, medical diagnosis, and therapy (21).

**3.1.1 Bacteria mediated Green Synthesis:**

|  |  |  |  |
| --- | --- | --- | --- |
| **Sr. No.** | **Bacterial strain used** | **Range of synthesized NP (nm)** | **Reference** |
| 1 | *Pseudomonas stutzeri* AG259 | Upto200 | (23) |
| 2. | *B. licheniformis* | 50 | (24) |
| 3. | *Klebsiella pneumonia* | 1-6 | (22) |
| 4 | *Bacillus methylotrophicus* DC3 | 10–30 | (25) |
| 5. | *Pseudoduganella eburnea* MAHUQ-39 | 8 to 24 | (26) |
| 6 | Bacillus safensis TEN12 | 22.77 to 45.98 | (27) |

* + 1. **Plant mediated Green Synthesis:**

|  |  |  |  |
| --- | --- | --- | --- |
| **Sr. No.** | **Plant used** | **Range of synthesized NP (nm)** | **Referernce** |
| 1 | *Conocarpus lancifolius* | 21-173 | (28) |
| 2 | *Origanum majorana*  (leaf extract) | 26.63 | (29) |
| 3 | Tabernaemontana divaricate  (leaf extract) | 40 | (30) |
| 4 | Syzygium cumini (fruit extract ) | 40 | (31) |
| 5 | *Juniperus procera* | 23 | (32) |
| 6 | Pisum sativum*L.* | 30 | (33) |

* 1. **Gold Nanoparticles**:

**3.2.1 Bacteria mediated green synthesis:**

|  |  |  |  |
| --- | --- | --- | --- |
| **Sr. No.** | **Bacterial strain used** | **Range of synthesized NP (nm)** | **Reference** |
| 1. | *Rhodopseudomonas capsulata* | 10-20 | (35) |
| 2. | *Shewanella oneidensis* | 10-20 | (36) |
| 3. | *Rhodococcus sp.* | 5-15 | (37) |
| 4. | *Escherichia coli* | 20-50 | (38) |
| 5. | *Desulfovibrio desulfuricans* | 50-100 | (38) |
| 6. | Delftia sp. KCM-006 | 11.3 | (39) |

* + 1. **Plant mediated green synthesis:**

|  |  |  |  |
| --- | --- | --- | --- |
| **Sr. No.** | **Plant used** | **Range of synthesized NP (nm)** | **Reference** |
| 1. | Gracilaria crassa | 32.0  ± 4.0 | (40) |
| 3. | Magnolia kobus(leaf extract) | 5–300 | (42) |
| 4 | Diopyros kaki(leaf extract) | 5–300 | (42) |
| 5. | Carica papaya(Fruit extract) | 12 ± 2.31 | (43) |
| 6. | Citrus limetta Risso (peel extract) | 50–80 | (44) |

* 1. **Iron Nanoparticles**

**3.3.1 Bacteria mediated green synthesis:**

|  |  |  |  |
| --- | --- | --- | --- |
| **Sr. No.** | **Bacterial strain used** | **Bacterial strain used (nm)** | **Reference** |
| 1. | *Aspergillus Sp. Kvp 12* | 50-200 | (45) |
| 2. | *Thermoanaerobacter sp. TOR-39* | 25–50 | (46) |
| 3. | *Bacillus subtilis* | 60-80 | (47) |
| 4. | *Actinobacter spp* | 10-40 | (48) |

* + 1. **Plant mediated green synthesis:**

|  |  |  |  |
| --- | --- | --- | --- |
| **Sr. No.** | **Plant used** | **Bacterial strain used (nm)** | **Reference** |
| 1 | (*Camellia sinensis*) green tea | 5–10 | (48) |
| 2 | (*Camellia sinensis*) green tea | 40–60 |
| 3 | *Azadirachta indica* (neem) | 50–100 |
| 4 | *Eucalyptus tereticornis*, *Melaleuca nesophila* and *Rosemarinus officinalis* | 50 - 80 |
| 5 | Grape leaves (methanolic extract) | 60 |

1. **Conclusion**

Aspects like industrialization, commerce, and population growth are crucial in causing water supplies to become more contaminated. Therefore, it is crucial to ensure clean providing clean water to the general people. For ensuring the water is pure and safe, there are more therapies are accessible and used globally. The traditional forms of therapy have unique difficulties, such as environmental risks, economic viability, time commitment, and energy utilisation, etc. To get around these restrictions, Nanotechnology is a field of technology that a wider range of applications in water therapy area.

Their unique properties like  high extent, high mechanical properties, greater chemical reactivity, lower cost and energy are resppnsible for elimination of precisely toxic metal ions, viruses, bacteria, organic and inorganic solutes from the waste water. Differing forms of nanomaterials include  metal nanoparticles, nanosorbents, bioactive nanoparticles, nanofiltration (NF) membranes; carbon nano tubes (CNTs), zeolites and clay are proved to be efficient materials for waste water treatment. It has been proved through various studies that Nanotechnology is a promising technology, and has demonstrated remarkable accomplishments in wastewater treatment.

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