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

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**Introduction**

For all the basis of life on the Earth and the origin of human civilization, water is considered as the most important component of all necessary substances (1). Clean water is a vital element for all living organisms. About 70% of fresh and clean water with high range of pollutants is consumed in industry, 22% in home sectors, and 8% in other forms. The main classes of pollutants are heavy metal ions and dyes. It is incredibly challenging to fully purify water once these heavy metal ions have gotten into it. Without purification or any treatment, water having high pollutant load should not be used for drinking purposes (2). Various sources like dye industry, textile house, poultry, etc. are responsible for the water pollution. This polluted water would be responsible for increment in health hazards at population level and also more social, economic problems would be caused (3). According to studies, about 780 million people across all over the world lack access to safe drinking water. Therefore in order to overcome this problem, pollutants present in water should be removed (2).

It is essential to remove these toxins using effective and environmentally safe ways. Many techniques have been employed in the literature to treat wastewater, including solvent extraction, ultra filtration, evaporation, and reverse osmosis. These techniques are known for their capability to remove impurities from water without making any harmful end products (2). Flocculation, disinfection, filtration, adsorption, ion- exchange, precipitation and electrodialysis, membrane separation, and aerobic, anoxic or anaerobic oxidation are the common methods which are used for the treatment of drinking water (4, 5). However, various chemicals such as chlorine compounds, permanganate, alum, ammonia, hydrochloric acid, sodium hydroxide, ferric salts, ozone, ion exchange resins, coagulation, regenerants are used to treat wastewater. In addition to this, intensive mechanical methods which require more energy and operation and thus requires engineering expertise and infrastructure (5).

Demonstrated accomplishments has been remarked by Nanotechnology in various fields and one of those fields is wastewater treatment. It has also been considered as promising technology for the same(5). Nanoparticles are considered as the fundamental component of nanotechnology. Nanoparticles are part of synthesis and development of various nanomaterials with size ranges 1-100nm and hence, proved as a part of an emerging field of science (4). At nanoscale, some special biological, physical and chemical characteristics are displayed by nanoparticles as compared to their respective particles at higher scales. Larger surface area of nanoparticles to the volume, increment in stability or reactivity during chemical process, enhancement in mechanical strength, etc. are few of the reasons behind this phenomena. Keeping these antique properties in view, nanoparticles are considered for various applications (6). Processes enabled by Nanotechnology are multifunctional and highly efficient modular and are envisaged to come up with affordable water with high-performance wastewater treatment solutions that rely less on large infrastructures. To overcome major challenges faced by existing treatment technologies, Nanotechnology provides new treatment capabilities that could allow the utilization of unconventional water sources economically to expand the water supply (7). How the nanoparticles would be synthesized or where they would be d is mainly depends upon the field at which they are going to be used (3). The Various properties of nanoparticlesticle are significantly different from traditional materials. These properties include visual, magnetic, and electrical properties of nanoparticles. In addition to these properties of nanomaterials, high catalytic activity, high adsorption and reactivity are also associated (2). Nowadays, “Green Technology” a new term has been introduced which aimat the healthier ecosystem which has now become the neetheof an hour. Given below are the key objectives of green technology:

1. To Minimize environmental risks
2. To Minimize health hazards at large scale

(iii) Replacement of already existing hazardous particle with nanoparticles which have minimum unwanted effects (3).

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

Generally, polymers or organic nanoparticles include micelles, dendrimers, ferritin and liposomes, etc. Nanoparticles which are mentioned above are all non- toxic and biodegradable in nature. Some of these polymers such as liposomes and micelles are also known as nanocapsules and it has been found that they are sensitive to thermal radiation as well as electromagnetic radiation which includes both light and heat. In drug delivery system, organic nanoparticles have been used widely because of their efficiency and are simple to inject on particular body areas, a process called as targeted drug administration (6).

* + 1. **Dendrimers**
* **Reverse Osmosis (RO) membranes-** These membranes effectively retain organic solutes having molar mass below 1000Da and organic solutes because of their pore size (0.1-1.0nm) (8).
* **Nano filter (NF) membranes-** They are known for removing organic solutes having a molar mass between 1000-3000Da such as natural organic material and hardness which comprises multivalent cations. However, both RO membranes and NF membranes require high pressure for their operation (8).
* **Ultrafine (UF) membranes**- Lower pressure (200-700 kPa) is required for these membranes. Unfortunately, it has also been discovered that these are not removing dissolved organic and inorganic solutes with molar mass below 3000Da effectively (8).
  1. **Inorganic nanoparticles -** However, direct drug and biomolecule administration is typically ineffective and plagued by issues such as DNA enzymatic degradation. Many carriers have been developed and investigated extensively in past decades which can be generally categorized into four major groups: inorganic nanoparticles, cationic compounds, viral carriers, recombinant proteins and organic cationic compounds (9). Inorganic nanoparticles do not include any carbon (6). Various versatile properties are possessed by inorganic nanoparticles which are acceptable for cellular delivery, also including rich functionality, wide availability, potential capability, and good biocompatibility of delivery which is supposed to be targeted (9). Under inorganic nanoparticles, various metals and oxides of metals have been categorized (6).
     1. **Metallized inorganic nanoparticles-** Nanoparticles with nanometric sizes synthesized from metals by either constructive or destructive methods are considered metal-based nanoparticles. Generally, all metals are responsible for the synthesis of nanoparticles. [6]. Among all the metals, the few most commonly used metals for the synthesis of nanoparticles are cadmium (Cd), aluminium (Al), copper (Cu), cobalt (Co), iron (Fe), gold (Au), silver (Ag), zinc (Zn) and lead (Pb). The nanoparticles which have been used at large scale for wastewater treatment are discussed below:
* **Silver (Ag) Nanoparticles:** Silver nanoparticle is one of the most important and widely used types of nanoparticles. Use of colloidal form of nanosilver has been known for more than 150 years, and since 1954 it also has been registered as a biocidal material in the United States. Nowadays, silver nanoparticles are one of the most important and widely used nanoparticles among all the types of nanoaparticles. Silver ions are also known for their capability of water purification in hospitals, pools, spas and community water systems. As the widely used element of choice for filtration, it is gradually taking the place of chlorine. Sludge is negatively impacted by silver nanoparticles, which have an impact on both aerobic and anaerobic microbes. In studies, it has been found that the concentration of silver ions and silver nanoparticles as low as 0.4 mg/L inhibited the growth of nitrifying bacteria. Also in sewage sludge, inhibition of anaerobic activity has been observed at 19mg/L silver nanoparticles which is mainly due to the sorption of silver nanoparticles to bacterial cell walls which are negatively charged, disrupting membrane permeability, deactivating cellular enzymes and ultimately leading to lysis of cell and its death. That is why; In order to remediate wastewater further, silver-based nanoparticles are highly helpful (3).
* **Gold (Au) Nanoparticles: Being** Gold nanoparticles are versatile materials, gold nanoparticles are known for their well-characterized physical and electronic properties. A common form of pollutants like heavy metals, detergents, fertilizers and pesticides can be removed by Au nanoparticles. The concept of gold at the nanoscale has been advancing through recent research on several fronts as the basis for cost- effective water treatment nanotechnology. That is why, the metal gold offers exciting potential to address the issue of water contamination. In addition, they are also simple to change in terms of surface chemistry (3). In recent studies, it has been observed that as a catalyst, palladium-coated gold nanoparticles are removing tri-chloroethane (TCE) from groundwater 2,200 times better than palladium alone (8). Au NPs also have the ability to bind with water-soluble organomercury compounds, Because Au NPs may attach to water-soluble organomercury compounds, it is possible that they will be successful for adsorpting out additional organic molecules that include heavy metals. (10).
* **Iron (Fe) Nanoparticles:** Since 1990s, nanoparticles made from iron have been known for the treatment of water and the reasons behind this application of FeNPs are: high specific surface area, wide distributions of reactive surface sites and unique adsorption. In order to synthesize FeNPs in a green way, leaf extracts of *Murraya Koenigii, Mangifera indica,, Magnolia champaca*  *Azadiracta indica,* can be used and also the ability to treat domestic waste water can be determined. Among all the plant extracts used for green synthesis of iron nanoparticles, *Azadiracta indica* demonstrated 82.35% chemical oxygen demand removal, 84.32% ammonia nitrogen, and 98.08% phosphate removal (11).
  + 1. **Metal Oxide Based Inorganic Nanoparticles:** Metal oxide nanoparticles (MONPs) have well-known localized surface plasmon resonance characteristics which add on the unique feature to MONPs termed as opto- electrical features and all of the precursors used to create these MONPs are metal-based. Among the metal oxide-based nanomaterials are manganese oxides, cerium oxides, iron oxides (nanosized), and zinc oxides. Titanium oxides, magnesium oxides, zirconium oxides, and aluminium oxides. According to studies, MONPs require on various elements like size, shape and aggregation for both dye removal from wastewater and antibacterial activities (2).
* **Zinc Oxides (ZnO):** ZnO nanoparticles were first synthesized by using sodium hydroxide and zinc acetate dihydrate through a method called simple co-precipitation. High chemical stability and excellent photocatalytic activity are the major reasons behind the good photocatalytic activity of ZnO in removing pollutants from wastewater (2). The photocatalytic activity of ZnO nanoparticles has been evaluated by using them as a model pollutant, and it proved the great photocatalytic activity of ZnO against the organic dye. The highest antibacterial activity of ZnO nanoparticles has been observed against Gram-positive bacteria (*S. aureus*) as compared to Gram-negative bacteria. According to studies, the synthesis of ZnO nanoparticles through the co-precipitation method is known to have great potential as a photocatalytic and an antibacterial agent for water purification through nanocomposite membranes. In terms of antimicrobial activity and antimicrobial potential for water treatment of ZnO nanoparticles, safety and photocatalytic activity have become important factors (12).

Zinc oxide (ZnO) nanorods covered with polyester fiber membranes and porous ceramic substrates were used to grow zinc stannate (ZTO) on them by using a moderate hydrothermal process. The nanorods aid in the growth of the zinc stannate by providing zinc ions. A study conducted by Danwittayakul, S., Jaisai et. al. has shown that by using porous ceramic with ZnO/10ZTO as a catalyst, degradation of 50% of methyl orange within 1 hour and ~ 95% methyl orange in 3 hours could be achieved upon exposure to UV light radiation. This degradation was due to efficient charge separation. Also, the ZTO islands formed on ZnO nanorods increase the photocatalytic activity in the exposed regions of ZnO nanorods which are rich in electrons (13).

* **Copper Oxides (CuO):** Copper oxide nanoparticles (CuO NPs) have been demonstrated to be useful in adsorption and in a number of applications due to their high surface area, tiny size, affordable production, and makeup which is non-toxic. Two chemical processes which are conventional have been considered as popularly employed techniques for the synthesis of nanoparticles of CuO. These processes are precipitation and heating techniques through the microwave. Copper oxide nanoparticles can remove fluorides from the aqueous phase that is more than three times its weight. 3152mg/g has been noted as the highest adsorption capacity of copper oxides in the case of fluorides. Adding to this, these nanoparticles can eliminate the presence of heavy metals, pharmaceutical compounds and dyes in wastewater (14).

Additionally, CuO's photocatalytic activities can be adjusted to accomplish effective pollutant degradation by manipulating physical characteristics including form, size, structure, and composition that could affect the nanostructure of the material. Nanoparticles of these oxides can photodegrade the contaminants without the addition of hydrogen peroxide effectively as they have already been proven an effective photocatalyst of visible range. (15).

* **Titanium dioxide (Tio2):** J.S. Sudarsan et. al. conducted research and the purpose of the research was a comparative analysis of the efficiency of nanoparticles with the conventional technique, wetland. In this study, UV source was required for irradiation of TiO2 and high effectiveness in the removal of heavy metals was observed, while no negative effects by the product were noted by during the process. 96% removal efficiency of TiO2 has been observed for metals like chromium and lead from polluted water. Also, there is no risk of oxidation in the case of iron (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 nanoparticles are magnetic in nature and are known for their capability of magnetic separation. Also, they can treat wastewater in large volumes. Hence, considered as most promising nanoparticles for the treatment of heavy metals (18). In a study performed by Nassar et. al., maximum adsorption capacity (higher than low-cost adsorbents) was noted at 36.0mg/g in the case of lead ions (PbII) by nanoparticles of Fe3O4. Additionally, these nanoparticles are known for their efficient adsorption capability of contaminants that are organic in nature. For the effective treatment of large-volume water samples and quick separation using a powerful external magnetic field, nanomaterials made up of iron oxide are now being investigated for organic pollutant adsorption. According to Iram et.al., hollow nanospheres of Fe3O4 have a maximum adsorption capacity for red dye at 90mg/g (19).

The covalent binding of 1,6-hexadiamine on the surface of Fe3O4 nanoparticles results in the formation of novel magnetic nano sorbent (MNP-NH2) which aids in the efficient removal of copper ions from aqueous solution. Hence, it is proved that a high level of efficiency can be achieved by modified nanoparticles. (20). On the surface of MNP–NH2, between Cu2+ and NH2 groups chemisorption takes place which is somewhere contributing to the efficiency of MNP- NH2.

1. **Synthesis of Nanoparticles in eco-friendly way**

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. A frequent demand for chemicals during the nanoparticles’ synthesis results in some of the hazardous substance’s presence that gets 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). Green synthesis is more environment friendly, economically advantageous, and easily scaled up as compared to chemical and physical methods for the production of nanoparticles (NPs) in large quantities. The use of chemicals which are hazardous in nature, high energy inputs, and high temperatures are not required during the green synthesis (22).

In this article, the green synthesis of metal-based inorganic nanoparticles: AgNPs, AuNPs, and FeNPs has been discussed. Green synthesis of nanoparticles mediated by a few plants and bacteria has been described below.

**Bacteria-mediated green synthesis of NPs:** Microbes are known to have the ability to synthesize nanoparticles either in an extracellular or intracellular manner. The three main processes that comprise the intracellular mechanisms are stability, reduction, and trapping. They essentially rely on ions of metal being transported inside the cell wall of the microbe. In this approach, through forces that are electrostatic in nature, the cell wall having a negative charge and metal ions with a positive charge do interact with each other. 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 synthesis of metallic and semiconductor nanoparticles in a biological way by using aqueous extracts of various plants’ species has been considered a versatile and suitable alternative to both physical as well as chemical methods of nanoparticle synthesis. Synthesis of nanoparticles from metal using extracts of plants is inexpensive and thus can be used as an economical and valuable alternative for the production of nanoparticles at a large scale. During the nanopaticles’ synthesis, it has been observed that the extracts of the plant act as both reducing and stabilizing agents (34).

* 1. **Silver Nanoparticles**

For the synthesis of silver nanoparticles in a greener way, entities that are biological like fungi, yeast, and bacteria as well as many plant biomasses and extracts of plants have been employed. These applications range from biology to catalysis and electronics, pharmaceuticals, medical diagnosis, and therapy as well (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 for 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 utilization, etc. To get around these restrictions, Nanotechnology is a field of technology that has a wider range of applications in the water therapy area.

Their unique properties are responsible for the elimination of viruses, both organic and inorganic solutes, metal ions that are toxic in nature, and bacteria from polluted water. These properties include high extent, chemical reactivity, mechanical properties, lower cost, and energy. Differing forms of nanoparticles include metal nanoparticles made up of metals, nanoparticles that are bioactive in nature, nanosorbents, nanotubes made up of carbon (CNTs), nanofiltration (NF) membranes, zeolites, and clay are considered an efficient material for the treatment of wastewater. It has been proved through various studies that Nanotechnology is a technology that shows promising results, and various demonstrated remarkable accomplishments have been demonstrated in the treatment of wastewater.

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