**Role of Nanomaterials for Treatment of Wastewater**

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**1. Introduction**

Water makes up over 70% of the world's surface and more than ninety-seven percent of the water on earth is in the sea, causing life on earth impossible without it. Seawater had an enormous salt concentration and wasn't fit for drinking before desalination [1]. Water is something that occurs naturally on the earth, and it is crucial for human beings and other living beings to have access to it in its purest form because life as we know would be impossible without it. Water is also known as a "universal solvent" due to its potential attributes, such as solubility power. The lack of safe water for drinking affects one-sixth of the world's population. Water contamination is the biggest issue facing everyone in the world today. It can be caused by a variety of factors, including suboptimal sewage treatment, industrial pollutants, problems with marine dumping, radioactive waste material, various agricultural practices, etc. [2]. Water is considered contaminated when unwanted contaminants infiltrate watercourses or reservoirs and make the water unsafe for consumption and other uses [1]. The requirement for clean water is continually escalating because of population growth and persistent drought. The environment gets approximately eighty percent of all wastewaters without any further treatment. As a result, 1.8 billion people rely on tainted water that is full of different bacteria and viruses. Consequently, they are more likely to become ill with a number of water-borne diseases like typhoid, diarrhoea, cholera, the disease polio and many more, which can be dangerous for one’s health. This demonstrates how urgently we need wastewater treatment. The effluents made from wastewater that contain micropollutants are another significant cause of pollution [3]. Furthermore, 3 to 10 billion gallons of waste that has not been treated are released annually from wastewater treatment plants. The chemical, physical, and biological treatment units are currently used to treat wastewater; however, it is necessary to do this in order to supply the need for clean water, to establish a more efficient treatment process. Aquatic and terrestrial species also suffer when wastewater is not properly handled [4]. Aquaculture organisations produces large volume of wastewater and are strongly reliant on water use. Organic contaminants, non-dissolving substances, and extremely concentrated heavy metals can all be found in wastewater. These pollutants have proven to be a significant obstacle in treating industrial wastewater sustainably. These contaminants need to be cleaned up using efficient and environmentally safe purification techniques before they can be disposed of [3].

Table 1: Highlights several water contaminants along with their causes and negative impacts

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Water Contaminants** | Microorganisms/ Pathogens | Agricultural Contaminants | Suspended solids and sediments | Inorganic Contaminants | Organic Contaminants | Radioactive Contaminants | Industrial Contaminants | Nutrients Contaminants |
| **Source of Contamination** | Virus, Protozoa,Bacteria | Chemicals from Agricultural industry | Land construction, destruction, and mining activities | Mining, metallic compounds, acids, industrial waste | Domestic Waste, plant waste | Distinct Isotopes | Municipal contaminant Water | From fetilizers, debris |
| **Adverse Effects of Contaminants** | Different water-borne diseases like typhoid, diarrhea, gastrointestinal problems etc. | Directly impact the availability of fresh water | Fish Spawning is harmed, fish and insects life are impacted in aquatic surroundings | Public health issues, aquatic plants and animals are highly effected | Carcinogenic in nature | Damage teeth, skin and bones, mutagenic in nature | Leads to air and water pollution | Disturbs the Eutrophication |

Nanotechnology is developing as an alternative to traditional wastewater treatment methods. The recently emerging science of nanotechnology is currently offering a potential method of filtering water with low cost, significant operational effectiveness in eradicating pollutants, and reuse capabilities. A range of industries, notably catalytic processes, medicine, sensing, and biology, effectively exploited nanomaterials in earlier eras when they were actively explored and produced [5]. Recently, when the world was having significant issues with its drinking water, professionals noticed that nanomaterials are an improved choice for treating wastewater as they possess specific characteristics such as nano size, a large area of surface, highly reactive characteristics, robust solution range of motion, potent, permeability feature, hydrophilic nature, dispersibility, and hydrophobicity. Numerous dangerous bacteria, organic and inorganic pollutants, and certain harmful metals like lead, Mo, etc. have apparently been successfully removed using various nanomaterials [6]. In accordance with the World Health Organization, waterborne illnesses cause four billion cases of various health issues each year, and around 1.7 million people passed away as an outcome of water pollution. In general, materials with structural elements between 1 and 100 nm in size (in at least one direction) are referred to as nanomaterials [7]. The properties of nanomaterials, such as their electrical, mechanical, optics, and magnetic abilities differ dramatically from those of normal materials because of their nanoscale size. catalysis, adsorption, and elevated responsiveness are properties shared by a wide variety of nanomaterials. The underlying principles of nanoscience as well as nanotechnology are nanomaterials. Globally, the research and development of nanostructures is a vast and multifaceted topic that has evolved quickly in recent years. The ways that products and materials are made, and additionally the variety and kind of capabilities that may be offered, have the potential for undergoing a revolution. It undoubtedly has a large economic impact, and in the coming years, this impact will likely grow. Since a nanometre corresponds to a billionth part of metres, the structures we are discussing are extremely small. As a result of this, we can create nanomaterials either "top-down" (by splitting or disintegrating massive solids into more tiny and fine fragment until they are constituted of only a few atoms) or "bottom-up" (by putting atoms together) [2]. There are several ways to make nanostructures; for instance, macro molecules, nanoparticles, buckyballs, nanotubes, and so on can all be synthesised artificially. Nanomaterials have great adsorption capabilities and reactivity because of their small sizes, which result in huge, specified surface regions. Additionally, nanoparticles have a high degree of mobility in solutions. Numerous forms of nanoparticles have been observed to be effective at eliminating germs, inorganic anion, and harmful metallic compounds [6]. Nanomaterials hold significant potential for use in the treatment of wastewater and water, according to several studies. Some imprinted polymers are useful for the process of treating contaminated water. Recently, advanced developments have been made to nanomaterials like nano-photocatalysts, nanomotors, nanomembranes, and nanosorbents (which include substantial capacity for sorption and carry many applications for water treatment methods) [7]. The most completely studied nanomaterials for wastewater and water treatment at the moment are carbon nanotubes (CNTs), nanoparticles composed from oxide of metal like (TiO2, ZnO, and iron oxides), zero-valent nanomaterials of metal (Silver, iron, zinc), and other nanocomposites. In addition to these organic microorganism-derived green nanomaterials, biowaste products including vegetable scraps, fruit peels, leftover agricultural products, and materials from plants can also be used for treating wastewater [8].

**2. Preparation of Nanomaterials**

To be able to achieve the relevant properties for the specified utilisation, choosing and preparing the right kind of nanomaterials is essential. For instance, the ability to adsorb, catalysis, reactivity, and greater surface area of nanomaterials at the nanoscale make them very useful for wastewater treatment. In this section, several nanomaterials' properties along with their production and functionalization are discussed [3].

**2.1 Evaluation of Nanoparticles**

Nanoparticles (NPs) are defined as entities having a single unit dimension of 1 to 100 nm. Even though they can exhibit extraordinary physical and chemical characteristics in comparison with their larger material counterparts, nanoparticles are undetectable to the human sight. Many NPs include only a handful of hundred atoms.

The chemical, physical, electrical, magnetic, optics, and other characteristics of NPs determine how well suited they are for a given application. Size, form, content, framework, area of surface and dissemination, chemistry of the surface, equilibrium, topography, and roughness are important chemical and physical qualities [8].

Nanoparticles' surface area, size, chemical composition, and alteration all affect their electrical properties. To characterise nanoparticles, a variety of microscopes including optics, X-ray, probe, electron, auditory, and neutrons kinds are available. For topological, image processing, crystal, and chemical analysis, a few of them are the scanning electron microscopy (SEM), the atomic force microscopy (AFM), transmission electron microscopy (TEM), and scanning tunnelling microscopy (STM) [9]. Two of the key problems characterized in the study of nanoparticles are shape and its dimension. Different methods are used to characterise nanoparticles that are scattered inside of particles with colloidal structures, liquids, or thin sheets of films. Coagulation, coating, and lubrication of lubrication surfaces can enhance the mechanical properties of NPs. Because of their distinctive mechanical properties, that involve the field of called tribology nanofabrication, nanomanufacturing, and surfaces engineering, NPs are being used in novel ways by researchers. Because of their excellent thermo-chemical stability, NPs make it easier to remove a few metallic material from water that has been contaminated [10].

**2.2 Manufacturing of nanoparticles**

The creation of colour is the first thing noticed once an NP is created. Due to their ability to capture and reflect some visible spectrum wavelengths, nanoparticles can exhibit colour. The creation of nanomaterials is accomplished using a variety of techniques, including the traditional Chemical vapour deposition, the sol-gel method, solvothermal, thermal, top-down, bottom-up, pulsed ablation with lasers, hydrothermal, burning, microwave, and gas-phase techniques are among the techniques used. Some dangerous substances, such as oxidising agents, reductants, stabilisers, and organic solvents, which are toxic and carcinogenic and constitute threats to the environment's health, may be used in the synthesis of NPs [8].

The biologically produced preparation of nanoparticles is a potential environmentally friendly solution to address such problems. These procedures use multicellular and unicellular organisms as capping agents, resulting in a greater number biocompatible metal nanoparticles than those made chemically [5]. The production of nanomaterials with precise size and form is now attainable by controlling the synthesis method and reaction conditions. While green nanoparticle production has received a lot of interest.

The most effective biological alternative is thought to be plants. Extracts from plants are increasingly regarded as a safe precursor for the creation of nanomaterials. They could be utilised in many sectors since they have the ability to decrease metal ions within ion channelling sites, both at the surface and within [4].



Fig 1: Preparation of nanoparticles by Top-Down and Bottom-Up Approaches

**2.3 Nanomaterial’s functionalization**

Functionalization is the process of modifying the surface chemistry of materials to add new features, aspects, capabilities, or qualities. It is a fundamental method frequently applied in the fields of chemistry, nanotechnology, biology, and textile engineering. Functionalization enhances NPs' qualities and abilities by surface modification, allowing them to contribute significantly to the medical profession. Professionals have long hypothesised that because nanoparticles have unique functional groups, they can target contaminants more effectively and selectively when combined with polymers. By manipulating their size and form, they have investigated the production and working principles of functionalized gold nanoparticles. They emphasised how gold nanoparticles can be used to create nanostructures with a variety of uses by having biological and chemical detecting capabilities [7].

In general, it has been discovered that gold nanoparticles (AuNPs) have excellent prospects for multifunctionality for enhanced applications. Carbon nanomaterials, in particular carbon nanotubes (CNTs), have received an enormous amount of attention lately because of their significant specific area of surface and the sites of adsorption that they offer. Regarding water and wastewater treatment, these compounds are especially helpful. The affixing of different functional groups is used to modify the surface of CNTs. Covalent or noncovalent functionalization of CNTs may generally be distinguished. The covalent functionality of CNTs is accomplished by switching the positions of the sp2 and sp3 atoms of carbon. This can be done using either "sidewall functionalization" or "ends and defects functionalization." The most common methods for this kind of functionalization include oxidation, esterification, and amination. The function of the covalently modified CNTs conductance may be hampered by the transformation of pre-existing carbon atoms from sp2 and sp3 along with it’s electrical, and mechanical properties. To resolving aggregation and separation challenges and aiding in the maintenance of their intrinsic properties, functioning of nanomaterials made from graphene is essential. Techniques for covalent and noncovalent modulation can be used to change the surface of graphene, much like they do with CNTs [3].

**3. Methodologies for Treating Water**

**3.1 Nano photocatalysts**

One of the most important methods for eliminating various microbiological pathogens and pollutant-trace pollutants from wastewater is photocatalysis. The term "photocatalysis" is derived from the Greek terms "photo" as well as "catalysis," that denote complicated breakdown in the presence of light [11]. A catalyst is typically a substance that modifies the rate of the reaction while undergoing minimal modifications to itself. Ultraviolet radiation, ozone, Fenton's reagent, and hydrogen peroxide are a few examples of highly reacting chemical-based oxidants that are created in-situ during catalysis. Thus, using the oxides created by an advanced oxidative system process, highly resistant organic molecules can be oxidised. This term may additionally be employed to describe a process that activates or stimulates a substance using UV rays, visible, or solar light [10]. Photocatalysts are substances that, independently of themselves, alter the pace of reaction during chemical transformation. A photocatalyst and a traditional thermal catalyst are fundamentally different from one another in that the later is made active by photons of light, while the earlier type is activated by heat. Nano photocatalysts are frequently utilised for wastewater purification because their increased surface ratio and shape-dependent properties aid to increase the reactivity of the catalyst. It has been shown that nano photocatalysts can boost oxidation capacity because they produce oxidizing species at material surfaces effectively, which helps to break down pollutants from polluted water.[9]

Almost all of the time, nanoparticles like zero-valence derived metallic substances, semiconductors, and a few bimetallic kinds are used to remediate contaminants from the environment like dyes made from azo compounds, chlorine dioxide, naturally occurring Cl2, insect repellents, nitroaromatics, etc. TiO2-based nanotubes have been found to be effective at removing a variety of impurities from waste water, such as chlorinated ethene, Congo red, colors derived from azo compounds, phenolic aromatic base impurities, toluene, dichlorophenol, and trichlorobenzene [12].

However, SiO2, ZnO, TiO2, Al2O3, the most common and significant ones are along with other metal oxide nanophotocatalysts. Titanium dioxide (TiO2) distinguishes out from all the other elements as a superb photocatalyst because it is affordable, non-toxic, chemically stable, and easily accessible on Earth. Anatase, rutile, and brookite are the three primary states of TiO2. Due to its 3.2 eV bandgap, antase is now considered as an ideal nanophotocatalyst material. ZnO is one of the other photocatalysts that has been created to successfully remove contaminants from wastewater and offer reusability [13].

In the instance of hybrid nanomaterials, the deterioration of the reference substance (dimethyl sulfoxide) and the photocatalytic performance of water treatment using CdS/TiO2 composite as catalyst were both investigated. Iron-doped nanomaterials are readily reusable as well as recyclable due to their ferromagnetism. Similar to this, significant photocatalytic reactivity of Pd- assimilated ZnO nanomaterial is being used to eliminate *Escherichia coli* from wastewater [14].

Nano photocatalysts still need additional modifications, despite recent efforts to replace oxides of metal with other substances like metallic substances or ions of metal, carbon-base substances, dye sensitizers, and several others to enhance their photocatalytic efficacy when subjected to visible light. There are two possible states for the nano photocatalysis process: heterogeneous and homogeneous. Heterogeneous nano photocatalysis has been intensively studied in the modern era due to its wide variety of applications in the disciplines of water purification and environmental-related fields. Intriguing benefits of heterogeneous nano photocatalyst include chemical stability, cheap cost of chemical use, lack of additives, and capacity to function at low concentrations. As a result, pre-industrial scale heterogeneous photocatalysis has recently been attained [15].

**3.2 Nanomembranes and Adsorption**

A special kind of membrane called a Nano membrane, made of various nanofibers, is used to filter out undesirable nanoparticles in the aqueous phase. This process acts as a pre-treatment for reverse osmosis and enables extraordinarily fast eliminating efficiencies with condensed fouling propensities. To build multifunctional membranes using different nanomaterials in different polymer-based membranes, numerous studies on membranes nanotechnology have been conducted. Water treatment using porous membranes included reverse osmosis, nanofiltration, and ultrafiltration [16]. The membrane has a composite layer atop a porous support. Adsorption happens when organic and inorganic substances stick to an adsorbent material's surface because of numerous physical and chemical adhesion mechanisms. The quick adsorption regeneration cycle and weak adsorption capacity of traditional adsorption methods make them difficult to employ, but over time, they are low-cost effective. However, the substantial surface region, improved responsiveness, and rapid kinetics of nanomaterial-based adsorption, including a carbon nanotube metal , metal oxides, and graphene, make the disinfection of wastewater in the industrial sector possible [1].

Nanocomposite adsorption produces no sludge as an output, leading to a one-step process with post-treatment cost reduction. Owing to their distinctive aromatic structure and chemical makeup, other important pollutants, such as establishing pharmaceuticals confinement (EPC), can be eliminated by adsorption.Arsenic (As) removal using a simple polyethersulfone/titanate nanotube sheet that also functions as an adsorptive membrane was shown to be effective. A superior-quality filtrate was created with an arsenic proportion < 10, which is much lower than the permitted arsenic limit for drinking water. This lends the adsorptive membrane a potent cleansing method for wastewater treatment in areas with high levels of arsenic contamination [17].

Because of its unique properties and structures, graphene and the nanomaterials created from it are being seen as attractive candidates to be utilized in water purification applications. They have incredibly quick adsorption kinetics because of their high volume to surface ratios and additional physiochemical traits including electrical interaction with pollutants. The ability of CNTs to remove a variety of contaminants from wastewater has led to their widespread recognition as an extraordinary adsorption material. The kind of sorbent, area of surface, and functioning of the sorbent all affect adsorption capacity. For the treatment of water, metal oxide-based nano adsorbents like zinc oxide (ZnO), titanium dioxide (TiO2), or iron oxide (Fe3O4) are widely utilized. Nano-metal oxides are being studied as active adsorbents for eliminating heavy metals due to their substantial surface area and potent specific affinity[4].

**3.3 Nanosorbents**

The vast range of qualities that nanosorbents possess, such as their high sorption capacity, make them more effective and acceptable for the treatment of water. The carbon-based nanosorbents that are reported the most frequently are carbon black, graphite, and graphene oxide.

There are also metal, oxides of metals and polymeric nanosorbents. To lessen the impact of toxins in the treatment of waste water, composites made of various materials, such as silver/polyaniline, silver/carbon, silver/TiO2, etc., are extremely important [6].

According to the method of synthesis, the carboneous material, such as CNTs, with a cylindrical shape nano structure, may appear as single-walled or multiwalled nanotubes. Due to their vast surface area, CNTs contain sustainable surfaces and detectable adsorption sites. Because CNTs have hydrophobic surfaces, it needs to be stabilized to avoid aggregation, which reduces the surface-active sites [1, 8]. Therefore, it is a substance that is effective at adsorbing pollutants. Like dendrimers, polymeric nano adsorbents are useful for removing heavy metals and organic contaminants from wastewater. Zeolites are substances where the absorbent framework has various nanoparticles like copper and silver particles can be implanted, are another significant nanosorbent. Zeolites have the benefit of controlling the quantity of metals and acting as an anti-microbial agent. Additionally, magnetic nanosorbents are a special tool for removing various organic contaminants from water and play a crucial role in water treatment [4].

**4. Nanomaterials for the Treatment of Water and Wastewater**

**4. 1 Nanoparticles of zero-valent metal**

**4.1.1 Nanoparticles of silver**

In order to remove heavy metals, silver nanoparticles (NPs) have been used since they may be compatible with green efforts. Priority is placed on reducing or completely eliminating the usage of dangerous materials while efficiently removing harmful metals from wastewater [15]. The elimination of cadmium (II), a type of bulky metal with severe toxicity that has been found to be harmful to both the natural world and human life, has been studied using silver nanoparticles (NPs). Using silver nitrate (AgNO3) and *Ficus Benjamina* leaf extract, silver nanoparticles (NPs) were created. Due to the expanded area and adsorption capability of adsorbents, it was shown that adsorbent dosage was closely correlated to cadmium removal [7]. Similar studies have been done on the soil immobilization of heavy metals using silver nanoparticles (NPs) made from cocoa pod extracts. The movement of heavy metals was hampered, and heavy metal removal was enhanced [12]. Due to their strong antibacterial properties, high adsorption capacity, and ecologically acceptable manufacturing processes, silver nanoparticles are a promising alternative for wastewater treatment. Compared to heterotrophic bacteria, silver NPs had higher inhibiting impacts on the denitrifying strains of bacteria. Different processes are used by silver particles to support their antibacterial properties [13, 14].

**4.1.2 Nanoparticles of iron**

Recent years have seen a substantial increase in scientific interest in several metallic micron-sized particles namely Fe, Zn, Al, and Ni due to their potential to treat water contamination. To eliminate heavy metals and arsenic, zero-valent ferrous NPs were investigated. Through removal processes such iron sorption, reduction, and co-precipitation, NPs were successful in removing a range of metal ions. It makes it easier to donate electrons by characteristics like a metal core and a sizable iron NP surface area. Additionally, the iron nanoparticles' high density enables recycling and gravity settling to separate them from the bulk solution [14].

Zero-valent particles of iron have been shown to have antibacterial properties when tested with bacteria. Investigations on antibacterial activity were conducted against gram-positive bacteria including *S. aureus* and *B. subtilus* as well as gram-negative microbes like *E. coli* and *Ps. aeruginosa*. Reactive oxygen species are created because of the zero-valent NPs. Because each Fe2+ and Fe3+ ions interact with the membranes of bacterial cells due to their corrosive characteristics, the zero-valent nanoparticles of iron successfully prevented bacterial growth. This growth inhibition has increased the possibility of using low-valent iron NPs in the systematic treatment of wastewater [15].

**4.1.3 Nanoparticles of zinc**

Although there is limited evidence on its application in wastewater treatment alone, zero-valent Zn (ZVZ) has already been demonstrated to have a superior reducibility over zero-valent iron (ZVI) [9]. Acid washing was used to create the ZVZ Nanoparticles in order to transform more bromate to more productive bromide at a greater dosage. Correspondingly, nitrate was effectively transformed to nitrite when ZVZ was made with acid washing, particularly hydrochloric acid. The ability of nitrite to be reduced even more to ammonium ions was another reason why the acidic circumstances were thought to be advantageous [11].

The work also exhibited that the produced ZVZ nanoparticles could be recycled repeatedly. ZVZ has a high reducibility and may be integrated with other substances, which could improve the effectiveness of its removal.

**4.2 Nanoparticles of metal oxide**

**4.2.1 Titanium Oxide (TiO2)**

Due to its environmentally beneficial and extremely stable qualities, oxide of titanium (TiO2) serves as a superb semiconductor with a variety of applications. Most wastewater treatment techniques have been biological in nature.

TiO2 was used to clean sludge and wastewater via anaerobic digestion, and this method revealed that the inclusion of TiO2 nanoparticles within cell membranes caused electron transfer. Because of the existence of TiO2 NPs, the study found that methane generation was 14.9% higher than expected [8].

Over 90% of the TiO2 NPs had remained in the sludge until the time everything was finished, and only a small amount had made it into the processed effluent. Additionally, the unidentified dangers of titanium dioxide particles in the atmosphere were significantly diminished. Using TiO2, the biological processes were successfully improved. TiO2 has also been included into a number of techniques for enhancing the efficacy of wastewater treatment systems [10].

Green synthesis has become a potential methodology because of the emphasis on durability as well as the expanding technical and financial opportunities in different applications. TiO2 NPs having an outer diameter of 18 nm were created using Syzygies cumin leaf extract and used effectively for eliminating chemical demand for oxygen as well as Pb2+ metal. According to the study, using synthesized NPs efficiently allowed for the elimination of COD and Pb2+ by 75.5% and 82.53%, respectively, through photocatalytic degradation [14].

**4.2.2 Zinc Oxide (ZnO)**

Due to their distinctive qualities, such as simple and broad bands in the near-UV band area, a powerful oxidization capability, and a superb photocatalytic property, ZnO NPs have emerged as another successful candidate for use in the field of photocatalysis in the treatment of water as well as wastewater in addition to titanium dioxide nanoparticles. Because ZnO NPs are biocompatible and environmentally friendly, they are suitable for the filtration of wastewater and water. Additionally, due to their band gap values are so comparable, ZnO and TiO2 nanoparticles have similar photocatalytic abilities. In contrast to TiO2 NPs, the NPs made of ZnO have the benefit of being less expensive [12].

ZnO-NPs have better bioactivity and are more effective at inhibiting microbial growth because they have a greater area of surface to volume ratio. Bacteria are eliminated as a result of the surface action of ZnO NPs. The ZnO particles' shrinking size produces more microbial harm, which boosts their antibacterial effectiveness. The abundance of oxygen-containing free radicals generated by ZnO-NPs break down the cell walls and membrane. The photocatalytic method to get rid of the dye also used ZnO-NPs. Under UV irradiation, the procedure was shown to be successful at removing dye from an aqueous solution [14].

**4.2.3 Aluminium Oxide nanoparticles**

The microbial community was discovered to be harmed by aluminium oxide nanoparticles (NPs). Numerous methods, including modifying bacterial DNA and altering the permeability and characteristics of the cell membrane, have been demonstrated to be effective in killing germs [18].

*Pseudomonas putida* was shown to be harmful to the aluminium oxide nanoparticles because they hampered their growth. The microbial enzymatic activity of aluminium oxide nanoparticles in activated sludge was also investigated. Dehydrogenase activity was shown to decrease and hydrolytic enzyme activity to rise, suggesting a possible effect on bacterial metabolism [19].

The treatment of wastewater has a lot of promise due to aluminium oxide nanoparticles' toxicity to the microbiological community.

**4.3 Carbon based Nanomaterials (CNMs)**

**4.3.1 Carbon nanotubes**

Carbon-based nanomaterials (CNMs) are a family of fascinating materials that are tempting for both fundamental study and an extensive variety of uses, particularly in sorption processes, because of their unique structural and electrical properties [20]. Their advantages for handling wastewater are the excellent ability to absorb a variety of impurity, rapid kinetics, huge surface area, and preference for aromatics.

Carbon nanotubes (CNTs), fibers of carbon, beads are merely a few examples of the different forms that CNMs can take. Of all of them, CNTs have attracted the most interest and have advanced quickly in recent years [21].

CNTs, which were found in 1991, have advantageous chemical, mechanical, thermal, and electrical characteristics that make them ideal for wastewater treatment. In addition to nanocomposites, devices for healthcare, microelectronics, storage of energy, pollutant treatment, and adsorption, CNTs have also been investigated for usage in various other applications. Carbon nanotubes (CNTs) are sheets of graphene manufactured in cylindrical rolls with a diameter as small as 1 nm. Due to their distinctive characteristics, as a novel adsorbent, CNTs have attracted a lot of attention. For a variety of contaminants, including as dichlorobenzene, ethyl benzene and Zn2+, Pb2+, Cu2+, Cd2+, and dye, CNTs show exceptional adsorption capacities and excellent adsorption efficiencies. They have a ton of porous structures and an incredibly high specific surface area, which accounts for this. As shown in **figure 1**, Carbon nanotubes (CNTs) are a relatively new addition that can be made of single-walled CNTs (SWCNTs) or multi-walled CNTs (MWCNTs) [22].

The number of layers based on which it is built serves to distinguish it. They are highly desired for in the field of wastewater treatment because of their mechanical design, useful electronic features, and one-dimensional structure. These catalysts are at the forefront of the industry due to their chemically stable and thermal properties. By fusing the iron oxide's magnetic qualities with the adsorption capabilities of CNT, chromium can be removed. The adhesion, mechanical, electrical, and optical properties of the material can all be changed by combining CNT with different metal compounds [21].

Membrane technology is another way by which CNT is used to cleanse sewage. CNTs are widely used and is the subject of in-depth research for filtration and purification methods for water in membrane technology.

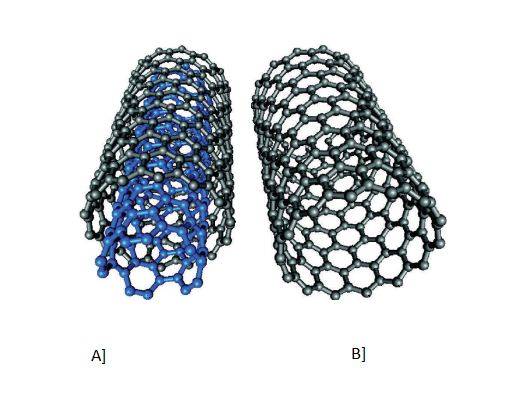


Figure 2: Structural Representation of a mutli walled CNTs and single-walled CNTs [10, 18]

**4.3.2 Graphene**

Graphene is a beneficial type of carbon that is composed of layered, structured carbon. Graphene is considered as one of the most efficient next-generation filtering membranes because of its increased surface area, numerous functional categories, affordability, reduced sensitivity, excellent selection, and remarkable permeability for a variety of chemicals, compounds, and ions. Due to all of these qualities and its simple manufacturing, graphene has become one of the more desired materials for pollution reduction in the waste water treatment industry [22].

Graphene oxide (GO), which is composed of two dimensions, is created when the graphite layer is oxidized chemically.

Graphene oxide is a superior alternative to graphene despite being more expensive and difficult to produce. Its chemical characteristics set it apart from graphene and enable it to function as a protective layer with a long lifespan, which is necessary for a broader variety of purposes that require mechanical and chemical characteristics [23].

Graphene sieves can be used to filter out ions from water. Numerous studies have found that the permeability nature is constrained, with a cut point near about 9 A [18, 23].

The detachment of hydrating ions from salty water is substantially more successful with a regulated expanding ability and pore diameters of 6.4 and 9.8 A [18].

It was discovered that this controlled swelling was successful in removing 97% of the sodium chloride, proving that graphene oxide can effectively separate ions from salt water. A graphene membrane that can filter out particulates larger than 1 nm may also be the upcoming major innovation in wastewater treatment technology. Heavy metals like copper, zinc, cobalt, cadmium, and lead have been demonstrated to be reduced or eliminated by graphene. Despite having reduced adsorption selectivity, it has strong adsorption abilities for several heavy metals [24].

Multi-bonding functional molecules also serve an essential but limited role in the elimination of toxic metals from wastewater via the application of graphene oxide adsorption. Methyl blue is also eliminated using GNT, a composite of the material graphene and carbon nanotube. It has also been demonstrated that graphene may effectively eliminate antibiotics from wastewater. Graphene is a powerful material for wastewater treatment, despite a few underlying difficulties.

**4.3.3 Carbon dots**

As an emerging class of carbon nanomaterials, carbon-dot particles (Cdots) have gained appeal recently. The carbon dots, which have a graphitic centre and several functional groups, offer extraordinary optical, electrical, chemical, and biocompatibility features. Microwave irradiation, ablation with a laser, electrolytic oxidation, hydrothermal reaction, ultrasonication, and the reflux technique can all be used to produce Cdots [18].

Cdots can be employed in the of detection of heavy metal ions, organic and inorganic pollutants elimination, and the optical elimination of untreated impurities due to their exceptional semiconductor features, high antibacterial capacity, photoluminescence, photoinduced electron transfer, and photoinduced electron transfer. The fascinating family of nanoparticles known as Cdots has the potential to be extensively exploited in sectors outside of biomedicine, such as photography and optical devices. Size-dependent electrical power, optics, electrochemical, and quantum phenomena serve as illustrative examples of their distinctive properties [25].

The solvothermal method was used to remediate wastewater containing varied proportions of catechol compounds and o-phenylenediamine by producing red, and bluish green Cdots. Analyses on Cdots' photo-Fenton reactivity focused on how quickly H2O2 breaks down into free hydroxyl radicals, which are then used to remove methyl blue. The results show that Cdots with a broader energy absorbance range have higher catalytic activity for the photo-Fenton process. Cdots' numerous functional groups and variety of polar groups on their surfaces make them an efficient adsorbent for the elimination of hazardous substances from wastewater. It was effective at removing uranium because it could generate a strong magnetic attraction with a large capacity for adsorption [21].

**4.4 Nanocomposites**

A nanocomposite material is created when two or more substances come together to form a single thing. At least one of the constituent materials must exist on the nanoscale. Over the past ten years, it has been utilized more frequently as an effective technique for eliminating wastewater pollutants like metals which are heavy and organic pollutants. Better hydrophilic nature, chemical and thermal endurance, porosity, and permeability are key features of more recent nanocomposite materials, all of which are crucial toxin remediation techniques [25].

*E. Coli,* a common contaminant detected in residential sewage, has been shown to be resistant to silver nanocomposite, making it an effective antibacterial agent. Enhanced adsorption rates and efficiency were also seen in a magnetic nanocomposite based on chitosan. In an experiment, chitosan and NPs with amine-functionalization were used. The eliminating of toxic substances via chitosan with ultrasonic radiation in mildly acidic water was made possible by the removable nature of this interaction, and produced magnetized chitosan nanocomposites may be the best choice for recycling bulky metallic substances elimination in the water treatment industry. Zeolite was used to evaluate a variety of agricultural runoff contaminants, including ammonia and breakdown products of humic acid, and the results were impressive [21].

The results demonstrated that at pH-natural conditions, zeolite can remove the gas ammonia along with humic acid from water. Due to the particular ionization radius of toxic substances including lead and cadmium, polymer materials added to well calibrated pore-sized membranes made of nanocomposite are highly efficient at removing them [22].

**5. Prospects and limitations of nanomaterial-based wastewater treatment methods**

The development of nanotechnologies has improved the wastewater treatment industry, despite certain existing difficulties.

Nano photocatalysts, nanomembrane filtration, nanomotors, and nanosorbents are just a few of the areas where research is being conducted to improve the effectiveness of large-scale water treatment systems and address their flaws. Future research must concentrate on cost effectiveness to create water treatment systems that are more successful. Due to this, the use of nanotechnologies for wastewater treatment might become more prevalent. Some NPs are harmful in and of themselves [9]. Only a few types of nanomaterials have seen widespread commercial use. The economic effectiveness of nanomaterials should be the main topic of future research.

Micromotor technology can be used with green materials like zinc, magnesium, and various other NPs to make them more ecologically friendly. Another important problem lies in the fact that there are no accepted criteria for assessing and contrasting the effectiveness of different nanoparticles in the wastewater management industry. Despite significant advancements in the application of Nanoparticles for the purification of wastewater, "real-time monitoring tools" for assessing the efficacy of nanoparticles in water that has been treated have not yet been developed. Future research must focus on developing a real-time approach to better understand how nanotechnology functions during treatment. With the extensive and regular usage of nanostructures in water and wastewater systems, the likelihood of cytotoxicity of nanoparticles to the natural world and humanity is also increasing. Additionally, there are numerous obstacles to overcome before consistent or acknowledged standards are created for detecting and evaluating nanoparticles in water as well as contaminated water [15]. Because each nanomaterial performs differently, it is challenging to select those that demand additional research and development. Future assessments of the effectiveness of nanoparticles in the treatment of wastewater and water are required.

Better selection, equilibrium, operational time frame, and efficiency of adsorption are advised to aid in the industrialization and manufacturing ramp the method of nanoscale technologies. Many worldwide and national research organizations may come up in the near future to develop various methods and recommendations to lessen the detrimental effects of NPs [16].

**6. Mathematical Modeling**

Mathematical modeling is a powerful tool in the study of nanomaterial-based wastewater treatment. It enables researchers to gain a comprehensive understanding of the fundamental mechanisms and interactions that occur during the treatment process. By using mathematical equations and simulations, scientists can optimize treatment processes, design efficient nanomaterials, and predict their performance under various conditions. As nanotechnology continues to advance, mathematical modeling will play an increasingly vital role in developing innovative nanomaterials and treatment technologies, paving the way for sustainable and effective wastewater management. Collaborative efforts between materials scientists, chemists, environmental engineers, and mathematicians will continue to drive progress in this field and lead to improved water quality and a cleaner environment for the benefit of society. Here are some common mathematical models used in the context of nanomaterial-based wastewater treatment:

**6.1 The first-order kinetic model**

The first-order kinetic mathematical models are commonly used to compare contaminant removal efficiency and mass reduction in wastewater treatment plants. It is a linear model used to predict pollutant removal in wastewater treatment systems. The model equation is as follows:

,

where

 is the concentration of the pollutant at the system outlet (mg/L),  is the concentration of the pollutant at the system inlet (mg/L), and H is the duration of hydraulic retention time of the system expressed in days. The first-order kinetic model equation provides the parameter k representing the rate of removal of pollutants or contaminants from wastewater.

**6.2 The Second-order kinetic model**

The second-order kinetic mathematical model was used to predict the substrate removal from the wastewater treatment system as follows:

,

where X is the biomass concentration in the reactor.

**6.3 Multiple Liner Regression Model**

Multiple linear regression is a statistical model with two or more independent variables (predictors). In this model, the different water quality parameters measured were used as “predictors”, and a specific water quality parameter outlet concentration was considered as the dependent variable (response). The linear regression equation is as follows:

,

where 𝑌 is the response variable, and 𝑋 is the predictor variable.

**6.4 Mass Balance Model**

Mass balance equations were used to model the removal of BOD5, COD, TKN, NH3, and ON in each treatment stage (ST, UAF, and HFCW), because these parameters are degraded primarily by microbial action. Monod’s equation (4) was used to express the specific growth rate of microorganisms as a function of substrate concentration 𝑆.

Where, 𝑆𝑖𝑛 is the substrate concentration at the inlet (mg/L), 𝜇𝑚𝑎𝑥 is the maximum growth rate (h−1), and 𝐾𝑠 is substrate affinity constant (mg/L). The mass balance for every stage and for every contaminant was written as:

**Rate of Transformation of S into the system**

**Outlet of S mass flow to the system**

**Inlet of S mass flow to the system**

**Accumulation rate of S in the system**

**= - +**

,

The accumulation and transformation terms are dependent on the volume 𝑉 of the reactor expressed in m3, whereas the inlet and outlet depend on the hydraulic load of wastewater 𝑄 (m3/day).

**7. Conclusions**

Due to their exceptional properties, which were made possible by their microscopic scale, such as improved catalysis and adsorption characteristics coupled with high reactivity, nanomaterials have recently attracted the attention of extensive research and development efforts across the globe. Nanoparticles have been employed to improve the quality of both drinking water and wastewater since numerous studies have shown that they may effectively remove a range of contaminants from water.

The focus was on the most fully studied nanomaterials, such as nanotubes made of carbon (CNTs), zero-valent metal nanoparticles (Ag, Fe, and Zn), metal oxide nanoparticles along with nanocomposites. Their uses in the purification of wastewater and groundwater were also explored in great depth. Given the rate of discovery and application, nanomaterials seem to hold great potential for the disinfection of water and wastewater.

For wastewater treatment to be viable and sustainable over the long term, it must use appropriate and affordable nanomaterials. Only a few different types of nanomaterials have gained commercial traction so far. To overcome the issues with nanomaterials, more research is still required. Since this will ensure their broad application in the processing of wastewater and water, future research should concentrate on improving the cost efficiency of nanomaterials. Low production costs are essential for this to take place.

Additionally, there are growing worries about nanomaterials' possible hazards to both humans and the environment as they are used in wastewater and water treatment on a larger scale. Data that is currently accessible in the literature suggests that some nanomaterials may have detrimental effects on the environment and human health.

Comparing the abilities of various nanomaterials to identify those that show promise and call for additional research is challenging. Therefore, it is necessary to improve the performance evaluation method for nanomaterials in wastewater and water treatment in the future.

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