

Efficacy and Challenges of Carbon-based Nanomaterials in Water Treatment: A review

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Abstract

Water is a vital element that supports life and is significant for global economic growth. Water sources are currently scarce because of uneven distribution across regions and contamination brought on by population development and industrial activity. The performance capabilities of advanced science and technology based on carbon-based nanomaterials to replace or act as alternative approaches for the present technologies are changing at a quick rate. Numerous studies have focused on the development of high-performance carbon nanomaterials for wastewater treatment. Carbon nanoparticles have developed into promising adsorbents for water purification in recent years. The distinctive qualities of carbon based materials (CBMs) make them highly desirable materials. Due to their unique physical and chemical characteristics, carbon-based nanomaterials (CBM) have demonstrated tremendous potential for usage in a variety of environmental applications. In this article, the efficacy and challenges of carbon-based nanomaterials in water treatment are reviewed. Recently carbon nanomaterials such as carbon nanotubes, graphene, carbon quantum dots, fullerenes have gained a lot of attention. The scientific community has shown a great deal of interest in both water filtration and desalination. The contributions of carbon-based nanomaterials to a wide range of applications in water treatment are critically evaluated in this review.

Keywords: Catalysis, Adsorption, CNTs, Waste water, Graphene

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1. Introduction

The world's population is increasing and factories and industries are expanding quickly, which has contributed to energy issue and environment pollution. Globally, environment pollution is a serious problem that threatens both industrialized and developing nations. Water pollution is one of the biggest environmental threats to both aquatic life and humans in the globe. The primary issue in providing freshwater is the contaminating effects of various organic and inorganic pollutants on water resources [1]. Freshwater supplies have become contaminated as a result of urbanization, population growth, industrialization, climate change and inappropriate use of water resources. Approximately 2.5 billion people do not have access to better sanitary facilities, according to the WHO (World Health Organization) and UNICEF [2]. Concerns about the ecology and public health are being raised by the water pollution, which endangers food production [3-4]. For the past ten years, various methodologies have been used extensively to remove both organic and inorganic pollutants from wastewater. These techniques include oxidation, precipitation, solvent extraction, distillation, bio-remediation, filtration, reverse osmosis, adsorption, coagulation, membrane technology, and photocatalysis [5-6]. However, several of those techniques have drawbacks, such as high

operational costs, high sludge production that generates secondary pollutants, and lack of economic viability. Nano-based technology, such as photocatalysis and adsorption has drawn a lot of interest among the mentioned conventional approaches because of their superior removal efficiency, reduced operating costs, simple designs, and environmentally friendly nature. Nanotechnology involves atomic-level manipulation of nanomaterials [1]. By examining a variety of new materials, nanotechnology created window of opportunity for water filtration and environmental improvement research [7].

For "real-time" and ongoing water quality monitoring, advanced nanomaterials are being deployed in the creation of cost-effective, high-performance water treatment systems. Nanomaterials have also been extensively used in effluence remediation, prevention, and treatment. While continuously monitoring the biological and chemical contamination from man-made, municipal or industrial waste, these recyclable materials can maintain the long-term water quality, affordability, and sustainability of the water supply [8-9]. In the area of treating wastewater, carbon-based nanomaterials have drawn a lot of interest. Researchers are paying close attention to these nanomaterials because of their

special characteristics, including their high surface area to volume ratio, small size, high thermal and chemical stability, high reactivity, accessibility and nanoscale catalytic potential [10]. More dynamic sites for material interaction with various chemical species from wastewater are provided by the increased surface area. There are numerous allotropic carbon-based nanomaterials, including graphite, diamond, fullerenes, carbon nanotubes, graphene, graphitic carbon nitrate etc [1].

Nanomaterials are effectively used for water treatment and remediation due to their high surface area, considerable chemical reactivity, mechanical qualities, cost-effectiveness, and low power consumption. These materials have appropriate size and porosity morphologies that are well-defined and controlled, making them potential good adsorbents. This paper highlights the use of carbon-based nanomaterials, namely carbon nanotubes, to remove aqueous pollutants and contaminants from waste water utilising advanced sustainable nanomaterials [8].

2. Historical back ground

The hollow graphitic carbon fibres with a diameter of 50 nm were first introduced in 1952 by Radushkevich and Lukyanovich in the Soviet Journal of Physical Chemistry. Using an electron microscope, Bollmann and Spreadborough demonstrated the structure of multiwall carbon nanotubes in 1960. In "Nature," they looked into the characteristics of carbon's friction caused by rolling graphene sheets. Oberlin demonstrated the CVD growth of carbon fibres on a nanometer-scale in 1976. The ground-breaking finding in this field was Kroto's discovery of fullerenes in 1985. Given that fullerene may be the first novel carbon allotrope to be identified in the 20th century, this finding seems to be quite significant. Richard Buckminster "Bucky" Fuller (July 12, 1895–July 1, 1983), an American architect, novelist, designer, inventor, and futurist who utilised geodesic sphere constructions in his work, is credited with giving fullerene its nickname. Carbon nanotubes are another significant and well-known type of carbon nanomaterial (CNTs). The use of nanotechnology and carbon-based nanomaterials during the past ten years may have enabled the world to undergo an industrial revolution unlike any other. This new technology has enormous potential for medical breakthroughs, the eradication of world hunger, the production of affordable products, and unfortunately, military usage [11].

3. Nanomaterials

The manufacture of a broad range of materials, including particulate materials having at least one dimension smaller than 100 nanometers, is made possible by the advanced field of research known as nanotechnology (nm). Chemical substances or materials that are produced and used at a very small scale, i.e., 1-100 nm in at least one dimension, are known as nanomaterials (NMs). Bulk materials are described as larger than 100-nm particles in all orientations. Although certain physical characteristics of NMs can depend on their size and form, they can differ from bulk materials whose physical characteristics are unaffected by their size. When researchers found that a substance's physicochemical properties, including its optical, mechanical, electrical and chemical properties, are influenced by its size, they realized the significance of NMs. Due to their distinctive features,

nano particle materials have drawn a lot of interest [12]. Nanomaterials exhibit a variety of unique optical, electrical, mechanical, antibacterial and magnetic properties depending on their kind, shape, size and structure which has led to numerous fascinating application [13].

4. Types of nanomaterials

Based on a variety of parameters, NMs can be divided into numerous groups. NMs are typically divided into categories based on their dimension, size, structure, condition, and chemical constitution [12]. Based on the variety of material they may be broadly classified into following types:

4.1. Carbon based nanomaterials

One-dimensional carbon nanotubes, zero-dimensional fullerenes and two dimensional graphene are examples of carbon nanomaterials made completely of sp^2 hybridized atom of carbon. Due to their special combinations of beneficial chemical and physical properties, such as excellent electrical conductivity, excellent heat conductivity, chemical stability, advanced optical properties, and high mechanical strength, carbon based functional nanomaterials have gained a considerable amount of attention from scientific community [14].

4.2. Metal based nanomaterials

Using either destructive or constructive techniques, metal-based nanoparticles are created from metals to nanometric sizes. The ability to produce nanoparticles exists in almost all metals. For the creation of nanoparticles, metals like aluminium, cobalt, cadmium, copper, iron, gold, lead, zinc and silver are frequently utilized. Metal NPs are produced using the metal precursors. Constrained surface plasmon resonance (SPR) gives these NPs their distinct optical properties [15]. The synthesis process typically affects the size of nanoparticles. They can be divided into several categories, including metal, metal-oxide, bimetallic, trimetallic, and other NPs [13].

4.3. Ceramic based nano materials

By heating and cooling, ceramic NPs, which are nonmetallic inorganic solids, are created. They can be amorphous, polycrystalline, dense, porous, or hollow, among other shapes and sizes. These NPs are gaining a lot of attention from researchers because of their applications like catalysis, photo-catalysis, imaging applications and photo degradation of dyes [15]. Typically, metal or metalloid oxides, carbides, phosphates, and carbonates make up ceramic nanoparticles. Ceramic nanoparticles based on silica and alumina are more often utilized. NPs, nanoscaffolds, and nanoclays are three different types of nanoceramics [13].

4.4. Polymeric nanomaterials

Due to a large improvement in surface area to volume ratio, polymeric nanomaterials with particle sizes in the range of 1-1000 nm at least in one dimension have gained a lot of interest in numerous scientific applications. They have superior qualities when compared to bulk polymers.

Superior optical, thermal, and electrical qualities can be seen in them. They are divided into natural polymer-based, polymer-based through biosynthesis, and polymer-based through chemosynthesis [13].

4.5. Biomolecules derived nanomaterials

A variety of biomolecules, including proteins, lipids, polysaccharides, nucleic acids, and others, have been successfully employed to create nanomaterials. Despite not previously being as well-known as inorganic nanoparticles, these materials have drawn considerable attention as a result of the growing use of biocompatible and biodegradable nanomaterials. Drug distribution is primary application for such materials [13].

5. Carbon based nanomaterials and its types

Known solid state allotropes of carbon with distinctive structures and characteristics include sp_2 bonded graphite and sp_3 bound diamond. In general, carbon nanomaterials' atomic structures and interfacial interactions with substances in other phases have a significant impact on their physical characteristics. Therefore, a common method to acquire desired features for specific applications is to develop and functionalize carbon nanomaterials viewed from a nanoscale. Functional carbon nanomaterials with nanoscale dimensions have received a lot of attention since they were first reported because they have a variety of chemical and physical characteristics including chemical stability, good thermal conductivity, good mechanical properties, improved optical properties and super electroconductivity. Carbon nanoparticles offer great capabilities for applications in material preparation, environment research, biology, storage system and modern research as a result of these special features [14].

Carbon-based nanoparticles (CBNs) are gaining popularity as nanomaterials in the fields of science and technology. Carbon can exist in a variety of allotropes, from well-known allotropic phases like amorphous carbon, graphite, and diamonds to recently found ones including as carbon nanotubes (CNTs), graphene oxide (GO), graphene quantum dots (GQDs), and fullerene [16].

6. Carbon nanotubes

Carbon nanotubes (CNTs) refer as 21st-century technology [17]. Since Sumio Iijima published his incredible finding in 1991— first high resolution TEM photos of "Helical microtubules of graphitic carbon"—CNTs have been among the most extensively studied carbon nanomaterial's. The diameter of these tubes, which is roughly 1/50000th the size of human hair or about equal to length of anthracene, is typically around 1 nm. Sidewalls of these tubes are composed of hexagonally organized sp_2 hybridized atoms of carbon. The tubes can have extremely high aspect ratios despite having very small diameters [14]. Because of their large specific surface area, high porosity, low weight, and favorable interactions with a variety of pollutants, CNTs are one of the most promising remediation materials [18].

6.1. Synthesis of carbon nanotubes

There are currently four main problems with the synthesis: (A) at massive scale manufacture of low cost and high-quality nanotubes, such as SWNT. (b) Selective manufacturing, which allows for precise control over the structure and electrical characteristics of the synthesized CNT. High-quality CNT is preferred for applications in both fundamental science and technology. (c) CNT organization that enables the placement and orientation of synthesized CNT on a flat substrate. (d) Being aware of the mechanisms behind the CNT processes. Numerous parameters, including catalyst, hydrocarbon, pressure, gas flow rate, temperature, deposition duration etc., are involved in the synthesis of CNTs [19]. There are three main ways to synthesize CNTs. These are laser ablation (LA), chemical vapor deposition (CVD), and electric arc discharge (EAD) [20].

6.1.1. Electric arc discharge method

In this procedure, graphite-based CNTs are created at the anode. High voltage beams of electron from arc that hits surface of graphite are needed. The electrical arc is produced by CNT plasmons, which cause CNTs to synthesize on the substrate's surface.

6.1.2. Chemical vapor method

In this technique, carbon and inert gas vapor are combined to create the substrate surface. It is heated to create carbon nanotubes, which are then dispersed throughout the surface of the substrate. On the surface of the substrate, nickel nanoparticles, iron, cobalt, or a mixture of these elements are used as catalysts. Around 700°C is the maximum temperature the furnace can attain. The catalyst particle size affects both the tensile strength and the diameter of CNTs. Only plasma annealing or etching of metal layer to mask the deposition of metal can regulate it [20].

6.1.3. Laser ablation method

In this process, production of CNTs occurred by directing a certain laser light wavelength at a graphite sheet through the use of a catalyst made of a transition metal. The two different kinds of CNTs, SWNTs and MWNTs, are both manufactured. In this operation, a 1 and a 2 laser beam from two different laser sources are used. A 1 laser beam is used as the initial strike, while a 2 laser beam is used as the second strike to create CNTs. It is advantageous since it creates CNTs for a particular purpose. Its disadvantage is that it is time-consuming and expensive process.

6.2. Classification and properties of CNTs

Two types of CNTs are multi-walled CNTs and single-walled CNTs

6.2.1. Single walled CNTs

These are cylinder-shaped, one-dimensional allotropes of carbon that have greater surface area and length-to-diameter ratio. SWCNTs are regarded as 1D nanomaterials due to their high ratio of length-to-diameter and small diameter. Single walled carbon nanotubes are thus named

because they have so many walls and hollow structures. In order to create hollow tubes, graphene sheets are wrapped around walls that are one atom thick. There are three alternative techniques to produce CNTs: zigzag, armchair, or chiral. The form is determined by position of carbon hexagons [20].

6.2.2. Multi walled CNTs

Multi walled carbon nanotubes are composed of several single walled carbon nanotubes which are packed closely together. Multi walled carbon nanotubes are still regarded as one dimensional type of carbon, however they are not as distinctive as SWCNTs. This is because there is a higher possibility of defects occurring. These disadvantages are offset by MWCNTs' higher dispersibility and reduced synthesis and purifying costs [20].

6.3. Properties of CNTs

A distinct type of carbon with a wide range of outstanding physical and chemical properties is the carbon nanotube. They exhibit exceptional electrical, thermal, and mechanical conductivity such as microelectronic interconnects, heat sinks, structural composites etc. Additionally, chemical characteristics like solubility and functionalization [21]. Some properties of CNTs are given below (Table 1).

Table 1. Properties of SWCNTs and MWCNTs [22-23]

Properties	SWCNT	MWCNT
Surface area	387.66	180.9
Total pore volume	0.662	0.345
Thermal conductivity	3000-6000	2000-3000
Average pore diameter	6.83	7.62
Specific gravity	0.8-1.3	1.8-2.6

6.4. Application in water treatment

In addition to dyes, hygiene products, phenolic compounds, petrochemicals, pharmaceutical waste, heavy metals, and organic compounds, water can also contain a variety of other contaminants. These pollutants are hazardous, stable chemically, cytotoxic, and inert. Among some of traditional water purifying techniques which are expensive and could be detrimental to health of human beings include reverse osmosis, chlorination, ozonation, and UV radiation. Using the traditional wastewater treatment

procedure, only certain contaminants are removed. Carbon-based material are mostly used in advance technologies which have concentrated on exploitation of CNTs in field of water treatment as filters or membrane, electrodes, adsorbents, and catalysts. Large surface area, electrical and thermal conductivity, strength and other enhanced characteristics of CNTs make them suitable for wastewater treatment. The treatment of sewage, sterilization, and desalination of seawater are all areas where CNTs have great potential. Numerous contaminants included in polluted water are totally degraded by it [20].

6.4.1. CNTs as adsorbent

CNT are the perfect adsorbent for the treatment of wastewater. Carbon nanotubes' adsorption behavior is affected by their site density, purity, surface area, porosity, functional groups, and CNT type. To remove different impurities, CNT bundles have a number of adsorption sites, including interior sites, grooves, interstitial channels, and exterior surface. According to reports, under identical circumstances, external sites are occupied before internal sites. Because the adsorbing substance can access external sites. The amount of carbon nanotubes that are not blocked makes the adsorption process successful. According to some researchers, removing the CNTs' caps increases the amount of sorption sites and adsorption capacity [17].

6.4.1.1. CNTS adsorption mechanism

Complex processes, including chemical interaction, adsorption-precipitation, and electrostatic attraction, appear to be responsible for metal ions' binding to surface functional groups present in CNTs. Generally, chemical linkages between functional groups present on surface of CNTs and heavy metal ions appear to be main cause of adsorption. CNTs have a low capacity for adsorption of heavy metal however, this capacity significantly enhanced after oxidation with NaOCl, KMnO₄ or HNO₃. Surface-oxidized CNTs have great potential as superior nano-adsorbents for controlling pollution. The CNTs' surface functional groups contain protons that interact with metal ions in the wastewater in an aqueous media. Once the adsorption of metal ions onto CNTs reached equilibrium, pH drop in the solution may be because of H⁺ ion release from the metal ion-adsorbed CNT surface. pH value dropping as initial concentration of metal ion rose suggests that as more metal ions bind to surface sites of CNTs, more H⁺ ions are liberated from those sites and released into the solution. The majority of contaminants are absorbed by open-ended CNTs' outer layer and interior regions. Functional groups present on surface and amount of surface area available are the main factors that cause this enhanced adsorption. The amount of CNT adsorption is affected by several factors, including pore density, purity, outer surface area, and surface functional groups. In addition to these factors, CNT ionic strength, pH and dispersion state also affect adsorption. Key parameters governing dye adsorption on CNT include pH and temperature [20].

6.4.2. CNTs in membrane filtration

By receiving substantial consideration in the development of membranes, CNTs have demonstrated significant advancement potential in nanotechnology. CNTs

are thought to be able to overcome some of the drawbacks of membrane filtration, including fouling and the conflict between permeability and selectivity [24].

6.4.2.1. Role of CNTs

In the area of water treatment, CNT-based membranes have potential to outperform or displace traditional membranes. CNT-based membranes boost selectivity and permeability by fusing the benefits of traditional techniques for separation of membrane with prospective capabilities of CNTs. The polar water molecules can move quickly through the hydrophobic hollow CNT tubes. CNT membranes can thus take the role of traditional membranes with little to no energy use. Three primary subgroups of CNT membranes are Bucky-paper, composite and Vertically Aligned membranes. The membrane can accommodate more water passage due to hydrophilicity of functionalized CNTs, increasing water permeability and improving water permeability of hydrophobic membrane. Many foulants are naturally hydrophobic, which reduces the chances that organic substances will adhere to surface of membrane. Increased membrane hydrophilicity is also related to improved antifouling properties. Hydrophilic modified membranes which are negatively charged will help in increasing effectiveness of antifouling by preventing organic molecules that are negatively charged from adhering to membrane surface. Pore density, CNT size, and the quantity of CNT walls are all factors that affect permeability. CNTs have a great potential as nanomaterials for improving properties like polymeric separation of membrane due to their distinctive properties, including excellent flexibility, low friction coefficient on internal walls, large number of Nano channels, high aspect ratio and interactions with aromatic compounds. In composite membranes, CNTs serve a number of vital roles, including better mechanical strength, operation stability over time, super hydrophobicity with improved wetting resistance, selectivity and higher permeability. In lab-scale batch tests using only moderate volumes of water, CNT-based membranes have proved successful in treating both wastewater and water. There needs to be a lot more work done on manufacturing process and scaling-up to improve CNT-based membrane technology. Additionally, in laboratory batch experiments, real wastewater must be used rather than simulated water for analyzing CNT adsorbent materials [20].

6.4.3. Water desalination

Desalination is a crucial technical remedy for dealing with the lack of fresh water in dry areas, coastal areas, and distant areas [25]. CNTs have great potential for water desalination because of their high ratio of surface area to volume, mechanical stability and chemical resistance. Recent theoretical and experimental developments in the desalination of water using CNT membranes, such as composited CNT membranes and VACNT membranes have shown tremendous promise in terms of high selectivity, improved salt removal efficiency, excellent mechanical properties and higher water flux [16].

6.4.3.1 Role of CNTs in water desalination

Normally, a phase change from liquid to vapor is needed to separate salt and water for water desalination. This method of desalination is often employed. Strongly hydrophobic CNTs significantly changed how water and membranes interacted, favoring permeability of vapor and blocking liquid entry in membrane pores. CNTs have quick adsorption and desorption properties due to which water vapor molecules may adhere to surface diffusion pattern in which solute jumps from a site to another by interacting with surfaces. This action may improve the distribution of vapor everywhere. By permitting diffusion to occur along their flat surface, the CNTs are also able to offer a different path for rapid mass movement. Inner tubes of CNTs, which improve vapor transmission, can also be used to carry water vapor directly. The electrostatic charge distribution has a substantial impact on how CNTs absorb ions and water. The water desalination with CNTs is schematically illustrated in Fig. 1. It has been discovered that changing the CNTs channel's alternating charge pattern may increase water intake while decreasing ion absorption. Antifouling, superior selectivity, good sieving capabilities, mechanical strength and increased water flux are just a few benefits that CNTs in desalination offer. Functionalized CNT membranes exhibit improved salt rejection efficiency due to chemical interactions, electrostatic interactions between salt ions and CNTs and Donnan effect [20].

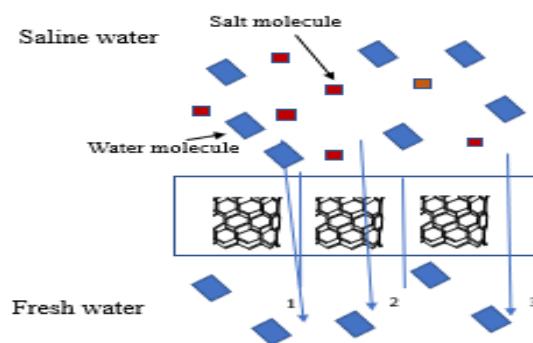


Fig. 1. Water desalination using CNTs [26]

6.4.4. CNTs for disinfection

CNTs show potential as antibacterial agents against a variety of aquatic microbes. Kang published the first evidence of the antibacterial activity of CNTs against *Escherichia coli* for both single-walled carbon nanotubes (SWNTs) and multi-walled carbon nanotubes (MWNTs). According to studies, the effectiveness of CNTs as an antibacterial agent depends considerably on their size and diameter. The antibacterial activity is also influenced by external parameters, including the dispersion power of CNTs, culture media, bacterial type, dose of CNTs, response time, and the mechanism of interaction between bacteria and CNTs. Additionally, CNTs increase antibacterial effectiveness by increasing dispersion and stability properties [27]. When CNTs adhere to surface of different microorganisms, they disrupt transmembrane electron transfer and break cell membranes or cell walls. CNTs disrupt proteins and destroy DNA inside of bacterial cells, as well as produce intermediates that harm cells. It's possible that

oxidative stress contributes to CNTs' toxicity to bacteria. SWNTs have a stronger antibacterial influence on microbial cells than MWNTs, which have a more subtle inhibitory action. The larger specific surface area and small diameter of SWNTs, enhance surface interaction between CNTs and bacteria cells and result in improved inhibitory effects, are believed to be the cause of difference in antibacterial efficiency between two types of CNTs [20].

6.4.5. CNTs in fuel cells

Fuel cells transform chemical energy to electrical energy. A typical fuel cell is shown in fig. 2. CNTs show better surface area and electrical conductivity in comparison to other supports. The performance of the catalyst can be improved with the use of CNTs. The fuel cell can achieve greater stability and acquire higher corrosion resistance performance by using CNTs [28]

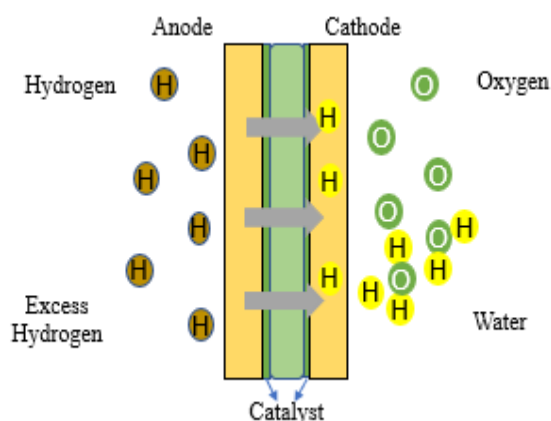


Fig. 2. Fuel cell

6.4.5.1 Role of CNT

MFCs have the ability to resolve a number of problems with traditional wastewater treatment. They lower energy input and superfluous sludge production while enabling energy recovery from wastewater. One of the most crucial MFC parts for producing electricity is electrode material. As electrode materials, carbon paper, plain graphite and carbon cloth have all been used. However, the energy or power generated by these electrode materials is limited. On their own, CNTs are used as cathode or anode material. Contrarily, CNT-based electrodes are frequently modified to improve their mechanical and chemical stability, increase their electrical conductivity, biocompatibility, and increase their electroactive surface area, all of which encourage electron exchange and development of biofilms. The power output is increased by adding CNTs to polymer anode. Increases in maximum power density, COD elimination efficiency, and Coulombic efficiency can all be seen when CNTs are added to carbon cloth electrodes. CNTs along with their composites have been used as MFC components for the past few years. Oxygen reduction reaction at cathode and the electrochemical activities of bacterial colony at anode are two

components of these newly developing nanomaterials that concentrate on enhancing MFC. By improving nutrient transfer, cell adhesion, and therefore denser biofilm formation, a CNT-based modification on anode surface improves electrocatalytic performance of bacteria [20].

6.5. CNTs toxicity

Although CNTs have a broad range of uses, toxicity levels and effects of CNTs on the environment and living things continue to be a global issue [20]. Numerous CNT characteristics, including length, aspect ratio, surface area, degree of aggregation, quality, concentration, and dose, affect the toxicity [29].

6.5.1. Factors effecting CNTS toxicity

CNT toxicity is related to CNT aggregation, surface modification, CNT dosage, shape, and size. Due to its superior physicochemical characteristics, enhanced biocompatibility, and increased dispersion, surface modified CNTs are used more frequently than normal CNTs. The amount of CNTs present is closely related to how poisonous the environment is. Different CNT forms could be more or less hazardous than others. Research indicates that SWCNT is more dangerous than MWCNT. The findings show that thin MWCNTs are less hazardous to cells and generate less reactive oxygen specie than thicker MWCNTs. According to results of numerous research, different CNT forms appear to have cytotoxicity of varying degrees and needle-shaped CNTs having most toxicity [20]. CNT's have some adverse effects on the environment and human health, as shown in Fig. 3.

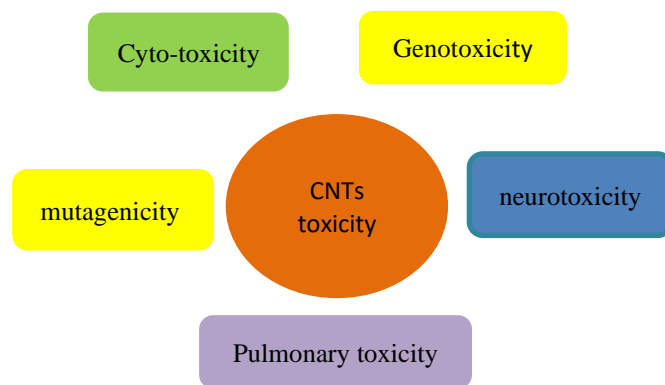


Fig. 3. Negative effects of CNTs [30]

6.6. Future scope and challenges in water treatment

6.6.1. Cost

Costs associated with CNT production and optimization Cost is frequently a limiting factor in a variety of applications. CNTs are a fairly pricey substance. A wide variety of CNT applications may be made possible by the capacity to synthesis huge quantities of CNTs at affordable costs. The usage of CNTs in conjunction with wastewater treatment techniques should be investigated to clear way for more effective wastewater treatment.

6.6.2. Toxicity

Besides their broad variety of uses of CNTs, there is still concern about toxicity levels and their effects on environment and living things. Greatest barrier to rapid and widespread adoption is its adverse impacts on environment and living things [31].

6.6.3. Industrial and large-scale application

Most CNT applications are limited to laboratory research. Further research is required to determine whether they could be used on an industrial scale and using cost-effective synthesis techniques, as well as to determine their potential toxicity [32].

6.6.4. Non-biodegradability

Designing ecologically friendly nanoparticles with environmental sustainability and biodegradability is crucial [33].

6.6.5. Effective regulatory system

For CNT dangers and hazards, there are currently no established safety regulations. The potential dangers of nanomaterials must be addressed and adequately handled by effective regulatory systems [33].

7. Graphene

One of the several forms of carbon is called graphene, which is a planar monolayer of carbon atoms structured in a two-dimensional (2D) honeycomb lattice with a carbon-carbon bond length of 0.142 nm [34]. Graphene found in different shapes, including nanoplates, nanoribbons, nanosheets, three-dimensional graphene, in addition to the unusual quantum hall phenomenon. All of them has incredible applications. In graphene, each carbon atom is sp_2 hybridized and has three bonds with other neighbouring carbon atoms. s , p_x , and p_y orbitals are combined to form sp_2 hybridization. In hexagonal phase, three different atoms of carbon bonded covalently with each other and are basically sp_2 hybridized, leaving one free electron for each carbon atom. This free electron is held in p_z orbital, which creates π bond and is located above plane. Interestingly, graphene p_z orbital is crucial to chemical and physical behaviour of this amazing material [35].

7.1. Structure of graphene

The $2p_z$ orbitals, which are parallel to planar structure, make up out-of-plane link in a typical sp_2 hybridization of two nearby carbon atoms on the graphene layer, while the sp_2 ($2s$, $2p_x$, and $2p_y$) hybridized orbitals make up the in-plane bond. Monolayer graphene exhibits remarkable mechanical properties, such as a 1 TPa Young's modulus and 130.5 GPa intrinsic tensile strength, thanks to the covalent bond that results. This bond has a short interatomic length of 1.42, making it even stronger than the sp_3 hybridized carbon-carbon bonds in diamonds. In monolayer graphene, the half-filled π band that allows free-moving electrons causes the conduction band and valence band with zero band gap to form. Additionally, in bilayer and

multilayer graphenes, the π -bonds offer a weak van der Waals connection between adjacent graphene layers [36].

7.2. Synthesis of graphene

7.2.1. Exfoliation and cleavage

Due to the superior in-plane mechanical, structural, thermal, and electrical properties of graphene, graphite and graphite nanoplatelets could be employed as workable and affordable filler is used instead of carbon nanotubes (CNT) in nanocomposites. These exceptional qualities are obviously essential at the nanoscale, and the exfoliation of the graphite down to a single graphene sheet in the matrices is crucial for the production of the conducting nanocomposites. However, achieving complete and homogenous dispersion of individual graphene sheets in a variety of solvents remained a challenge. Aggregation is the main difficulty in the manufacture and handling of massive quantities of graphene sheets, just like CNT and other nanomaterials. The surface area particular to graphene is enormous. Graphene tends to form irreversible agglomerates or even restack to create graphite through Van der Waals interactions if not kept well apart from one another. Because the majority of graphene sheets' special features are only connected to individual sheets, preventing aggregation is crucial [34].

7.2.1.1. Liquid-phase mechanical exfoliation

Researchers studying graphene have started using these liquid-phase techniques to separate individual graphene sheets from bulk graphite [37]. In oxygen plasma, a sheet of highly oriented pyrolytic graphite (HOPG), which is readily available, was dry etched to several 5 μ m deep mesas for mechanical exfoliation, a straightforward peeling operation. The mesa was then adhered on a photoresist, and layers were peeled off with Scotch tape. After being removed from the photoresist in acetone, the tiny flakes were placed to a silicon wafer. The composition of these tiny flakes was discovered to be monolayer or several layers of graphene. In contrast, Raman spectroscopic investigations show that chemical oxidation of graphite and the following exfoliation result in the generation of substantial amounts of graphite oxide monolayer due to the invasive nature of the chemical process. These structural flaws caused graphene's electrical structure to be disturbed and became semiconductive. According to XPS tests, it is practically impossible to rebuild the graphene structures through chemical reduction or heat annealing (up to 1000°C). Therefore, where it is necessary to maintain the graphene structure, physical exfoliation procedures are preferred [34].

7.2.1.2. Intercalation of small molecules by mechanical exfoliation

By inserting tiny molecules between the layers of graphite or by non-covalently attaching molecules or polymers to the sheets, graphite intercalation compounds can be created that significantly reduce agglomeration in the material (GICs). Guest molecules in interlayer galleries do not affect layers of graphite in GICs. The in-plane electrical conductivity increases when guest molecules and graphite layers interact through charge transfer, but when molecules form covalent bonds with the graphite layers, as in fluorides

or oxides, conductivity decreases because conjugated sp^2 system is broken [34].

7.2.3. Chemical vapor deposition (CVD)

A lot of effort is done into producing graphene on a wide scale using the chemical vapour deposition (CVD) method [38]. On metal surfaces, carbon typically disperses at high-temperature phases before segregating at low-temperature phases. By lowering the energy barrier of the reactants, metal substrates demonstrated an amazing role during CVD development of graphene films. Copper catalyst was often used because of its fascinating solubility with carbon and promising outcomes in the creation of high-quality CVD graphene. Methane is used as precursor during high-temperature (>1000 °C) synthesis of graphene. However, because of substantial energy consumption and potential thermal deterioration of graphene, which can impair performance of optoelectronic devices, this is not cost-effective. Alternative methods based on liquid or solid hydrocarbon precursors, such as LPCVD and PECVD, have been employed to get over these restrictions. In these methods, the temperature is considerably decreased to 300°C [39-40].

7.2.4. Chemically derived graphene

Currently, it has become possible to obtain graphene-based single sheets in large quantities by chemically converting graphite to graphene oxide. According to the Hummers method, graphite is typically oxidized to produce graphite oxide (GO) using oxidants including concentrated sulfuric acid, potassium permanganate and nitric acid. GO is significantly more oxygenated than pure graphite and contains epoxy and hydroxyl groups on sp^3 hybridized carbon on the basal plane, as well as carbonyl and carboxyl groups on sp^2 hybridized carbon at the sheet margins. GO is therefore extremely hydrophilic and easily exfoliates in water, produce a stable dispersion that consists primarily of single-layered sheets (graphene oxide) [34-41].

7.3. Applications in water treatment

7.3.1. Capacitive deionization using graphene-based electrodes

A novel technology called capacitive deionization (CDI) has been successfully applied in numerous water treatment and purification applications. Compared to other modern technologies, the CDI technology has demonstrated enhanced efficiency in several applications [42]. Extensive work is put into establishing revolutionary high surface area carbon electrodes with superior properties like high ion transport and extraordinary ion removal capacity. These electrodes come in a variety of forms, including graphene-based electrode materials, hierarchical porous carbon architectures, and electrodes derived from MOFs [43]. CDI is utilized in this procedure to desalinate water. Graphene is component of CDI and its nanocomposite is employed as electrodes in this approach, which does not use it as the primary filtering mechanism. Electrostatic adsorption serves as the CDI's primary driving mechanism for eliminating ions in this process. Electrosorption, also known as CDI, is a technique utilized mostly in desalination applications in

which ionic species are adsorbed on electrodes when direct voltage is delivered through electrodes. Adsorbed ions released back into our solution if external voltage is reversed or shorted [44]. Benefits of this method include following low cost, simple regeneration, great removal efficiency, and energy efficiency. There are a number of procedures that must be followed and several methods that must be used to prepare electrode. Preparation of resol (RGO-RF) and graphene comes first. Required electrode is then constructed and transformed into a capacitive deionization device for desalination applications employing Polytetrafluoroethylene (PTFE) for binding. RGO-RF offers superior NaCl adsorption properties compared to traditional RGO. Additionally, it was discovered that employing Resol will improve the particular surface because a greater specific area is needed. It was also demonstrated that the CDI approach exhibits Langmuir adsorption [45]. Numerous investigations have revealed energy efficiencies between 60 and 95 percent. Additionally, because they offer a good surface area and improved conductivity, composite materials like three-dimensional macroporous graphene, graphene/CNT etc are also widely investigated for desalination purposes in this field [3].

The CDI technique also employs the popular flow-through capacitor (FTC) approach. Due to their stability, strength, and low resistance, CNTs have demonstrated to be quite efficient in this manner. The BET surface area is one of the key factors in this approach [46]. Because BET surface area and CNT nanotube diameter are reversely correlated, decreasing diameter will increase BET surface area, which increase removal effectiveness by up to 95%. Additionally, hot-pressed CNTs can be carbonized to improve the surface texture of the material with a removal effectiveness of more than 90%, an increase in specific capacitance from 2.4 to 10.6, and a decrease in equivalent resistance from 15.1 to 2.2 that improve CDI performance [7].

7.3.2. Water purification

Graphene is a fantastic and promising nanomaterial for water desalination (WD) and purification due to its porous structure and wetting properties [47]. A schematic diagram showing water purification using graphene is illustrated in fig. 1. Due to its excellent surface features, extensive surface area, structural traits, high tensile strength, minimal thickness, charge density, and mechanical strength, graphene offers a significant promise for desalination and other purifying methods [48]. Because conventional reverse osmosis membranes have a poor water permeability, the desalination process calls for more operating power. By adding nanopores to its surface, graphene is altered in this novel membrane. In this procedure, well-designed pore channels can help water flow and speed up flow. Additionally, by altering the size of the pores, additional compounds, dependent on their molecular size, can be filtered in addition to salt using this technology. The pores use physical principles like charge and hydrophobicity to reject ions and other molecules of solute [7-49].

Graphene has a number of advantages over other membranes used in water desalination. The first and the most significant benefit is that it is only one atom thick, its

thickness may be disregarded. Researchers have discovered an effective method for producing necessary pores on graphene sheets, despite the fact that it has a minimal thickness. Graphene has high mechanical strength in contrast to its thinness. These two characteristics result in low pressure requirements and faster water transport. A gallium cannon is utilized in this procedure. However, it is discovered through experimental research that a maximum pore diameter of roughly 7 \AA should be used for desalination purposes. Such a technique produced a single layer of graphene with five trillion 0.4 nm holes/cm. After pores are produced, some

hydrophilic bonding created at pores to improve water flux that passes through pores. This is because there will be a greater amount of hydrogen-bonding arrangement inside the pores. Because of its excellent water permeability in contrast to top RO membranes now in use, this innovative water purification membrane was significantly better than conventional reverse osmosis membranes. Additionally, it was revealed that pore size and pressure were both important factors in salt rejection. It was demonstrated that enhancing size of pore and pressure will both reduce salt rejection [7].

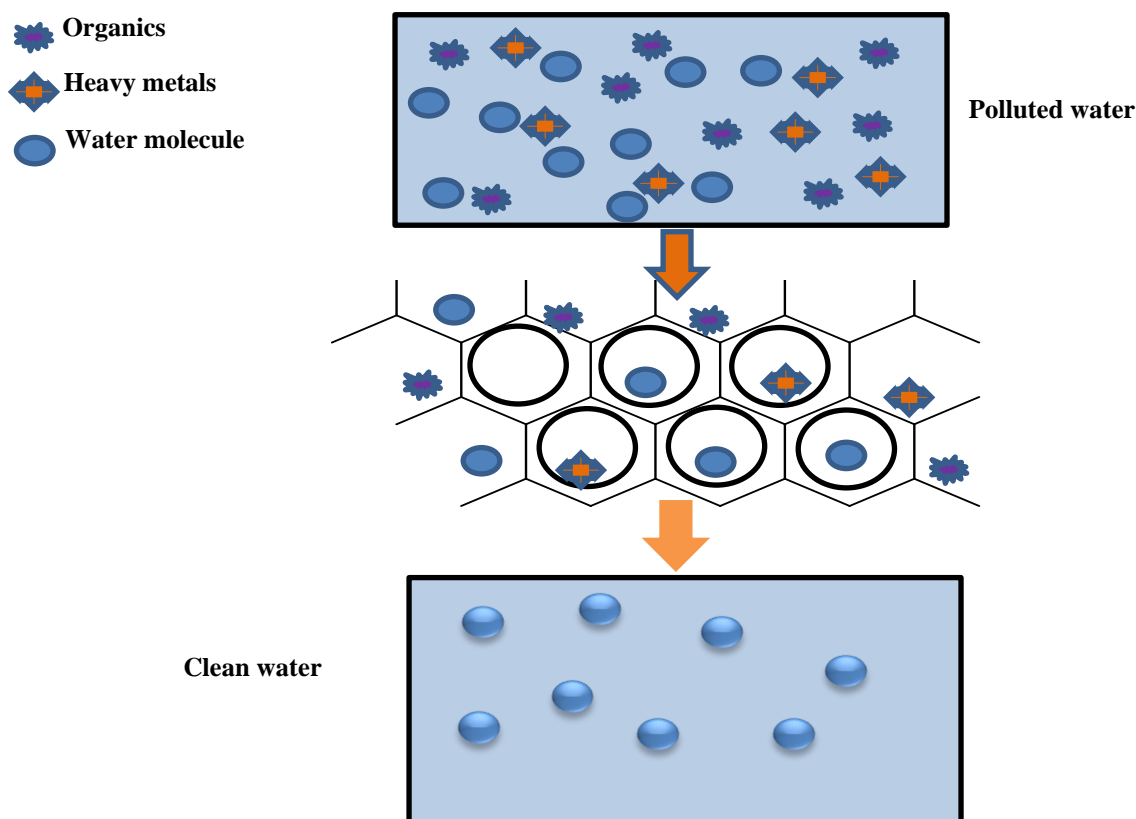


Fig. 4: Graphene for water treatment [50]

7.3.3. Graphene as adsorbent

In-depth research has also been conducted on use of graphene for adsorptive elimination of contaminants from water [51]. Graphene is an attractive alternative to more conventional adsorbents like activated and mesoporous carbons because it theoretically has a very high surface area. For this effect, use of graphene and its derivatives as adsorbents for pollutants removal has been investigated [52]. First of the following elements that affect graphene's adsorption capabilities is the contribution of each individual adsorption site [53]. In graphene, there are three potential locations for the adsorption of various contaminants. Because oxygen atoms have a far higher affinity for metal ions than does skeletal carbon, one is locations on the oxygen functional groups. The locations of C electrons on graphene sheets are thought to be another. The second is the active location on the outside of the embellished nanoparticles on graphene sheets [54].

7.3.3.1 Adsorption of anionic pollutants

The ability of graphene to bind to many contaminants is excellent. Wastewater frequently contains the anionic contaminants fluoride, arsenic, and chromium. According to some theories, anions could be adsorbed on adsorbents through nonspecific or selective adsorption. Fluoride is removed from aqueous solutions using graphene as an adsorbent. Greatest adsorption capacity of graphene under the same circumstances was 35.59 mg g^{-1} . Fluoride adsorption by graphene was primarily a distinct process, indicating that the graphene's adsorption mechanism was an ion exchange between fluoride ions in solution and hydroxyl ions on the material. Therefore, surface-exchange processes were mostly used to absorb fluoride ions [54-55].

7.3.3.2. Adsorption of cationic pollutants

In polluted water, cationic contaminants like Pb, Hg, Cd, Cu, Ni, Co, and Zn are frequently found. Three

adsorption mechanisms, electrostatic contact, ion exchange, and complex formation are the foundation for adsorption of metal ions. By using electrostatic, ion exchange, and coordinate methods, it is possible to attach ions to the many oxygen groups that protrude from GO sheets. For those cationic pollutants, adsorption is promoted by a high pH value. This is due to competition between proton and metal ions on -COO and -O sites under a low pH situation, which will lead to a decreased adsorption capacity [54].

7.3.4. Graphene as photocatalyst

Numerous 2D graphene nanosheets-supported semiconductor composite photocatalysts have been developed and used in a variety of photocatalytic areas because of their distinctive optical, electrical, and physicochemical capabilities. By serving as an electron acceptor, graphene reduces electron hole recombination [56].

Additionally, by π - π stacking, graphene promotes the interaction of metal oxide with organic pollutants [52]. Building composite photocatalysts made of heterogeneous graphene and semiconductors is one of the most promising directions. Since Fujishima and Honda's discovery of photoelectrochemical (PEC) water splitting over TiO₂ electrodes in 1972, heterogeneous photocatalysis has been increasingly popular as a green and promising technique. The creation of novel semiconductor-based photocatalyst materials and their potential applications in a variety of fields, including H₂ generation, watersplitting, CO₂ reduction, environmental remediation, organic synthesis, and bacterial disinfection, have made exciting significant steps over the past few decades. Under adequate light irradiation with incident photon energies that are equivalent to or greater than that of the semiconductor's band gap, the electrons in a particular semiconductor can be photo-chemically stimulated to its CB in heterogenous photocatalysis, leaving a positive hole in the VB. Highly effective photocatalysis methods are made possible by the heterogeneous photocatalysts. The bulk of photocatalysts, however, have low quantum yields, low rates of using visible light, and low levels of stability, which have become many significant obstacles in designing and creating heterogeneous photocatalysts for use in practical applications [56].

7.3.5. Graphene as disinfectant

The potential antibacterial properties of pure graphene and graphene oxide without any added functional components have also investigated. The effectiveness of graphene oxide as an antimicrobial agent was found to be strongly influenced by lateral dimensions and morphology of the sheets, with the larger sheets exhibiting higher antimicrobial activity due to their broad cell surface coverage, as opposed to the smaller sheets. Larger graphene sheets (>0.4 m²) completely warp bacterial cells, blocking all of the active areas and preventing the growth of new cells. However, smaller graphene oxide sheets (0.2 m²) adhere to cell membrane, but because they cannot completely occupy and isolate the cell surface, their effectiveness is much diminished. While dispersed graphene oxide sheets can exhibit improved antibacterial activity due to a higher exposed surface area, aggregated graphene oxide sheets can

also be inhibited in their antimicrobial activity. The impact of graphene oxide on microbial population found in wastewater was investigated. Results support hypothesis that graphene oxide reduces the microorganism's metabolic activity, which in turn limits cell multiplication and finally results in cell death. Reduced metabolic activity results in lower oxygen consumption, which lowers biological oxygen demand value (BODs). The graphene oxide-produced reactive oxygen species were also in charge of inhibiting microbial cell growth [52].

Additionally, Bacteria that oxidizes ammonia and organisms that accumulate polyphosphate, which are in charge of removing nutrients nitrogen and phosphorus from polluted water, have been demonstrated to be inhibited by graphene oxide. As an antimicrobial agent for the disinfection and sensitization of water, composites of graphene and reduced graphene oxide with metals and metal oxides such as Fe, Ag, Fe₃O₄, and TiO₂ have been investigated. Gollavelli and colleagues recently created a Fe₃O₄ graphene composite and showed that it has effective antimicrobial characteristics against E. coli however still being low in toxicity to zebrafish. High surface roughness of magnetic graphene, which leads to its penetrating of cell membrane as a result, and the bactericidal effects of Fe₃O₄ nanoparticles were both thought to be responsible for its antibacterial properties. An edge-dominated structure is far more effective for anti-microbial applications than planar/epitaxial graphene, hence an appropriate preparation method, such as a plasma accelerated chemical vapor deposition procedure, is needed to produce the product. Similar to this, high surface area structures like aerogels and xerogels based on graphene should be used for heavy ion removal using adsorption approaches. Vast surface area of graphene and micro and structure nanoporosity enable highly effective adsorption of organic dyes, potential hydrocarbon spills and heavy metal ions [52].

8. Fullerenes

Fullerenes are extremely symmetrical, cage-shaped molecules made exclusively of carbon atoms that were first discovered by Curl, Kroto and Smalley 20 years ago [57]. Fullerenes are 0D nano-carbons with pentagonal and hexagonal rings that are found in closed-caged structures. They are represented by formula C_{20+n}. Within the fullerene family, spherical fullerene is extensively researched. Over 3000 atm of pressure can be withstood by C₆₀, and after the pressure is released, the material will resume its former shape. The C₆₀ species is harder than diamond thanks to its effective bulk modulus of 668 GPa, high refractive index, low dielectric constant, huge molecular volume, high surface to volume ratios, strong affinities of electrons [58].

8.1. Structure

20 hexagonal and 12 pentagonal rings make up foundation of closed cage icosohedral symmetry of fullerenes. All carbon atoms are sp₂ hybridized and connected to three other atoms via bonds. The 6:6 ring bonds, which are "double bonds" and are shorter than the 6:5 bonds, are the shorter of the two bond lengths in the C₆₀ molecule. Due to its ability to avoid double bonds in pentagonal rings and consequently have delocalization of poor electron, C₆₀ is not "superaromatic." As a result, C₆₀ behaves like an electron-

poor alkene and interacts easily with entities that have an abundance of electrons. Stability of molecule is caused by geodesic and electronic bonding elements in the structure. C₆₀ is a very symmetric molecule [59].

8.2. Physical properties

Fullerene is 1.65 g cm⁻³ in density, 9.08 k cal mol⁻¹ in standard heat of production, 2.2 (600nm) in index of refraction, sublimates at 800K, and has a resistance of 1014 ohms m⁻¹. Additionally, it has been discovered that the fullerenes are soluble in typical solvents like benzene, toluene, or chloroform. A crimson solution can be made by mixing some fullerene soot with toluene and filtering the result. Crystals made entirely of carbon are produced as the solvent evaporates. Fullerenes were discovered in carbon soot according to an HPLC trace [59].

8.3. Advantages

Researchers have examined C₆₀'s potential for application in the environment and discovered that it is useful for treating water. Due to its low inclination to aggregate and high surface area, C₆₀s are a viable option for use as adsorbents in the treatment of sewage. Due to its inexpensive production costs, simplicity of use, and accessibility of various adsorbents, C₆₀ is chosen. Best material is C₆₀ because it is substantially more efficient than soot or activated carbon at adsorbing organic molecules in water (a suitable adsorbent, which has a porous structure and large surface area). Interactions of the chemicals in dispersion solutions are primarily what allow C₆₀ to adsorb substances. Additionally, C₆₀ has a large surface-to-volume ratio, a high electron affinity, more surface flaws, minimal biological toxicity, and is most importantly a photoactive molecule. C₆₀ exhibits a hydrophobic characteristic, but can be functionalized to become a hydrophilic or amphiphilic material [58].

8.4. Fullerene based Polymer Nanocomposites membrane in water treatment

The advantages of C₆₀ for water treatment were demonstrated when hydrophilic functionalized C₆₀ species were made, which are used to destroy harmful bacteria which are found in water by employing photocatalytic ability of C₆₀. Additionally, sorption is one approach for removing heavy metals from wastewater effluents, including lead, zinc, cadmium, nickel, copper, cobalt, mercury and arsenic. Surface flaws and the material's lattice structure are frequently linked to the sorption capacity of metals. When treating wastewater, conventional materials consist limited metal sorption capacity and metal removal effectiveness. By employing C₆₀, a porous structure was created with increase in manufactured adsorbents' hydrophobicity, and results demonstrated an improvement in their ability to bind metals. For instance, the sorption capacity for heavy metals like lead and copper rose by 1.5–2.5 times utilizing 0.001-0.004% of the C₆₀ in activated carbon. Additionally, electronic characteristics of composite materials' based on C₆₀ are used because they showed superior retention times and greater specific capacitances (135.5 Fg/g). A Langmuir model-based C₆₀-based nanocomposite-PS film that was more effective at removing Cu²⁺ ions. The manufacture of C₆₀-based polymer

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films boosts their hydrophobicity, improving their adsorption and making recycling easier.

Water disinfection has been reported to use membranes with antibacterial properties created by grafting PVP onto C₆₀ that show the safety of doing so. The C₆₀s function in the membranes as nano-adsorbents and increase the adsorption effectiveness of the membranes. The removal and adsorption characteristics of the naturally occurring hormone estrone were investigated using hydrophobic PPO membranes integrated with different C₆₀ compositions. The outcomes demonstrated the significance of internal organization membrane pore size. Incorporating C₆₀ into hydrophobic polymers increased permeate flux by 8 times as compared to membranes made of virgin polymer. Because of C₆₀'s adsorption properties and steric hindrance effects, 10 wt% C₆₀-PPO nanocomposite membranes demonstrated good permeate clearance of at least 95% during long-term filtration [60].

For removal of the organic matter, TFN membrane with 0.5 wt% C₆₀(OH)₂₂₋₂₄ displayed excellent antifouling performance. With better particular desalination performances, Perera created TFC membranes for forward osmosis that comprise C₆₀(OH)₂₄₋₂₈. The constructed C₆₀(OH)₂₄₋₂₈ based TFN membranes were shown to have excellent desalination capabilities, including salt permeability, reverse salt flux, water reflux, water permeability and antifouling propensity. When different C₆₀(OH)₂₄₋₂₈ loading was added to the polyamide top surface, pure water flux increased, salt rejection decreased, and antifouling performance improved. With loading of 400 ppm C₆₀(OH)₂₄₋₂₈, a water flux of 26.1 L/m²h was measured, which is higher than that of pure TFC membrane. Shen used IP to load fullerene into a new TFN membrane. The membrane demonstrated outstanding antifouling properties, stability and excellent Mg²⁺/Li⁺ separation efficiency with a separation factor of 13.1. This membrane contained 0.01% (w/v) fullerene. It was claimed that these membranes could be particularly effective at recovering Li⁺ from saltwater [58].

8.5. Future scope and challenges in water treatment

Numerous initiatives have been made to enhance the water permeability, separation efficacy, and antifouling performances of nanofiller-polymer membranes. Researchers have also looked into surface changes, cost-effectiveness, and the long-term durability of these membranes. It is known that carbon nanomaterial's acting as nanofillers have distinct characteristics from those of pristine polymer membranes. The current issues can be resolved by controlling loading of carbon nanomaterial's, interaction between polymer carbon nanomaterial's, their dispersibility, and other minor parameters in order to increase stability and separation efficiency of polymer nanocomposite membranes, particularly in aggressive and adverse environments [58].

The price of fullerene, which is comparatively high, may prevent its widespread use. On top of that, the standard arc-discharge technology only allows for the mass production of C₆₀ and C₇₀. As a result, it is anticipated that greater fullerenes and their derivatives would have a relatively poor

yield and be considerably more expensive. However, as the corresponding technology develops and more research is devoted to the manufacture of fullerene, its price will decline [61].

9. Carbon quantum dots

A new family of carbon nanomaterial's called carbon quantum dots also known as graphene/graphene oxide quantum dots and carbon dots, have a variety of special features. They typically have sizes between 3 and 20 nm and are quasi-spherical nanoparticles with amorphous to Nano crystalline centers. At their surfaces and basal planes, CQDs have significant quantities of epoxy, hydroxyl, and carboxyl groups. Depending on the synthesis process, the O content can range from 5% to 50% in weight. These groups give varied capabilities for further functionalization and surface passivation, as well as high water solubility [62].

9.1. Methods used to fabricate CQDs

Fabricating CQDs has been done using a variety of strategies and procedures. One of them involves sonicating multi-walled carbon nanotubes for two hours in a solution of strong nitric and sulfuric acids, followed by eight hours of refluxing at 80°C. After reaction, the acidic medium was diluted with sodium hydroxide before being dialyzed with a dialysis membrane to eliminate the extra acidic solutions. Concentrated acids were used to reduce the precursor materials' size and functionalize them. Based on various heat settings, this method can also provide CQDs a potent photoluminescent effect [63].

The ultrasonic procedure has also been applied to the creation of CQDs. This procedure involves dissolving glucose in water first, then adding sodium hydroxide solution. In certain experimental studies, the glucose was oxidized using intense sulfuric acid or hydrogen peroxide. For four to five hours, ultrasonic waves were applied to the mixed solution. Based on that technique high energy that can cause chemical and physical changes as well as disruption of carbon bonds was produced by agitating the solution's particles with ultrasonic energy. Additionally, this process can increase the amount of free radicals and bubbles produced, increase the reaction's reactivity, control morphology, and possibly even lessen surface flaws of CQDs [63].

When compared to electrochemical and hydrothermal approaches, microwave-assisted extraction of CQDs is a quick and inexpensive process. This technique, which relies on microwave heating rather than direct heating, is regarded as one of the hottest research fields today. Microwaves and carbon-based materials can interact quite strongly. This feature improved the method for creating efficient and localized heating, making the carbonization processes advantageous and making the formation of distinctive nanostructure morphology simpler. This method has been studied in several research for the green synthesis of quantum dots. For instance, it has been reported that the internal structure of carbon dots can be altered effectively and under control utilizing branching polyethyleneimine and citric acid. Such a strategy encourages the development of versatile carbon dots with simple fabrication techniques between catalytic and luminous capabilities [53-64].

9.2. Application in water treatment

9.2.1. CQDs as photocatalyst

Due to carbon quantum dots' (CQDs') low toxicity, water stability, increased surface area, economic viability, strong biocompatibility, and chemical inertness, the modification of semiconductor photocatalysts with CQDs is of utmost importance[65]. Recent research have examined Carbon Quantum Dots materials (CQDs) for the development of superior photocatalysts in combination with a semiconductor material like ZnO in order to overcome the drawback of semiconductor materials as photocatalytic degradation for organic pollutants. CQDs offer a fantastic prospect for photocatalytic application due to their strong electron conductivity and controllable Photoluminescence. The adsorption of dye molecules onto the surface of photocatalyst particles, however, can be enhanced by the surface functional groups of CQDs. Additionally, CQDs function as electron donors and acceptors, resulting in efficient electron and hole separation. Based on these characteristics, CQDs can enhance the photocatalytic activity of ZnO by acting as the only photocatalyst, spectrum converter, electron mediator, and photosensitizer [66].

According to a study, CQDs are used to photocatalytically degrade organic pollutants. To create a composite photo-catalyst (CQDs/NH₂-MIL-125), CQDs were joined to the metal-organic framework NH₂-MIL-125. Based on that research, microwave irradiation was employed to create CQDs using ascorbic acid as the starting material. Various amounts of photocatalyst compound (CQDs/NH₂-MIL-125) were homogeneously dissolved in distilled water and heated at 90°C for three hours. This photocatalyst was mixed with Rhodamine B solution (10 mg/L) and swirled in dark for 40 minutes before stirring while being exposed to Xenon lamp radiation for 200 minutes. Using UV-Vis spectrophotometer, the solution samples were examined every 20 minutes to gauge the RhB degradation. The presence of CQDs in the Xenon light caused the RhB to be removed almost completely within 120 minutes, according to the results. A steadily increasing CQD concentration gradually increased the photocatalytic efficiency. The CQDs can be thought of as an intensifying luminous material, according to this result. Additionally, it can promote photocatalytic activity, which can help to improve the separation of electrons from holes [67].

Using CQDs/TiO₂ composite nanofibers, another study demonstrated photocatalytic destruction of methylene blue dyes. In that study, CQDs/TiO₂ composite nanofibers degraded nearly all of the MB dyes in 95 minutes while TiO₂ nanofibers degraded approximately 71% of MB in that time. This finding demonstrates that CQDs/TiO₂ composite nanofibers outperform TiO₂ in terms of photocatalytic effects. CQDs absorb light during the photocatalytic degradation activity when exposed to UV light and reemit it at a lower wavelength. The TiO₂ nanofibers will be excited by the shorter wavelength to produce electron-hole pairs. As a result, CQDs serve as acceptors and transporters for electrons produced by photons. Hydroxyl groups at the catalyst surfaces captured the electron-hole pairs that resulted from the excitation of electrons, producing OH• radicals as a

result. The degradation of dyes depends on the hydroxyl radical. Superoxide radical anions O_2^- have been produced as a result of a reaction between the excited electrons and the dissolved oxygen molecules. Hydroperoxyl radicals (HO_2^\bullet) and hydroxyl radicals (OH^\bullet) can be produced during protonation. All of the dye molecules will be broken down into nontoxic gases such as carbon dioxide and water molecules by the powerful oxidizing action of these radical molecules [63-68].

9.2.2. CQDs as fluorescent probe

Because of their superior optical and luminous qualities. Several metal ions can be used as fluorescence probes using CQDs. According to a study, CQDs can be used as a fluorescent probe to detect Hg (II) in water samples. The water samples had various levels of Hg (II) solution added to them. Using a spectrophotometer for photoluminescence, water samples were examined. The outcomes demonstrated that 1.26 ng/mL was limit of detection for Hg (II) when CQDs were used as fluorescent probe. By adding different quantities of Hg, the CQDs solution's fluorescence intensity was gradually reduced (II). It is hypothesized that functional groups present on surfaces of CQDs that contain oxygen could coordinate Hg (II) ions. The procedure caused the fluorescence quenching by causing non-radiative recombination, excitations via electron transfer between oxygen-containing group of CQDs and Hg (II) and electrostatic contact. Other researchers used different Cu^{2+} ion concentrations to assess the sensitivity of CQDs in more detail. Following the addition of Cu^{2+} , the fluorescence intensity gradually diminished as a result of Cu^{2+} chelation with carboxyl and carbonyl groups on CQD surfaces [69].

According to a different study, CQDs can be used as fluorescent probe for exact detection of Fe^{3+} ions. On the basis of that research, ethylenediamine solution and biomass tar were used as starting ingredients for hydrothermal synthesis of nitrogen doped-CQDs (NCQDs). By determining the intensity of the FL in the samples at various Fe^{3+} concentrations, fluorescent quenching impact on NCQDs was examined. The FL emission intensity was dramatically reduced when Fe^{3+} ions were introduced to the NCQDs solution due to the fluorescence quenching effect of Fe^{3+} ions adhering to NCQDs surfaces. In order to quench photoluminescent of the NCQDs, a complex chelate is formed when functional groups on surfaces of NCQDs specifically bind to metal ions. The NCQDs can function as a fluorescent probe with exceptional sensitivity to Fe^{3+} ions thanks to abundance of functional groups containing oxygen on their surfaces. Therefore, Fe^{3+} ions could extinguish fluorescence emissions of NCQDs using the energy of electron transfer [63].

9.2.3. CQDs as adsorbents

Through adsorption method, CQDs are used to remove both inorganic and organic contaminants. CQDs were changed into nitrogen-doped-CQDs in a study, and their surface activity was assessed by adsorbing Pb^{2+} and Cd^{2+} ions

from wastewater. N-CQDs are effective at removal of Pb^{2+} and Cd^{2+} ions from water through surface adsorption because of their wide surface area, variable surface chemistry, and non-corrosive nature. The interactivity (chemical and physical interactions) among particles can be increased by the surfaces or edges of CQDs. CQDs can be thought of as an effective adsorbent in the removal of harmful compounds from wastewater due to the abundance of functional groups and diverse polar moieties on their surfaces. The metal ions can be bound by a variety of functional groups, including amine and carboxyl groups, through π -stacking interactions and electrostatic attraction. A study created a nanocomposite (PECQDs/MnFe₂O₄) adsorbent by combining polyethyleneimine-functionalized CQDs with magnetic materials (MnFe₂O₄). This nanocomposite demonstrated a strong magnetic field and a high capacity for adsorption, both of which can be effectively used in the removal of uranium [63].

pH of solution had a significant impact on the adsorption capacity. The adsorption capability decreases with decreasing solution pH. Metal ions and hydrogen ions compete for the same adsorption sites in an acidic solution. Because they oppose one another, high hydrogen ion concentration in acidic solution can prevent metal ions from adhering to the adsorbent. Adsorbent surface, however, becomes negatively charged at higher solution pH levels because of the deprotonation by hydroxyl ions. Two important parameters in the adsorption process are typically polarity and surface area of adsorbent materials. Due to its substantial surface area, which can reach as high as 1690 m² g⁻¹, CQDs have been employed extensively in adsorption studies. Electrostatic adhesion, chemical chelation, and physisorption between metal ions and adsorbent can be used to influence the metal ion adsorption process [70].

CQDs composited with zinc-aluminum layered double hydroxide have been used to adsorb cadmium while the adsorption kinetics have been examined. A large number of active adsorption sites were provided by the variety of functional groups on CQDs/ZnAl-LDH composite, which increased the adsorption capacity for cadmium. Cadmium had a maximum capacity of 12.60 mg/g on the CQDs/ZnAl-LDH combination at 20 minutes. Using the pseudo-second-order model, the CQDs/ZnAl-LDH composite showed strong correlation coefficient value (0.9998). The result supported hypothesis that majority of the adsorption process was heterogeneous by fitting well with intra-particle diffusion models and Freundlich model [70].

9.3. Future scope and challenges

One of the most important fields for humans has undergone a major change and is now carbon dots. However, there are still some unknown gaps and places. There has been much discussion on the source of fluorescence emission, but more study is required. The function and impact of carbon dot structures on their properties have not yet been described by scientists, but this constraint has not stopped them from conducting in-depth study for synthesis and applications, notably in the biological sciences. Despite the numerous uses of CQDs in biomedicine, it is still not understood how they affect the bloodstream, and more research is strongly advised.

Although quantum dots have been studied in bioimaging, the presence of heavy metals prevents them from being used in this field due to major health issues and environmental concerns. Additionally, the topic of biosensing applications is still a mystery because only a small number of research have shed light on the use of CQDs and GQDs in this area. Therefore, additional studies could provide answers to numerous problems and disclose new applications. It is simple to create CQDs from a variety of natural carbon sources, but these materials lack the homogeneity and purity necessary to create homogenous CQDs [71].

Another issue related to the carbonization of CQDs throughout various synthetic processes, such as pyrolysis and electrochemical, was the carbonaceous agglomeration. Additionally, surface characteristics that are important for solubility and particular applications may change as a result of synthetic processes or post-treatment. Furthermore, there were still a lot of issues with the conventional green techniques used to make GQDs. Strong acids or other organic solvents were typically needed, and there might be challenging post-processes. Therefore, there is a pressing need to create environmentally friendly methods that rely on natural resources that are renewable and are simple to separate [64].

10. Conclusions

Global concern is growing over the issue of inorganic and organic pollution in water supply. It is more crucial to get rid of these contaminants from the water system since they offer a bigger damage to ecosystems and living things. There have been a significant variety of techniques used to remove pollutants from wastewater, but adsorption and photocatalysis using nanotechnology are becoming more and more common. Adsorption and photocatalysis are examples of nanotechnology that hold great potential for overcoming the drawbacks of other traditional approaches. Due to their exceptional qualities and potential applications for removing organic and inorganic contaminants from wastewater. Nanomaterials made of carbon have gained a lot of interest. Utilization of carbon based nanomaterials and their derivatives as adsorbents and catalysts for removal of inorganic and organic contaminants from wastewater was highlighted in this review. In this review, just four different kinds of carbon-based nanomaterials are covered. In both laboratory scale and real world wastewater treatment, usage of these nanomaterials as adsorbent and catalyst have demonstrated astounding properties. Active sites on material's surface and the potent interactions between active adsorption sites and contaminants provide materials a greater capacity for adsorption. Increased efficiency of photocatalytic processes is attributable to greater light harvesting and decreased photo-induced electron and hole recombination. However, more modifications to these nanomaterials are required for a successful commercialization to enhance their properties, lower the cost-effectiveness and scale up manufacturing.

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