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Review Article

An Overview of Nanomaterials in Water Purification, Health Effects and Future Aspects

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Abstract:

The lack of pure water has become a major threat to humans today. Apart from the currently available purification methods, the world is focusing on cutting-edge technologies with promising results. As a rapidly developing field, nanotechnology is vital for many industries. Nanomaterials have emerged as a trending topic in environmental research, because of their high surface area, nano- and micro- interface characteristics and remediation potential. From the last few decades onwards, nanofiltration methods have taken high attention. Synthetic nanomaterials like carbon nanotubes and metal oxide nanoparticles are highly in use commercially, while clayand polysaccharides are naturally occurring nanostructures that are being used in water filtration for a long time. Under synthetic nanomaterials, carbon nanomaterials are advantageous in the treatment of wastewater due to their wide surface area and selective character for aromatics. A variety of metal, metal/nonmetal oxide nanoparticles, such as zeolite, silica, titanium dioxide, and silver nanoparticles, have also been incorporated into polymeric matrixes. Due to their non-toxicity, biodegradability, etc., natural nanoparticles have drawn a wide attention. This paper critically examines the nano filtration techniques now in use, their modifications, and their toxicity, particularly with regard to synthetic nanoparticles.

Keywords: Water purification, nanotechnology, nanomaterials

1.0 Introduction

The environment is continually in danger as a result of increased globalization and industrialization, and therefore, people are dealing with a wide range of problems[1]. Among them, access to clean water is a critical global issue resulting significant impact on public health such as chronic kidney diseases, water borne diseases like diarrhea and cholera. According to the United Nations (UN), 30% of the world's population lacks access to reliable and safe drinking water services, prompting the organization to include clean water and sanitation as goal number six on its list of sustainable development goals[2]. About 1.2 billion of people lack access to safe drinking water, while about 2.6 billion have little or no sanitation, and millions of people die annually from diseases transmitted via unpurified water[3].

Water can exist as natural water sources like surface water and ground water and industrial water sources like effluents from industry. Water can be contaminated by toxic metal ions, radionuclides, organic and inorganic solutes, bacteria and viruses[4]. In developing and industrialized nations, the most number of contaminants are reached the water due to human activities[3]. In this context, water-borne bacteria and enteric viruses become a major threat in getting diarrheal and parasitic infections in people who follow poor sanitation[3]. Heavy metals have higher density, and they exist naturally in the environment with very low concentrations. Heavy metal content is higher in industry effluents and contamination with water is a significant environmental and public health concern. Heavy metal ions must be removed from wastewater because of their environmental concerns, such as toxicity, and high inclination to agglomerate[5]. For instance, the Environmental Protection Agency (EPA) states that the maximum allowed concentration of hexavalent chromium (Cr^{6+}) and lead (Pb^{2+}) in drinking water is 0.05 mg/L. Pb^{2+} poses serious health risks to people, including harm to the brain and immunological systems. The adverse health effects of Cr^{6+} exposure include lung cancer, eardrum perforation, and skin and nasal irritation[6]. Cadmium and Arsenic are also highly toxic heavy metals and cause skin, lung, and kidney cancers; hence, levels in drinking water should be kept below 3 µg/L and 10 µg/L, respectively[7]. The development of appropriate and effective water purification technology is vital for ensuring human access to clean water.[8] Chlorination, filtration, and disinfection are the most used water purification techniques at the moment. However, due to poor maintenance of the treatment process, irregular supply of water, contamination and lack of chlorination, this has become an issue. In this context, nanotechnology can play a vital role in water purification[8].

In recent years, the scientific world has found the development of nanotechnology to be one of the most exciting subjects for interdisciplinary research. The study of atomic scale phenomena is known as nanotechnology or nanoparticles, which are molecular aggregates with sizes ranging from 1 to 100 nm[9]. The development of nanotechnology has created countless opportunities for water filtration[10]. The different nanostructured materials have been developed with properties including high aspect ratio, reactivity and controllable pore volume as well as electrostatic, hydrophilic, and hydrophobic interactions that are helpful in adsorption, catalysis, sensors, and optoelectronics[10]. In this regard, nanofiltration membranes (NF) are frequently used in water treatment to remove materials in size between 0.001 and 0.1 micrometers using a low-pressure membrane method[11]. Nanofiltration lies between reverse osmosis and ultrafiltration which is most commonly used for softening. In addition, it is regularly employed to remove microorganisms and micropollutants. These have been implemented effectively in enterprises, demonstrating their dependability. Since nanofiltration easily removes natural organic matter, it is also used in manufacturing units where surface water is treated. In comparison to reverse osmosis membranes, nanofiltration membranes are more effective in removing natural organic matter and colour[2].

This review critically presents the nanofiltration methods developed so far, the impact of these materials on an effective filtration system, and the limitations of these techniques. Furthermore, concerns about carbon nanotubes, synthetic nanoparticles, polysaccharide nanofiltration membranes, clay nanoparticles and modifications also have been investigated, along with health issues.

2.0 Synthetic nanomaterials in water purification

Synthetic nanoparticles are produced for a specific purpose and have a defined chemical composition and size distribution. Synthetic nanomaterials are grouped as carbonic, metal oxides, semiconductors and metals depending on their chemical and physical characteristics.

Among them, carbonic nanomaterials include fullerenes, carbon nanotubes and carbon black, while metal oxide nanoparticles include titanium dioxide (TiO_2), aluminum oxide (Al_2O_3), iron oxide (Fe_2O_3) or (Fe_3O_4), and zinc oxide (ZnO). Semiconductor nanoparticles include silicon (Si), indium phosphide (InP or InGaP), and cadmium-tellurite (CdTe). Additionally, the group of metallic nanomaterials includes the elements gold (Au), silver (Ag), iron (Fe), and cobalt (Co)[12] . They have various types of applications, particularly water purification.

2.1 *Carbon nanotubs (CNTs)*

The element carbon plays a significant role in nature. Due to its ability to exist in sp^1, sp^2 and sp^3 hybridization, it forms various crystalline and amorphous materials like graphite and diamond. Carbon nanotubes (CNTs) and graphene were discovered, followed by fullerenes[13]. Figure 1 shows the structure of a graphene sheet and a carbon nanotube. The remarkable physicochemical properties of CNTs have made them the subject of nanotechnology, particularly in water purification [9].

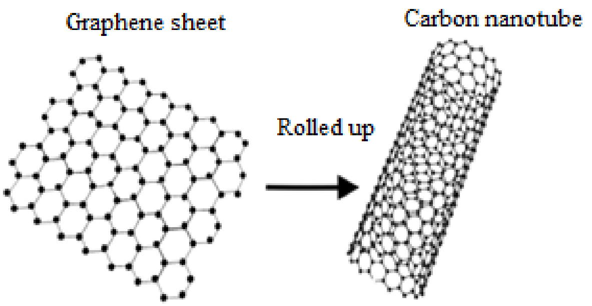

Fig 1. The structure of a graphene sheet and a carbon nanotube [13] Jose Varghese, R. *et al.* (2019) *Introduction to nanomaterials: Synthesis and applications*, *Nanomaterials for Solar Cell Applications*. Elsevier Inc. doi: 10.1016/B978-0-12-813337-8.00003-5.

CNTs are one-dimensional nanomaterials with a unique set of mechanical, electrical, and chemical characteristics[14]. Adsorption, photocatalysis, sensing and monitoring, disinfection, and desalination are some examples[9]. Carbon nanotubes seem to have a sorption capacity, allowing them to eradicate certain pollutants from wastewater[2]. The carbon backbone's bonding structure and the relative simplicity of chemical modification make CNTs and CNT composite materials effective adsorbents for pollutant sequestration from water[14]. For example, according to a study done by Bang et al. 2004, using the CNTs and other fullerenes, the equilibrium was attained for the adsorption of As (V) in 63 minutes and As (III) in 240 minutes[29]. Single-walled carbon nanotubes (SWCNTs) have a cylinder-like form and are made up of just one graphene shell. On the other hand, multi-walled carbon nanotubes(MWCNTs) are made up of several layers of graphene sheets[9,10] .

Over ten years of research have been devoted to the use of CNTs as nanomembrane filters for selective water transport, leading to the hypothesis that they can be utilized for water filtration[14]. The hydrophobic, smooth inner walls of the CNT give it a special ability to carry water[10]. Moreover, the reduced size and improved water permeability in CNTs have opened up extensive research opportunities in water purification as a replacement for polymeric membranes for desalination[10]. SWCNTs and MWCNTs both have been utilized for the direct desalination of water as well as for the indirect removal of problematic chemicals that impede the desalination processes. MWCNT with pore diameter of 7 nm and four to five orders of magnitude has shown quicker water flux with molecular simulations than the prediction by traditional fluid calculations[9,10]. Figure 2 shows how the desalination process occurs via CNT membranes[9].

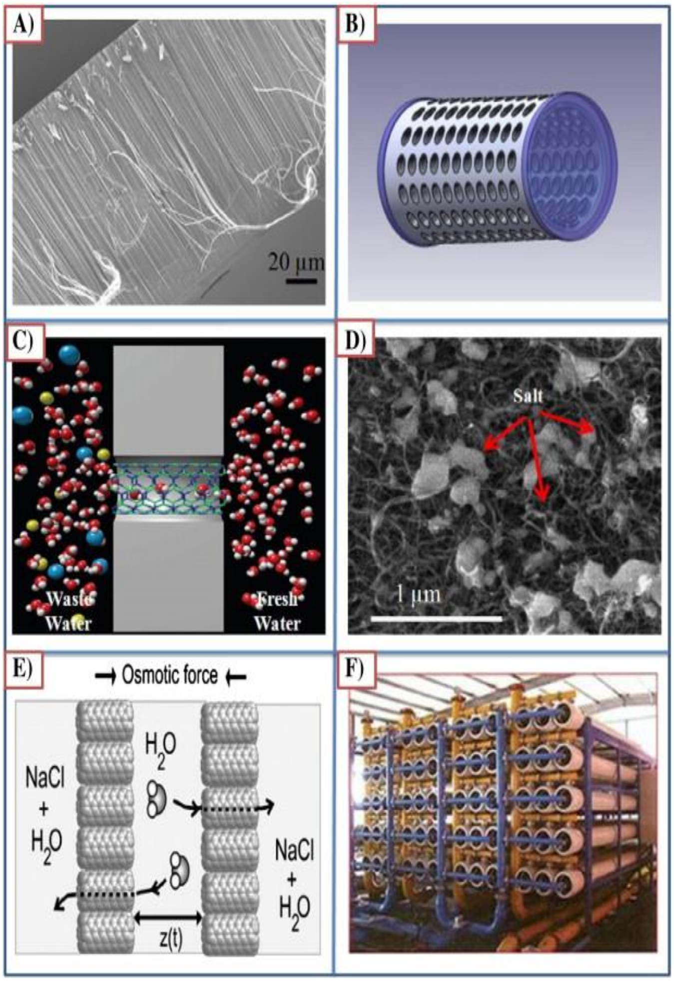

Fig 2. Structures of some CNT membranes (A) A cross-sectional scanning electron microscope (SEM) image of a pristine CNT membrane; (B) CNT based water filter with cylindrical geometry; (C) movement of water molecules through a CNT channel; (D) SEM image of scattered NaCl nanocrystals on CNT membrane surface; (E) movement of pure water molecules through CNT-membrane in osmotically imbalanced compartments, and (F) engineered CNT membranes in industrial set up (Das, R. *et al.* (2014)

The neutralization of bacteria and viruses or the exclusion of these species from water by nanofiltration is one of the promising uses of CNTs in water purification. An antifouling ability to prevent bacterial adhesion and biofilm formation is another desirable quality for modern water treatment materials. To achieve neutralization and antifouling water purification platforms, many CNT composite materials have been researched[14]. For example, CNT filters were successfully created, according to Srivastava *et al*[11]. These filtration membranes are made up of hollow cylinders with walls made of carbon nanotubes oriented radially. They demonstrated that the filters removed pathogens like *Escherichia coli* and *Staphylococcus aureus* from contaminated water effectively[11]. Aggregated CNTs deposited onto a porous polymer membrane can effectively filter bacteria from aqueous solutions, where the amount of CNT loading also affects the virus filtration capacity. Due to the nanoscale characteristics, CNTs can be used in size exclusion membranes, capable of blocking the transportation of certain microorganisms across the membrane[14].

CNTs' antibacterial mechanism is still not fully understood and several mechanisms have been postulated. One postulation explains that CNTs attach to the surface of microbial cells, disrupting transmembrane electron transfer and damaging the membrane and cell wall. The second mechanism presents that CNTs penetrate bacterial cells, damaging DNA and causing protein dysfunction, while another method explains that secondary products such as harmful reactive oxygen species are produced[16].

2.1.1 Modifications for CNTs for better efficiency

Since CNTs and activated carbons (AC) have a similar chemical structure, oxidative acid treatment with HNO_3 or H_2SO_4 is a frequent technique for adding or changing the surface functional groups, and therefore, it serves two main goals. The first goal is to shorten or cut the tubes and open the CNTs' ends. This can help to homogenize the CNT mixture and enhance the surface area of the CNTs, increasing the control over the physical properties. The introduction of oxidative functional groups (carboxylic acids, alcohols, and epoxides) along the margins of the CNTs, especially around the openings, is the second result of acid treatment. This allows the CNTs to be further chemically changed. Because of CNTs' nanoscale characteristics, this material offers a promising way to create size exclusion barriers that can prevent the passage of specific microorganisms over the membrane[14]. A porous polymer membrane with aggregated CNTs placed over it can efficiently filter out bacteria from aqueous solutions, and the capacity to filter out viruses depends on the amount of CNT loading[14].

2.2 Graphene based nanoparticles

Graphene is a two-dimensional nanomaterial composed of sheets with a single layer of carbon atoms[17]. It is present as an intriguing nanomaterial with certain advantages over AC and CNTs when it comes to the purification of water. Graphene is a desirable material to use for water purification due to the highly accessible surface area for contaminants to adsorb[14]. Much of the research on graphene for water filtration has been on nano-perforated graphene sheets as size-exclusion filtration membranes. Recently, more sophisticated alternatives to AC for the filtration of water have been investigated, including graphene adsorbents and antimicrobial compounds[14]. There are three ways to implement molecular sieving for membranes made of graphene, as explained by Han et al. For type I, the graphene sheet is pierced to create nanopores, and by varying the pore size, it is possible to sieve various molecules. Graphene sheets are laminated or stacked for type II. Type III uses graphene as a composite filler in conjunction with other matrix components[18]. The latter two techniques use the same filtration mechanism to separate various molecules by varying the graphene-based membrane's interlayer spacing. Graphene oxide (GO) is widely used to make type II and type

III composite materials because it has more hydrophilic groups available, which leads to better chemical properties[18]. Figure 3 shows the main three types of graphene-based membranes.

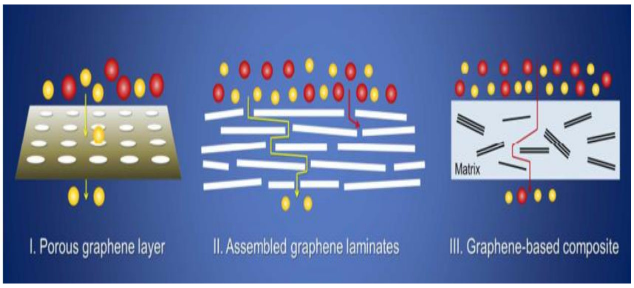

Fig 3. Main types of graphene-based membranes: type I. single porous graphene layers; type II. assembled graphene laminates; type III. graphene-based composites. [18]. Han, Z. yang *et al.* (2021) 'A review of performance improvement strategies for graphene oxide-based and graphene-based membranes in water treatment', *Journal of Materials Science*, 56(16), pp. 9545–9574. doi: 10.1007/s10853-021-05873-7.

Graphene is often transformed into GO in water purification applications by an acid treatment procedure, such as the Hummers or enhanced Hummers procedures[19]. The graphene sheet is exposed to a significant amount of hydrophilic oxygen-containing groups, such as hydroxyls and epoxides, as a result of the conversion to GO. Membranes with high water permeability and flux can be made using the improved hydrophilicity, which considerably increase water flow through GO materials[14]. However, the high surface energy of GO sheets, which can produce aggregation through van der Waals interactions have limited the use of GO as an adsorbent[20]. In order to improve the separation effectiveness of GO-based adsorbents, modified GO has been used in aqueous media including three-dimensional GO sponges, a magnetic GO/polyvinyl alcohol composite gel, and magnetic GO-modified poly acrylic acid with reported Methylene blue (MB) dye adsorption capacities[19]. GO is utilized as a host for creating various nanocomposites that may accommodate a variety of applications because of its huge surface area. However, the high dispersibility of GO causes many difficulties in removing from aqueous solution even after the adsorption of contaminants. The best way to overcome the aforementioned issue is to magnetize GO, which enables easy separation of magnetized GO using an external magnetic field. Additionally, magnetic materials have a strong adsorption capacity toward pollutants in addition to the benefit of easy and quick separation from aqueous solution. Therefore, finding an appropriate magnetic adsorbent material that will dominate the technique's selectivity is a crucial element for effective separation. In order to remove organic dyes and inorganic hazardous metals from water, many researchers have created metal oxide nanocomposites based on GO, such as Fe_3O_4/GO, decreased magnetic GO, Mn_3O_4/GO, and other hybrid nanocomposites. After wastewater treatment processes have reported that nickel ferrite GO composite is a better reaction media than iron ferrites, because it has higher catalytic and electron transfer efficiency through the Ni^{2+} in the nickel ferrite[21]. These magnetic nanocomposites can have a wide range of applications, because they are easily recovered from the aquatic solutions. The removal of heavy metals has found extensive use for nickel ferrite-based nanocomposites due to their excellent catalytic and charge transfer efficiencies. The astounding removal effectiveness of magnetic nanoparticles/graphene or GO composites for contaminants like chromium, copper, cadmium, lead, cobalt, and organic dyes has also been proven by a group of researchers[21].

2.3 Metal oxide nanoparticles

Rare metal oxides possess distinctive optical, electrical, magnetic and catalytic properties, which made them available for numerous practical uses, including temperature sensors, solar energy conversion, gas sensors, photocatalysis, and electrochemistry, most importantly in water purification[22, 23]. As a result, various metal and metal oxide nanoparticles, such as zeolite, TiO_2, Ag nanoparticles, and MnO_2, have been incorporated into polymeric matrixes for the preparation of nanofiltration membranes. Those have improved the membranes' flux and rejection, mechanical and thermal stability, and anti-fouling and anti-bacterial properties[2]. Reducing toxic high valence heavy metal ions into low valence ions is referred as photocatalytic removal, since the low valence metal ions are generally less toxic than high valence metal ions[22].

Another important factor involves in metal oxide nanoparticles in water purification is antimicrobial disinfection[24]. The surface of both Gram-positive and Gram-negative bacteria are negatively charged. Electrostatic interactions cause positively charged nanoparticles to be drawn to the surface of negatively charged bacterial cell walls. Positively charged metal-based nanoparticles form a solid bond with membranes, disrupting cell walls while increasing permeability[25]. Additionally, nanoparticles can release metal ions into the extracellular environment, which enter the cells and interfere with biological processes. Reactive oxygen species (ROS) can be produced inside the cell by metal ions or nanoparticles[25]. Since glutathione oxidises from the oxidative stress, bacteria's antioxidant defence system against ROS is suppressed. When the metal ions are free to interact with cellular components like proteins, membranes, and DNA, cell functions are disrupted[25].

In particular, TiO_2 is the best semiconductor photocatalyst due to its high stability, low production cost, and safety for both the environment and people[23]. Titanium materials with high surface area and pores have considerable promise for enhancing photocatalytic activity. Furthermore, mesoporous titanium with a crystalline structure and even mesoporous doped TiO_2 photocatalysts were created and demonstrated effective photocatalytic activity, and those can be used in water purification[26].

Water contains arsenic as a result of both anthropogenic and natural activity. Arsenic in water often exists in two valence states: oxidized (+V oxidation state, As (V)) and reduced (+III oxidation state, As (III)). As (V) is a major species in natural water sources and is less hazardous than As (III)[27]. In investigations performed by Peng *et al.*, 2005 equilibrium adsorption of As (III) and As (V) by using nanocrystalline CeO_2 combined with CNTs, the adsorption was occurred within 4 hours, and the adsorption followed pseudo-second-order kinetics[28]. In another study the elimination of As (III) using a crystalline hydrous titanium dioxide was conducted and discovered that within the first 30 minutes of contact time, 70% of As (III) adsorption will be completed[30].This clearly indicates the efficient adorption of As when using the TiO_2 nanoparticles. Figure 4 shows the SEM images of metal nanoparticles and nanocomposites.

Due to their large specific surface area and high activity in most catalytic processes, recent studies focus on creating and utilizing GO-modified photocatalysts**.** Early research focused on the various synthetic methods for producing graphene and offered the synthesis and physiochemical characterization of TiO_2-GO and titanium oxide nanoparticle-reduced graphene oxide (TiO_2-RGO) composites[31].

Magnetic nanoparticles are a class of nanoparticles that can be manipulated using magnetic fields. Unique physical and chemical characteristics that are not present in their bulk counterparts can be found in magnetic nanoparticles[32]. Iron and iron oxide magnetic nanoparticles (MNP) with chemically modified surfaces have gained interest recently as potential solutions for a variety of biotechnological and environmental applications, particularly in water purification[33]. Iron-based nanoparticles have been used extensively in recent years to remove arsenic from soils and water environments[27]. In order to remove pollutants from aqueous solutions, such as arsenic and fluoride, nano-agglomerates of mixed oxides, such as iron-cerium, iron-manganese, iron-zirconium, iron-titanium, iron-chromium, cerium-manganese, etc., have been successfully synthesized. Iron can be reduced by metals like zinc and tin[34]. These metals undergo oxidation throughout the decontamination process. Iron has also been mixed with other metals to get comparable outcomes. Trichloroethane and trichloroethene can be broken down by iron-nickel and iron-copper bimetallic particles, respectively[35]. As (III) to As (V) undergoes photo-oxidation within minutes, as demonstrated by Bissen et al.[36]. In their research work, As (III) was oxidized by UV light in the absence of TiO_2, and no reverse conversion of As (V) to As (III) was seen. However, the reaction was far too slow to be practical for water treatment[36].

Several researches indicate the utilization of composite structures that resemble MnO_2 carbon fibres as sorbents for water purification applications[37]. According to a study by Li *et al*. 2018, polyacrylonitrile (PAN) and polypyrrole were electro spun into a hierarchical nanofiber mat. Then it was mixed with $KMnO_4$ solution to deposit MnO_2 and utilized as an adsorbent to remove Pb^{2+} from aqueous solution[38].

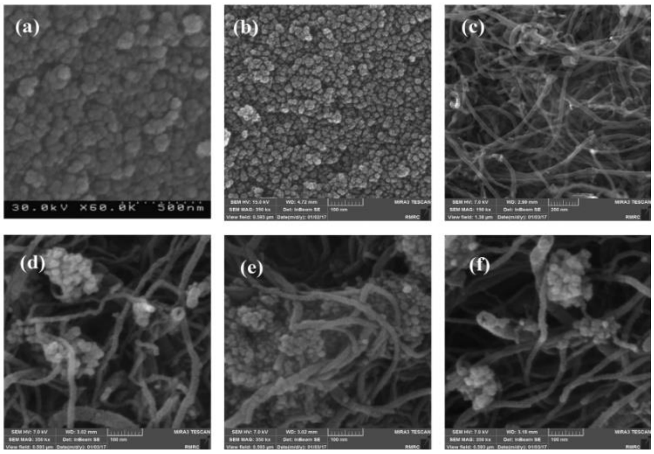

Fig 4. FESEM images of CdS nanoparticles (a), TiO2 nanoparticles (b), pure MWCNT (c) CdS/MWCNT nanocomposites (d) TiO2/MWCNT nanocomposites (e) MWCNT/CdS/TiO2 nanocomposites (f).[26] Askari, M. B. *et al.* (2018) 'Comparison of optical properties and photocatalytic behavior of TiO2/MWCNT, CdS/MWCNT and TiO2/CdS/MWCNT nanocomposites', *Optik*, 157, pp. 230–239. doi: 10.1016/j.ijleo.2017.11.080

Furthermore, it has been demonstrated that polydopamine-assisted MnO_2 -loaded PAN fibres have a greater adsorption ability for Pb^{2+} ion removal applications. Li *et al*. 2018 demonstrated the formation of heteroatom-rich carbon fibres using hierarchically organized PAN/MnO_2/graphene fibres to achieve remarkably high power and energy densities for energy storage applications[38].

3.0 Natural nanoparticles in water purification

Natural polymers have been used for a long time for water filtration. Charcoal has been used historically with positive outcomes. As an adsorbent, activated carbon is frequently used to remove heavy metal contamination in water. Since activated carbon lacks specific selectivity for metal ions, its application is typically constrained by its adsorption capacity and utilization in powder form. Another popular class of natural polymers is polysaccharides.

3.1 Polysaccharide nanofibrous membranes

Polysaccharides are one of the most prominent classes of biomaterials on Earth. Cellulose and chitin are examples of polysaccharides and have favourable environmental effects [39]. Polysaccharide nanofibers have received a great deal of attention, because of their abundance in nature, simplicity in functionalization, biodegradability, sustainability and structural variety[40]. Cellulose fibres exhibit different structural hierarchy. They are made up of nanofiber assemblies with lengths of several micrometers and diameters ranging from 2 to 20 nm. These single cellulose fibers, which are about a nanometer in diameter, are also known as nanocrystals, whiskers, nanowhiskers, micro fibrillated cellulose, or microfibril aggregates[39].

3.1.1 Nano cellulose

Nanocellulose (NC) is an environmentally friendly substance that exists as nanocrystals and nanoscale fibrils[41]. It is made up of D-Glucopyranose repeating units joined by 1-4 glycoside links. It is typically produced by microorganisms (algae, fungi, bacteria), aquatic animals, and cell-free enzyme systems. It is also typically removed from natural cellulose materials such as plant cell walls and cotton linters using mechanical, chemical, or enzymatic treatments[41]. Nano cellulose has recently been acknowledged as one of the most innovative materials with applications in a variety of industries[41]. Researchers consider NCs, because of their desirable physicochemical characteristics, such as intrinsic abundance, strength, stiffness, renewability, biodegradability, biocompatibility, and sustainability[41]. Moreover, nanofibers with high purity have been extracted from cellulose materials using a variety of techniques. These techniques include chemical (acid hydrolysis), biological (enzyme-assisted hydrolysis), and mechanical (grinding, and high-pressure homogenizing) treatments[39].

3.1.2 Preparation of nanofibers

Ultra-sonication and chemical treatments have been used to separate chemically pure cellulose nanofibers from one another[42] . For example, a study has used an ice bath for ultrasonic therapy while keeping the output power of the ultrasound at 400 - 1200 W to examine the impact of ultrasonic intensity on nanofibrillation[42].

Bacterial cellulose (BC) is a particularly appealing biopolymer, because it is simple to produce and purify. Also BC lacks collateral biogenic components like lignin, hemicelluloses, and pectin. To date, BC has undergone significant analysis and characterization, since its structure was first described more than a century ago. *Acetobacter xylinum* has been utilized to make bacterial cellulose from a variety of substrates, including glucose from corn syrup[42]. More recently, rice bark supplemented with glucose has been used as a substrate to make cellulose nanospheres[42]. Bacterial cellulose has a high level of inter- and intra-hydrogen bonds between neighbouring chains of glucan, which contributes to its high crystallinity. These connections between the glucan molecules result in a regular crystalline arrangement, which gives cellulose its distinctive diffraction pattern, swelling, and reactivity[42].

New biomaterials often display combinations of properties that a single polymer could not achieve. As a result, the combination of two or more polymers has gained popularity[43]. For example, cellulose mixed with chitosan can be identified. The significant reinforcing impact of the nano-sized cellulose has been reported to give nanowhiskers (CNWs) or nanofibrils (CNFs) improved mechanical and chemical characteristics[43]. Chitosan (CS), also known as poly-(14)-2-amino-2-deoxy-d-glucose, is a natural polysaccharide material with exceptional performance[44]. In addition, the Chitin, the second-mostprevalent natural polymer in the world, is deacetylate to produce it. Chitosan has been widely used in a variety of industries, including the food, cosmetics, biomedical, and pharmaceutical industries. However, an essential stage in the treatment of water is the effective separation of the adsorbents from the water before the sorbates and adsorbents are recycled. However, reducing the adsorbent to a very small size to increase surface area and adsorption efficacy makes adsorbent separation extremely difficult[44]. Therefore, improving the ability to separate the small-sized adsorbents is a very intriguing project. Magnetic separation technologies (MST) also have recently attracted the research interest[44]. Regardless of the size of the water, magnetic substances can be effectively removed from it with the use of magnetic force. However, the majority of materials, including chitosan, lack magnetism which limits the usage on water filtration. Thus, the non-magnetic materials should somehow be linked with a magnetic component, to obtain the MST function[44].

3.2 Clay nanoparticles used in water purification.

Clay is a fine material produced from soil or natural rocks that contains many minerals together with trace amounts of metal oxides and organic content[44]. Chemically, clay is made up of tiny crystallites of alumino-silicates in a variety of ratios, with alkali and alkaline earth elements replacing iron and magnesium[44]. Clays are divided into various classes according to their chemical makeup and particle morphology, including smectite, chlorite, kaolinite, iolite, and halloysite. It has been observed that a variety of clays, including bentonite, kaolinite, illite, sepiolite, montmorillonite, and pyrophyllite, are effective at removing contaminants from water[45]. Nano clays have been researched and developed for a variety of applications due to their widespread availability, comparatively low cost, and relatively little environmental impact[46]. Adsorption is the main mechanism of nano clays in removing contaminants from water. Due to their simple processing, efficient cation exchange, huge surface area, and comparatively low cost and toxicity, polymer/nano clay composites are able to deliver a high adsorption capacity for water treatmen[46].

Nano clays are layered mineral silicate nanoparticles having layered structural units that, when stacked, can create intricate clay crystallite. The sheets that form an individual layer unit are octahedral and/or tetrahedral. Aluminum or magnesium are arranged in six-fold coordination with hydroxyl and oxygen from a tetrahedral sheet to form octahedral sheets. Tetrahedral sheets are made up of silicon-oxygen tetrahedra joined to nearby tetrahedra, sharing three corners while each tetrahedron sheet's fourth corner is covalently coupled to an adjacent octahedral sheet. Figure 5 shows the structural geometry of common nano clay minerals[46].

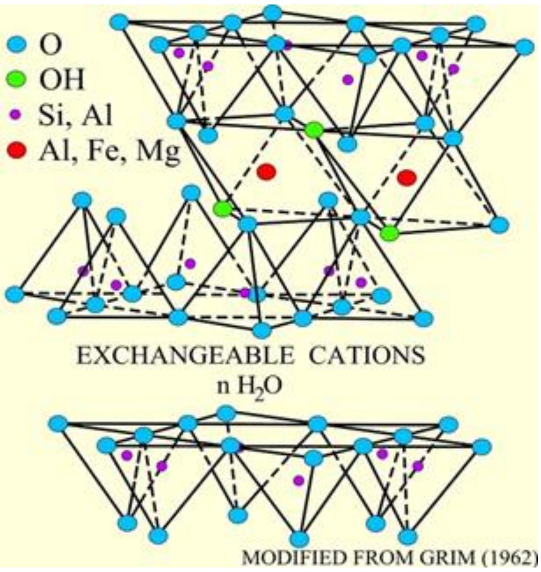

Fig 5. Structural geometry of common clay minerals. Awasthi, A., Jadhao, P. and Kumari, K. (2019) 'Clay nano-adsorbent: structures, applications and mechanism for water treatment', *SN Applied Sciences*, 1(9), pp. 1–21. doi: 10.1007/s42452-019-0858-9.

The arrangement of these sheets affect several defining and distinctive characteristics of nano clays. Over 30 different types of nano clays are used in various applications based on their mineralogical composition and characteristics[46].
Kaolinite group clay minerals, such as dickite, nacrite, kaolinite, and halloysite, are formed from breakdown of feldspar[47]. The dickite and nacrite clays were formed hydrothermally from a kaolinite combination. The kaolinite group is mostly composed of alumina (octahedrons) and silica (tetrahedrons)[47]. An investigation by Omar et al. 2007, on adsorption capability of kaolinite for the removal of lead ions from aqueous solutions showed interesting results. For instance, as the temperature increases, the adsorption potential was found to be proportional. The measured adsorption kinetic data at different temperatures proved that surface adsorption together with intra-particle diffusion control is responsible for the rate of adsorption[47]. Modified kaolinite has also been proven to absorb certain heavy metals. For instance, Unuabonah, Adebowale, and Ofomaja used a two-batch adsorption method to enhance the number of adsorption sites on kaolinite treated with sodium polyphosphate. Increased adsorption capability is also demonstrated for the removal of lead, zinc, and cadmium from aqueous solutions using kaolinite clay treated with sodium polyphosphate[48].

The largest and most important class of phyllosilicate clay minerals is smectite. Smectite clay and montmorillonite (MMT) are now used interchangeably. Minerals in the kaolinite group are considerably different chemically from smectite. Smectite clay mineral has equidimensional and elongated symmetry. Iron montmorillonite (nontronite), magnesium montmorillonite (saponite), and lithium montmorillonite (hectorite) are all present in the elongate smectite structure. The smectite group's unique characteristic is the substitution of octahedral and tetrahedral sheets. Although it has been shown that organo-MMT clays may remove copper (II) as a function of pH, organo-clays in general have not attracted much attention as heavy metal adsorbents due to their competition with organic cations for adsorption sites. Also, these clay minerals are more hydro-plastic, and using such compositions compromises the mechanical resilience of membrane filtering systems[47].

The main component of bentonite is a mineral called montmorillonite, which is composed of aluminum phyllosilicate. The Bentonite clay is created by alternating glassy substances. In addition to quartz, feldspar, and gypsum, bentonite clay minerals also contain kaolin, mica, attapulgite, and illite. $Al_2H_2Na_2O_{13}Si_4$ is the common molecular formula for bentonite clay. Sodium and calcium bentonite are the two main varieties of bentonite clay. Calcium bentonite clay is a non-swelling type that contains Ca^{2+} as an exchangeable cation with the presence of a double layer of water, and sodium bentonite clay has one Na^+ ion as an exchangeable ion with a single water layer[46].

4.0 Health effects in nano filtration methods

The problem of nanoparticle toxicity is brought to light by our limited understanding of nanoparticle activity and environmental fate[1]. Although the realm of nanotechnology is still in its infancy, the average individual is unaware of the dangers posed by MNPs, which creates significant health hazards[24]. Two difficulties with nanotechnology are the toxicity of nanoparticles and the possibility of exposure. A biological or chemical impact on the environment or humans is the first significant concern. Leakage, spillage, circulation, and concentration of nanoparticles can harm people and the environment[1]. Many organizations, including the Environment Protection Agency (EPA), the Organization for Economic Co-operation and Development (OECD), the European Union (EU), and the Center for Disease Control and Prevention (CDC), have been monitoring on the effects of nanomaterials on environmental safety[49]. To begin with, CNTs and other engineered nanomaterials (ENMs) can only have clinically significant impacts if they can enter the body or a biological system in a sufficient quantity. In addition, they must be able to affect biological processes directly or indirectly, as well as biochemical and cell biology activities. According to recent studies, CNTs can enter the body through the skin, respiratory system, or digestive system. Once entered the body, they can then accumulate in various organs and potentially cause various harmful biological effects[50]. Due to its significant tensile strength, thermal conductivity, electrical characteristics, and wide range of commercial applications, CNT is very marketable. The fact that CNTs have traits with asbestos fibers that cause disease such as a high aspect ratio, a big surface area, and a lack of solubility raises serious safety concerns. Multiwalled carbon nanotubes (MWCNTs) have been the subject of toxicology investigations in rats and mice that demonstrated adverse effects other than pulmonary inflammation[51]. Pulskamp et al. 2007, research showed that metal catalyst impurities contributed to the cytotoxic nature of unpurified CNTs. They exposed rat macrophages (NR8383) and human A549 lung cells to SWCNTs and MWCNTs. The dose- and time-dependent increase of intracellular reactive oxygen species was detected along with the decrease in the mitochondrial membrane potential of both cell types[52].

Reactive oxygen species (ROS) and chemical reactivity are related to nanoparticle toxicity. Carbon nanotubes and metal oxides can both produce ROS. ROS can lead to inflammation, oxidative stress, and functional problems with DNA, membranes, and proteins. Enzymes and proteins within the body may malfunction as a result of nanoparticle adhesion. Changing a CNT's shape, size, or content can change how harmful it is at the nanoscale. Numerous research has shown that larger diameters and longer lengths have more toxicity than smaller ones[49]. Nanometal oxide particles (NMOs), such as Fe_2O_3, Al_2O_3, MnO_2, MgO, TiO_2, and CeO_2 NPs, have a high surface area and a specific preference for adsorbing hazardous heavy metals from liquid environments. The production of novel innovations to coordinate MNPs and evaluate their efficacy for evacuation of harmful metals and pollutants under various trialing situations are hotly disputed topic today. Moreover, Al_2O_3 and ZrO_2 have the capacity to produce ROS. These can cause apoptosis, and prevent the growth of vital bacteria[24]. When iron NPs interact, they have the ability to permeate the skin, create local discomfort, and significantly affect the central nervous system[24]. TiO_2 NPs from applied sources may introduce potential risks into aquatic and terrestrial water due to their toxicity, raising severe concerns about their use in water filtration, because it poses a significant environmental risk[24]. Additionally, they affect the nervous system and cause ROS, cell death, mitochondrial attack, and cell destruction[24].

Comparing polysaccharide nanofibers to carbon or metal nanofibers, they offer superior environmental characteristics[41]. Although the products containing natural nanoparticles are not toxic the human involvement in extracting, producing, and processing those may bring adverse health effects to the society[53]. For example, in clay nanoparticles, the effects of platelet toxicity (Bentone MA, ME-100, Cloisite Na+, Nanomer PGV, and Delite LVF) on the human lung were studied by a team of researchers. They demonstrated that the impact of toxicity on the variation in the dose level and the time-dependent of both types of clay nanoparticles, and they employed automated cells for the first time in real-time impedance imaging compositions processing those may bring adverse health effects to the society[53].

5.0 Current hurdles and future aspects

When considering the nanofiltration methods that are discussed in the review, are currently under some hurdles that the future world must take into consideration.

When it comes to the CNTs, there are some main huldles that have been pointed out. The first difficulty is the challenging procedures for producing CNTs with homogeneous pore size and dispersion. The existing CVD approach frequently fails to produce uniformly distributed, size-controlled pores. Another major issue is the shrinkage of the CNT membranes' pore size and diameter. Only single-walled carbon nanotubes (SWCNTs) and double-walled carbon nanotubes (DWCNTs) produced on epoxy or mixed composite matrices can result in smaller pores with higher desalination capabilities. The addition of desired functional groups at CNT tips is another challenge[10]. These things should be taken into consideration in the future.

When it comes to the metal oxide nanoparticles, the green synthesis of metal oxides has taken a significant attraction. The biogenic manufacturing of nanomaterials utilizing plants and microorganisms can be done in several environmentally benign and biological ways. When creating sustainable nanostructures like nanoflowers, nanowires, nanorods, nanotubes, and nanoparticles, capping/stabilizing and reducing agents such as flavonoids, terpenoids, proteins, vitamins, glycosides, carbohydrates, polymers, alkaloids, and various antioxidants are present in such sources[54]. There are many environmental applications for the production of nanoparticles using living creatures like plants and microbes, including water filtration[54]. The green synthesis of nanoparticles will play a significant role in future.

The current world is focusing mainly on natural nanoparticles because of their non-toxicity, and environmental friendliness. When considering clay nanoparticles, because of changes to the surface geometry and an increase in surface area, they are suitable materials for a variety of applications. More experimental research in the field of polymer clay nanocomposites for water treatment is required to obtain distinct results. For intended uses, composites for water decontamination are necessary.

Additionally, the use of nanotechnology can boost the capacity of water filters since these materials have a high surface-to-volume ratio and a large number of active sites for the removal of contaminants. Therefore, more study is needed to establish an appropriate understanding of the interaction between nanocomposites' structure, properties, and formulation for improving the performance of water systems[45].

6.0 Conclusion

Water contamination has become a major concern that is being worsened over time. Among various methods currently available, nanotechnology is a modern and promising way of water remediation. Since nanoparticles are composed of various important characteristics like high adsorption, antimicrobial activities, and photocatalytic activities, they have gained a high attraction in water purification. Nanoparticles can be identified as either synthetic or natural. CNTs which are coming under synthetic nanoparticles are highly used for the desalination process. As the majority of water can be found as seawater this is a

very efficient process. Further, the researches have showed positive results that CNTs have the ability to remove bacteria like *Escherichia coli* from the contaminated water. Metal oxide nanoparticles and graphene oxide nanoparticles both have high adsorption capacity which allows them to capture contaminants from water. In addition, metal oxide nanoparticles like ZnO, and TiO_2 possess high photocatalytic activity which mainly allows for the removal of toxic heavy metals. According to past researches TiO_2 has shown promising results when removing As from contaminated water. However the major factor that need to concern when using nanoparticles is their toxicity which can affect both flora and fauna species.
Long-term exposure to these substances can lead to various chronic diseases that are even not totally understood yet. Therefore, natural nanomaterials like cellulose, chitin and clay nanoparticles have taken a significant attraction. Nanocellulose is more popular, because of high abundance and low toxicity. Even bacterial cellulose and chitin have shown promising results in water purification. Past researches have indicated that clay nanomaterials are capable of removing toxic metals like Pb, Zn, Cd from water. To improve the efficiency of water purification, the scientists are focusing on combination of these polymers.

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