Recent Developments in Nanomaterials Based Adsorbents for Water Purification Techniques

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Abstract: Currently, most advanced technologies employ nanomaterials due to the modern tailor-made properties these materials exhibit compared to their bulk counterparts. Nanomaterials have attracted researchers around the globe in the last few decades due to their unusual properties due to the presence of a greater number of carriers at the surface, which affects the chemical and physical properties of these materials. Ensuring pure drinking water for domestic purposes is the biggest challenge in current times. Industrialization is increasing with time due to human needs. The extensive use of fertilizers to enhance agricultural productivity has hazardous effects on the ecosystem. Water pollution will significantly impact living beings on the land and aquatic beings, followed by terrestrial, aerial flora, and fauna. In a world full of technologies, there are many methods to purify water (water filters, RO purifiers, etc.). Still, nanotechnology plays a vital part in purifying water on a large scale. Nanotechnology methods came up with new materials and analytical techniques that can treat the by-products that are toxic to the environment. Heterogeneous photocatalysis used with metal oxide nanostructures causes no harm to the ecosystem. Nanomembranes and Nanostructures will play an active role by acting as a trap for many Nano pollutants. This review presents nano cellulose, nanocarbon tubes, and nanomembranes used in water purification and analytical techniques by addressing the current economic water purification techniques.

Keywords: nanoparticles; ion-exchange techniques; water softening; purification and separation of chemicals.

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1. Introduction

The nanoparticles with one billionth (10⁻⁹) of meter particle size significantly impact the growth of present-day technologies in the 21st century [1]. The surface characteristics of these materials play a significant role in designing technologies in various fields, which has driven the interest of research teams in nanotechnology.

Most of the nanomaterials can be classified as colloids. The nanoparticles have the attractive property because of the van der Waals forces, making them behave as a colloid. These colloids are formed by steric stabilization by the absorption of the surfactants and polymers.
The stabilization can be done with coating on the surfaces [2]. It will significantly reduce water pollution with the new nanostructure and materials because of its surface property. It is a multidimensional and complex problem that interested most researchers in developing different materials at various water purification stages shown in Fig. 1. New methods in water purification are essential for the modern world to address current issues.

Figure 1. Drinking water treatment scheme for treatment plant [DWTP] [3]. Reprinted (adapted) with permission from ACS Environmental science & technology; 10.1021/es800768h. Copyright (2008) American Chemical Society.

The primary source of waste generated water pollutants by hospitals, industries, agriculture, and household activities contains non-metabolized and metabolized particles. Polluted water contains these chemicals, medicines, detergents, and additives, which considerably impact human health, especially children and aged people. According to WHO, millions of people have no supply of pure drinking water [4]. The drinking water cost has grown significantly over the past few decades because of climate changes, increasing energy costs, population growth, and environmental factors. Traditional water treatment cannot remove the contaminants from water, which affects water quality [5]. The contamination can be surface or bulk ions, which can penetrate aqua filters.

The challenges bring focus on looking for alternative methods and pollution remediation methods [6]. Keeping this issue in mind, various DWTPs are proposed and operate experimentally at different field levels. The primary techniques are screening, filtering, coagulating, centrifugation, sedimenting, separation, and flocculation. The secondary methods are anaerobic and aerobic techniques. The tertiary methods are crystallization, distillation, extraction of solvents, evaporating, precipitating, oxidation, exchange of ions, nanofiltration, reverse osmosis, ultrafiltration, adsorption, microfiltration, and electrolysis [7]. The demand for cost-effective pure and potable drinking water is gaining worldwide attention using sustainable methods.

The expected population explosion of humankind creates much pressure on the supply of pure drinking water with a present threshold of 1700 m³/person-year. Heavy metals in the water are one of the serious issues these days. A study has been carried out in China, which has the fastest growth in the economy, has only 40% of the groundwater, which is usable, and 28% of the improper to be used for industrial purposes [8]. Nanomaterials have gained importance in water purification as they can be used as membranes by forming a solid matrix. These membranes can exhibit improvement in the properties of chemical separation and mechano-thermal stability with the proper selection of nanomaterials. This review will discuss the emerging technologies of Nanotechnology-based materials and their analytical applications intended for water purification.
1.1. Technologies for water purification.

The traditional water purification methods [Fig 1.2] are distillation, chemical methods, coagulation and flocculation, biological treatment, treated with UV, RO, ultrafiltration, nanofiltration, microfiltration, and carbon nanofiber methods. However, these traditional technologies will purify the water to the extent that it cannot be potable for drinking purposes. The new technology which has emerged by using the concepts of Nanotechnology can provide a solution to obtain potable water. Nanotechnology is used in absorbing nano metals and non-metal oxides, effective photocatalysis, membranes for filtering and hindering microbial growth, and disinfection.

![Figure 1.2. Water purification process.](image)

2. Nanomaterials for Water Purification

2.1. Area specific effectiveness

The nanomaterial's effectiveness for efficiently removing the water's impurity is highlighted in the Table. 1.

| Nanomaterial | Effective in removing/ treating |
|--------------|---------------------------------|
| Ag/TiO₂ nano filter membrane [9] | Bacteria |
| Alumoxane derived Alumina membrane [10] | dye |
| Alumina membranes derived from polystyrene sulfonate [11] | Cations with divalent nature |
| Amino acid homopolymers derived silica membranes [12] | Metals |
| Polymeric or alumina membranes with Au nanoparticles [13] | 4- Nitrophenol |
| Titanium oxide filters [14] | PAHs |
| TiO₂/ Al₂O₃ composite membranes [15] | Direct black 168 dye |
| TiO₂ nanophotocatalytic nano membrane [16] | Methyl orange, azo dye |
| Silicon carbon filters [17] | Trihalogenmethanes, PHAs |
| Nanocrystalline zeolites [18] | Tolerance, nitrogen dioxide |
| Synthetic zeolite [19] | Humic acid |
| Graphitized CNT [20] | 1,2 Dichlorobenzene |
| CoO₂–CNTs [21] | Metal ions |
| CNT [22] | p- Nitro-phenol |
| Polyethyleneimine with Carbon NPs [23] | Metals |
| CNT hydride [24] | arsenate |
| CNT sheets [25] | Metal ions |
| CNT/Fe [26] | Toluene, Benzene, dimethyl |
| MWCNTs and SWCNTs [27] | Roxarsone, Trihalomethanes |
| Mesoporous aluminosilicate spheres with nanosized Fe₃O₄ [28] | mercury |
3. Nanomaterials for water purification

3.1. Zeolite-based nanomaterials.

These naturally occurring materials can also be prepared artificially on a large scale or at a laboratory level. More than 40 zeolites are naturally available, among which clinoptilolite is the most accessible. These are three-dimensional structures with a -ve charge produced with Si⁴⁺ structure replaced with Al³⁺ [31-34]. Generally, they contain silicon, aluminum, and oxygen in their formation of structures. The zeolites are synthesized with coal fly ash or silicon-aluminum solutions and used for adsorbents in column filters. Some of the zeolites are inexpensively synthesized; among them, NaP1 is most extensively used, with a chemical formula of Na₆Al₆Si₁₀O₃₂, 12H₂O, and Na[I] ions. This zeolite is mainly for the heavy metals present in the waste of acid mines. Zeolite-coated ceramic membranes have gained importance for their filtration sensitivity to a range of ultra-filtration by having solute particles of the size, which can be filtered by NF or even RO membranes [35-40]. The containment will be a function of ratio, temperature, types of ions, and water. The familiar zeolites are inverted to sodalite [SOD], [MFI] - class, and the Linde type A [LTA]. Fig 2 presents the fabrication process and the structure of ZIF-8 with CNTs [41-45].

![Fabrication Process and Structure](image)

**Figure 2** (a) fabrication, (b) SEM, (c) HRTEM, (d) photo (e) XRD (f) different magnified SEM, (g) and (h) EDX of ZIF and CNTs hybrid framework [41]. Reprinted (adapted) with permission from ACS Sustainable Chemistry & Engineering; 10.1021/acssuschemeng.7b02376. Copyright (2017) American Chemical Society.

3.2. Inorganic-organic TFN [Thin Film Nano] membranes.

These membranes are mainly known for their enhanced mechanical, chemical, thermal stability, permeability, and permittivity properties. To make use of the properties exhibited by nanomaterials, the nanoparticles are introduced into a macroscopic material. During the
processing, nanophases are dispersed across the material. This decreases the mass fraction of the NPs [46].

Recent research is focused on incorporating Nanomaterials into microfiltration as well as ultrafiltration membranes. It improves permeability, decreases porosity to capture the Nanosized particles, fouling, pollutant degradation targeting, and enhances thermal and mechanical stabilities. Increasing water permeability did not have a direct effect on the decrease of TDS [47].

3.3. Carbon nano tubes (CNT).

Carbon nanotubes (CNT) are the most popular type of nanoparticles due to their excellent properties. CNTs have better efficiency for the reduction of organic chemicals than activated carbon. The external surfaces of CNTs act as adsorption spots [48-52]. Some research indicates that CNTs aligned in one direction will serve as an active center for active or gating for water transport [53]. A molecular dynamics study states the effectiveness of CNTs for desalination of water in RO systems.

In the aqueous environment, the surface area decreases because of the high hydrophobicity and high interstitial spaces. They are the better absorbents for heavy metals (Fig 3). As they have a small interparticle distance, the adsorption kinetics are high-speed. CNTs, along with nitric acid and KMNO₄, help remove Cd²⁺ ions from the aqueous solution. They have 0.25 X 10¹² pores per cm² [54]. The more practical approach of aligning Dehler et al. filters with CNTs along with hydrophobic membranes.

![Figure 3 CNTs performances for efficient water treatments [55]. Reprinted (adapted) with permission from ACS Environmental science & technology; 10.1021/es500506w. Copyright (2014) American Chemical Society.](https://biointerfaceresearch.com/)

CNTs have antibacterial mechanism properties and electrochemical behavior where microorganisms are trapped through oxidation, bypassing small intermittent voltage[56-59]. Electrophoresis of the viruses towards the CNTs can give the electric potential, negatively impacting the organic matter in the CNT filter as a virus trap. CNTs and fullerene can generate ROS in water as they are photosensitive, and activation can be activated [60]. There is enough research and development done where single-wall CNTs (SWCNTs) and multiwall (MWCNTs) are directly involved in water desalination. Md. Eaqub Ali and others [61-65], in
their research, showed that the smooth and the internal core of CNTs could be used for filtration.

The general type of CNT is pristine CNT. It has an aggregating property that significantly lowers water output and pollution rejection capabilities from membranes containing metal catalysts, physical heterogeneous, and impurities [66].

The application of purification of water through the CNTs can also be linked with the surface tension. CNTs coated with polytetrafluoroethylene [PTFE] have no wetting property, which gives better purification property. By applying the voltage, the hydrophobicity of the nanotubes can easily be manipulated to a new value. The hydrophobic nature changes to hydrophilic incrementally with +2.6 v potential used [67-70].

3.4. Graphene

Another type of Nano carbon-based material is Graphene oxide [GO]. Henriques found a new way by making GO foam, which removes 96% of mercury in 24 hours, which was tested on the river and seawater samples. Synthesized with the precipitation method, the GO membrane can remove cadmium and ionic dyes.

From the commercial point of view, graphene is economical than CNTs with limited commercial applications because of their high price [71]. Graphene has a thick layer lattice, which is an allotrope of carbon with SP² bonded carbon atom’s hexagonal structure. It is impermeable to small molecules with high mechanical properties. In most practical and industrial applications, graphene has increased importance as a desalination membrane [72]. Mishra and Ramaprabhu carried out the experimental work on seawater's desalination by a supercapacitor. f-HEG loading resulted in 55% arsenic at the electrode and sodium removal from sodium arsenate up to 66%. They found high adsorption capacities, even at 142, 139, 122 mg/g. This provides a commercial platform for the development of compactable supercapacitors. The graphene nanocomposite also can be used as a functional electrode for CDI [73]. The graphene electrode consists of reduced rGO-RFshowed more significant potential in adsorption.

The new one-pot method revealed excellent results on adsorption of salt removal with an efficiency of ~ 93% and different electropositive capacity of 5 mg g⁻¹, specific capabilities up to 292 F g⁻¹, and adequate recycling capacity [74].

Desired size Nanopores can be fabricated on graphene by ion bombardment, electron beam irritation, oxidation, chemical etching, di-block copolymer templating, and doping [75]. Salt rejection up to 5.5 A is possible through the molecular dynamics study through the graphene membranes shown in (Fig 4). Theory shows the use of regular-sized pores for RO.

![Figure 4](https://biointerfaceresearch.com/)

**Figure 4.** Illustration of a) sheets and b) the membrane of GO [76]. Reprinted (adapted) with permission from ACS Applied Materials & Interfaces; 10.1021/am5040945. Copyright (2014) American Chemical Society.
Graphene gave the flexibility to embed in the matrix with all the free-standing membranes. It acts like an incorporated polymer matrix. Incorporating is a highly efficient method than surface coating. The above work showed that graphene Nanopores, which are – ve, have an excellent capacity to reject salt ions. The integration of graphene oxide sheets with the polymers has shown an increment in the sheets [76].

3.5. Metal-based nano absorbents

Metal-based Nano absorbents, in general, are primarily metal-oxide NPs. These have a higher tendency to absorb heavy metals over activated carbon [77]. Previous researchers showed a nanoscale effect because of its increment in the surface as we go down to much smaller and lower sizes into a nanometre. Yean showed this size effect in 2005, where he experimented by decreasing the size. Shorter interparticle distance and the greater surface area are responsible for the adsorption capacity [78].

In his next research, the same researcher showed the comparison between the Nanotubes and the Nanorods and proved that Nanorods are more efficient in the adsorption of other metal ions. Nano hematite can carry out the reduction of heavy metal lead ions by endothermic and exothermic Zn reactions. These allow heavy metal adsorption effectively. Nano maghemite and nanomagnets are considered superparamagnetic in iron oxide-based Nanoparticles. Magnetism is taken as an advantage in this case. Metal oxide nanocrystals porous pellets can also be used in industries; fine powders and pellets are used, which is advantageous [79]. Conjugation of MgO and TiO$_2$ also increases the effectiveness of absorption. Long reactive iron nanoparticles in a size range of 10-100nm explain the effectiveness of chlorine-containing compounds neurotoxicants. They are pre absorbed to zero-valent Fe, with the formation of ethane by reduction $\text{C}_2\text{Cl}_4 + 4\text{FeO} + 4\text{H}^+ \rightarrow \text{C}_2\text{H}_4 + 4\text{Fe}^{2+} + 4\text{Cl}^-$. 

3.6. Polymeric biomimetic hybrid protein membranes.

Biomimetic polymeric proteins are suitable for extensive selective transport of solute and the solution (water) to pass through the biological membranes. Cross-linking of the matrix can be achieved through UV light irradiation, which helps to cross-link the matrix. It can be done by free radical initiators such as azobisisobutyronitrile [79]. Kaufman et al. demonstrated the lipid bye layer's usefulness. A recent approach has shown that AQOs are first incorporated into proteoliposomes. The resulting structure will have a cross-linked polyimide coating film. AQP containing proteoliposomes is introduced into a thin film of polyamide during the interfacial polymerization process and acts as a gateway for the selective RO membrane. As a naturally occurring polymer, cellulose is one of them having novel biopolymer-based Nanocomposites with unique properties. This had an interwoven structure. It can form a porous membrane with high mechanical strength [80,81].

3.7. Polymeric nano absorbents.

Recently research gained interest in polymeric nano adsorbents as well. These shells will have a good adsorption capacity of up to a pH of 5.5 by removing the heavy metals. This has recyclability four times. Another study showed that bimetal doped Nano and micro functional polymeric adsorbents showed more significant fluoride and arsenic adsorption potential. A suspension is prepared with it. To obtain bimetal-doped, Nano-adsorbent Al and
Fe ions were substituted. It demonstrated better adsorption towards fluorine concerning arsenic [82]. It has its specialty for water purification of iron oxide aggregation in a solitary manner and a stabilizing scaffold for reactive nanoparticles to remove arsenic. Tomographic images of AFM for raw and propionate lignin Nanocomposite depict that after propionate smoothing. Poly-amidoamine has excellent properties of uranium adsorption [83-86].

3.8. Nanofiber membranes.

Nanofiber membrane is synthesized with the electrospinning method using hundreds of polymers. Its characterization, Preparation, and selectivity depend on the situation presented in the literature[87-90]. This has hydrophobic nature, which reduces the fouling.

This can remove the bacteria and viruses based on their size, and it is capable of ultrafiltration and reverse osmosis techniques. Sato et al. and others [91-95], in their research, removed E.coli maintaining the continuous flow. Nanofibers help eliminate the microorganisms by having a negative surface charge they dispersed over a micro-glass for nanoparticle-based filtration; this is another approach for nanofiber processing.

Alumina was used for the making of porous membranes Fig. 5 (a). The study on the pour sizes gives information about the porous ceramic membranes, which are around 60 nm [96] Fig.5 (b).

![Figure 5.](image)

3.9. TiO2 Nanoparticles.

TiO2 nanoparticles are also in use to treat wastewaters with inactive microbes. Incorporating Nano TiO2 into TFC active membrane layer with five wt.% slightly increases permeability [97]. This polymeric membrane will have long-term efficiency. Embedding the functional Nanomaterials into the membranes will significantly improve the properties like mechanical permeability, fouling resistance, thermal stability, and creating new functional groups for removing contaminants and self-cleaning membranes [98-100].
3.10. Ag nanoparticles.

Silver has been a familiar and good antibacterial for ages. This can be used as a remedy for the decontamination of water. The features contain antimicrobial activity, easy to fabricate, and are safe. Nanosilver has to be taken in proper doses. If not, it becomes toxic, and its toxicity depends on the shape, size, and coating. In another study shows that silver ions favor E.coli growth. The incorporation of Nanosilver into ceramic microfibers acts as a barrier for pathogens [101-103].

3.11. ZnO nanoparticles.

ZnO has an excellent property of absorption of UV light. ZnO NPs will work effectively as an antibacterial agents. The antibacterial action is still unknown; it may depend on the particle size effects [104]. The reason might suggest the photocatalytic effect of H₂O₂ on the microbial activity of ZnO. Even though it has an easy nature for dissolving, but it has a limited application in practice.

3.12. 2D nanoparticles.

The unique absorption property of 2D Mxene made it a more exciting point of exploration in wastewater treatment. Mxene shows more effective for reducing heavy ions. The application of Mxene started with its unique property of having various functional groups and more surface area compared to other metals used in purification methods. Mxene nanosheets will remove Chromium (iv) ions by reducing Chromium (iv) ions into Chromium (iii), the positively charged Mxene surface with the high number of the hydroxyl group at low pH will attract the negatively charged chromium ions through electrostatic attraction and also showed more excellent application in the removal of oxidants in the wastewater [105].

Removing non-biodegradable heavy metals from that aquatic life was a challenge for a few years, but the Mxene nanosheets made it easier by trapping the heavy metals in the space between its layers; the larger surface area will also play a significant role in absorption between the layers this happens mainly due to the presence of titanium which has the more excellent capability of attracting the heavy metals by forming the covalent bands with respective elements.

4. Conclusions

Nanotechnology enables us to make water purification with a low-cost approach to the popular RO membranes, especially for longer cycles of reuse and desalination. TFN membranes, Zeolite-coated ceramics, Carbon-based materials, Metal-Based Nano absorbents, Hybrid protein-polymer biomimetic membranes, Polymeric Nano absorbents, Nanofiber membranes, TiO₂ Nanoparticles, Ag Nanoparticles, ZnO nanoparticles, Magnet based have made their contributions to the purification. These different particles or elements have been developed through the incorporation of nanotechnology.

The zeolite-coated ceramic membranes give a promising selectivity, with high separation capabilities that can replace polymer membranes earlier. TFNs with nanosilver coating will have good hydrophobicity, have good resistance to fouling. These are titania nanoparticles with membranes of self-cleaning properties.
CNTs have the remarkable property of self-alignment with the potential application, having a more extraordinary ability to adapt the functionality that can be manipulated according to the need. The challenges faced are temporary where we lack economic support and a significant amount of research in the multidisciplinary streams of nanotechnology. Hence, introducing nanotechnology will help robust solutions for water purification for both incremental and revolutionary purposes.

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Conflicts of Interest
The authors declare no conflict of interest.

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