Role of Nanomaterials in the Treatment of Wastewater: A Review

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Abstract: Water is an essential part of life and its availability is important for all living creatures. On the other side, the world is suffering from a major problem of drinking water. There are several gases, microorganisms and other toxins (chemicals and heavy metals) added into water during rain, flowing water, etc. which is responsible for water pollution. This review article describes various applications of nanomaterial in removing different types of impurities from polluted water. There are various kinds of nanomaterials, which carried huge potential to treat polluted water (containing metal toxin substance, different organic and inorganic impurities) very effectively due to their unique properties like greater surface area, able to work at low concentration, etc. The nanostructured catalytic membranes, nanosorbents and nanophotocatalyst based approaches to remove pollutants from wastewater are eco-friendly and efficient, but they require more energy, more investment in order to purify the wastewater. There are many challenges and issues of wastewater treatment. Some precautions are also required to keep away from ecological and health issues. New modern equipment for wastewater treatment should be flexible, low cost and efficient for the commercialization purpose.

Keywords: nanocatalysts; nanomembranes; nanosorbents; nanomaterial applications; waste water treatment; nanomaterial challenges

1. Introduction

Water is a natural source on the earth and its availability in pure state is very essential for human beings as well as for other living creatures because the concept of life is unbelievable without water. Water is also called universal solvent due to its potential properties like solubility power etc. Currently, major problem of whole world is water contamination, due to several reasons like inadequate sewage treatment, industrial wastes, marine dumping issues, radioactive waste material, some agricultural perspectives etc. [1,2]. Water pollution has an adverse effect on environment, and it can also responsible for air pollution that reflects very dangerous results on human health. Water pollution also carries an adverse impact on economic growth and socials perspectives of the concern societies/countries. Recently, a UN report stated that purified and freshwater availability is a global issue and become a challenge in 21st century for whole world because the survival of living creatures is not safe with contaminated water [3,4]. Contaminated water means that unwanted materials come into water bodies or reservoirs and make it unsuitable for drinking and other purposes. To overcome this emerging problem, there are many chemical, physical and mechanical methods. Moreover, researchers are still working by exploring different new technologies to improve water purification methods with low cost [5,6]. Newly, emerging field nanotechnology provides a potential offer to purify water with a low expense, high working efficiency in removing pollutants and reusable ability [7]. In past era,
nanomaterials are successfully applied to several places like in a field of medical science, catalysis, etc. Recently, when the world facing serious issues of drinking water, experts found that nanomaterial is better option to treat wastewater because it has some unique properties like nano size, large surface area, highly reactive, strong solution mobility [8], strong mechanical property, porosity characters, hydrophilicity, dispersibility and hydrophobicity [9–11]. Some heavy metal like Pb, Mo, etc. organic and inorganic pollutants and various harmful microbes are reported to be successfully removed by using different nanomaterials [12–16]. Currently, WHO (World Health Organization) reported that almost 1.7 million people died due to water pollution and four billion cases of different health issues were reported annually due to waterborne diseases [17]. Table 1 indicates different kinds of water pollutants with sources and their adverse effects.

| Water Pollutants       | Source of Pollutants                          | Effect of Pollutants                                                                 | References |
|------------------------|-----------------------------------------------|--------------------------------------------------------------------------------------|------------|
| Pathogens              | Viruses and bacteria                          | Water borne diseases                                                                | [18]       |
| Agricultural Pollutants| Agricultural chemicals                        | Directly affect the fresh water resources                                           | [19]       |
| Sediments and          | Land cultivation, demolition, mining operations| Damaging fish spawning, affecting aquatic environment of insects and fishes          | [20]       |
| suspended solids        |                                               |                                                                                      |            |
| Inorganic Pollutants   | Metals compounds, Trace elements, Inorganic salts, Heavy metals, Mineral acids, | Aquatic flora and fauna, Public Health problems                                      | [21]       |
| Organic Pollutants     | Detergents, Insecticides, Herbicides.         | Aquatic life problems, Cacogenic.                                                   | [22]       |
| Industrial Pollutants  | Municipal pollutant Water                     | Caused water and air pollution.                                                     | [23]       |
| Radioactive Pollutants | Different Isotopes                            | Bones, teeth, skin and can cause                                                    | [24]       |
| Nutrients Pollutants   | Plant debris, fertilizer.                     | Effect on eutrophication process.                                                   | [25]       |
| Macroscopic Pollutants | Marine debris                                | Plastic pollution.                                                                  | [26]       |
| Sewage and contaminated water | Domestic Wastewater                          | Water borne diseases                                                               | [27]       |

Recently, there are more advance developments occurred in nanomaterials such as nanophotocatalysts, nanomotors, nanomembranes and nanosorbents (Nanosorbents contain high sorption capacity which carries many applications for water treatment methods) and some imprinted polymers are effectively usable for treatment process of contaminated water. In short, the study of nanomaterial applications in water purification is considered to assess positive perspectives [16]. Therefore, we have summarized the role of nanomaterials for wastewater treatment to overcome the water crises in this review article. Nanoengineered materials provide a potential and significant water treatment approaches which can be easily adaptable, but some imperfections still need for further attention which are specially summarized in this article. Moreover, we also addressed the limitations, advantages, disadvantages and future perspectives related to these nanomaterials. Furthermore, the toxicity of nanomaterials and their several applications in wastewater treatment are briefly discussed which might be useful for researcher to plan new strategies.
2. Water Treatment Methodologies

2.1. Nanophotocatalysts

The word “photocatalysis” is composed of two Greek words “photo” and “catalysis” which mean decomposition of compounds in the presence of light. Usually, in scientific world there is no consensus definition for photocatalysis [28]. However, this term can be employed to define a process to activate or stimulate the substance by using light (UV/Visible/Sunlight). Photocatalyst which changes the rate of reaction without any involvement by itself during the chemical transformation process. Furthermore, the key difference between traditional thermal catalyst and photocatalyst is that the prior is activated through heat while the final is activated through photons of light energy [29]. Nanophotocatalysts are commonly used for wastewater purification, as they help to enhance the reactivity of catalyst due to having a greater surface ratio and shape dependent features [30].

The nano size-based materials show different response as compared to bulk materials due to their distinct quantum effects and surface properties. It assists to increase their electric, mechanical, magnetic chemical reactivity and optical properties too [31]. It has been showed that the nanophotocatalysts can expand the oxidation ability due to effective production of oxidizing species at surface of material which helps in degradation of pollutants from the polluted water effectively [32].

Nanoparticles like zero-valence based metal, semiconductor and some bimetallic type etc. are mostly used for treatment of environmental pollutants e.g., azo dyes, Chlorpyrifos [33–35], organochlorine pesticides, nitroaromatics, etc. [36]. There are also several reports in literature which illustrated that TiO$_2$ based nanotubes can effectively be used in removal of pollutants (organic pollutants such as azo dyes, Congo red, phenol aromatic base pollutants, toluene, dichlorophenol trichlorobenzene, chlorinated ethene, etc.) from waste water [37–41]. However, the most common and significant metal oxide nanophotocatalyst are SiO$_2$, ZnO, TiO$_2$, Al$_2$O$_3$, etc. [42–44]. Among them, Titanium dioxide (TiO$_2$) is one of excellent photocatalyst from all existing material due to its several reasons such as low cost, toxic free property, chemical stability, and its easy availability on earth. Moreover, TiO$_2$ exist in three natural states, anatase, rutile, and brookite. So far, anatase considered as good nanophotocatalyst material [45]. The bandgap of this state is 3.2 eV and it can absorb ultraviolet light (below 387 nm) [46]. However, other photocatalysts like ZnO have also been produced to eliminate contaminants in wastewater and presents reusable ability effectively [47–51]. In case of composite nanomaterial, the degradation of reference substance (dimethyl sulfoxide) for evaluating the photocatalytic performance of water treatment by using CdS/TiO$_2$ composite as catalyst under the irradiation of visible light also investigated [52]. The iron doped nanomaterials have ferromagnetism ability which helps to recycle and reuse it easily [53–56]. Similarly, due to some characteristics like high photocatalytic reactivity Pd incorporated ZnO nanomaterial have been used for the removal of *Escherichia coli* from wastewater [57]. Although, new efforts have been targeted on metal oxides in order to increase the photocatalytic performance under visible light irradiation through modifying them with other elements like metals or metal ions [6,33] carbonaceous-based materials, dye sensitizers [58] and many others but still there is a need for further modifications in nanophotocatalysts.

Furthermore, nanophotocatalysis process may occur in two states heterogeneously or homogeneously. The most intensively studied state is heterogeneous nanophotocatalysis in modern era, due to its wide scope in water decontamination and environmental related applications. In case of heterogeneous photocatalysis, it implies the prior development of an interface between fluid (both reactants and products of reaction) and solid photocatalyst (such as metal or semiconductor) [59,60]. Generally, the word “heterogeneous photocatalysis” is mostly employed where a light-based semiconductor photocatalysts are used, which is in interaction with gaseous or liquid phase [61]. The heterogeneous photocatalysis based applications are strongly depend on the scaled-up reactor based on advance developed designs with improved efficiency [62]. The major task in reactor designing is effective illumination of nanocatalyst and mass transfer optimization, particularly in case of liquid phase. The transfer of photon can be improved by using light-emitting diodes and optical fibres,
but productive revolutions in this field are still lacking. Moreover, an extensive effort has been focused toward the progress of solar photoreactors [63–65]. According to literature, the positive role of nanophotocatalyst has been demonstrated in research laboratory for air cleaning and water treatment. At the commercial level it is still not a perfect way to minimize the problem. Moreover, the present lack of extensive commercial applications is due to absence of effective photoreactor configurations and lower photocatalytic competence of photocatalysts. Despite all, heterogeneous nanophotocatalyst recommend fascinating advantages i.e., inexpensive usage of chemicals, additive free, work even at lower concentration, chemical stability (e.g., TiO$_2$ stable in aqueous medium) [66]. Therefore, recently heterogeneous photocatalysis is achieving the pre-industrial scale.

2.1.1. Advantage and Disadvantages of Nanophotocatalyst

Nanophotocatalysis has reflected a vital role for the mineralization of dangerous organic substances at 25 °C and proved very effective and efficient method for detoxification of water with help of nanophotocatalysts [67]. Furthermore, mostly nanophotocatalysts show some advantages such as they are less toxic, having low-cost, chemically stable, easily accessible and excellent photoactive properties with nano size i.e., 1–100 nm range [68]. Generally, nanophotocatalysts present various advantages such as stability (chemical/physical), low cost and eco-friendliness. Among them, TiO$_2$ having good photostability but many nanophotocatalysts, such as zinc oxide, metal sulfide materials, copper-based materials, and so on exhibit relatively low chemical stability due to photocorrosion [69]. As light shine on them, they oxidized or reduced depend on materials and their oxidation states changes by generating holes or electrons, which leads to decomposition of photocatalysts and decreases the efficiency of photocatalysts. Therefore, there is a strong need to synthesize a nano composite in order to achieve stable photocatalysts for long-time performance.

The major advantage of nano-sized is related to quantum-size effect, which enhance the energy bandgap and reduce the particle size [70]. Moreover, as a process photodegradation also have several advantages such as low cost, reusable, and generally complete degradation. In addition to all of the developments, still nanophotocatalyst facing some issues i.e., toxicity and recovery of catalysts from mixture. These type of issues limits the applications and scope of nanophotocatalyst at higher level [71]. So, the scientific community is now focusing others nanocomposite of different material which can reduce the toxicity while using in water treatment process. So, it is suggestible for the scholar community to synthesize new photocatalysts which can work in visible ranges for sustainable result and promote the doped photocatalyst with different material such as graphene and its derivatives to reduce the toxicity effect. To overcome the catalyst recovery drawback, one significant approach could be used i.e., magnetic nanophotocatalysts in wastewater treatment. When magnetic nanophotocatalysts are used, the recovery of catalyst can be achieved through external magnetic fields, therefore, permitting the many recycling of nanocatalyst and achieved more effective and naturally responsive water decontamination processes. Furthermore, the approach regarding nanophotocatalysis for removal of pollutants from water has been described as a very effective approach and some unique applications of nanophotocatalysts are shown in Figure 1.
2.1.2. Future Perspectives of Nanophotocatalyst

A wide research on nanomaterials is ongoing in field of nanophotocatalysis which led to few progress in reactor designing and developments regarding the modifications in nanophotocatalysts. Although many developments in nanophotocatalytic materials occurred, still some important inquiries required related to characteristics of nanophotocatalytic materials. The major challenges in intensification process is mass transfer limitations and higher consumption of photons [72]. The concept of nanocomposites is ideal in solving the electron pair recombination problem which can be prolonged by combining the nanocomposites with nanophotocatalytic reactor structures. The new modern reactors are known as microfluidic reactors which open a new door for intense characteristics study in reaction phase and synthesis phase. Microfluidic reactors are those reactors which are working on micro level with reactants [73,74]. The key features of micro-reactors are large surface-to-volume ratio, improved diffusion effect and great mass transfer coefficient factor, highly stable hydrodynamics, less Reynold’s flow, and informal handling which makes them more ideal material than conventional reactors. However, still it is difficult for photocatalysis to apply on large scale in actual wastewater.

Moreover, the synthesis of significant structures such as nanorod, nanosphere, nanoflowers, nanoflakes and nanocones with enhanced functional and structural properties could be opened an extensive area of study. Several structures of nanomaterials with potential properties could be produced through the measured synthesis approaches. However, the future research, should be explored by producing new photocatalysts. The synthesis of novel nanophotocatalysts with excellent efficiency, inexpensive, eco-friendly and high stability is crucially needed. Moreover, to exploit pollutant treatment effectively, several approaches should be joint with sensible match, such as electrocatalysis, photocatalysis, adsorption and several thermodynamics processes. The preparation of nanocomposites in the presence of ZnO, TiO$_2$ was well explored in early decades for the treatment of water pollutants. The nanocomposites preparation by using carbaneous material, polymer and ceramic materials are still in initial stage. It can generate ideal nanocomposites with improved properties. The heterogeneous photocatalytic for wastewater remediation is inhibited by some main technical problems that need to be study effectively. Finally, a significant photocatalytic treatment with better solar-driven, excellent efficacy and less site area requirements can be comprehended in future with fast assessment.

Figure 1. Potential applications of nanophotocatalysts.
2.1.3. Photocatalytic Degradation and Mineralization Pathway

Nanomaterials also got much attention in degradation as well as mineralization of toxic organic pollutants due to having remarkable physiochemical properties. In photocatalysis, there are two types of processes that occur, namely mineralization and degradation of organic pollutants [5,75]. In the process of degradation, the organic pollutants are splitting or decomposed into several products while in the case of mineralization, the complete destruction of organic pollutant took place into water, carbon dioxide and some inorganic ions. The possible pollutant degradation mechanism in the presence of light is shown in Figure 2 [75]. Briefly, a semiconductor like TiO₂ absorbs the light which is greater or equal to TiO₂ band gap width, it carries to electron–hole pairs (e⁻⁻ h⁺). If the separation of charge is continued, the electron–hole may travel to the surface of catalyst where they contribute with sorbed species in redox reactions. Particularly, h⁺cb react with water (surface-bound) to generate the hydroxyl radicals and simultaneously e⁻cb selected by oxygen to produce the radical anion (superoxide radicals) as designated below in equations.

\[
\text{TiO}_2 \ + \ h\nu \ \rightarrow \ e^{-}_{cb} \ + \ h^{+}_{vb} \quad (1)
\]

\[
\text{O}_2 \ + \ e^{-}_{cb} \ \rightarrow \text{O}_2^{-} \quad (2)
\]

\[
\text{H}_2\text{O} \ + \ h^{+}_{vb} \ \rightarrow \text{OH} \ + \text{H}^+ \quad (3)
\]

Figure 2. General mechanism of toxic organic compound degradation through nanophotocatalysts.

After pollutant degradation by using nanomaterials in the presence of light, HPLC-MS or GC-MS was employed to analysis the produced degraded products. Here, it is necessary to confirm regarding the obtained degradation products, whether these products are more toxic or less toxic as compared to parent compound using toxicity test.

As discussed above, mineralization concept is actually synonymous of complete photodegradation. It defines the degradation of a compound into CO₂ and H₂O. Sometimes others minerals also released during mineralization of compounds such as sulphate, ammonia, sulphite, fluoride, sulphide, chloride, phosphate, nitrite, etc. [76]. Generally, the rate of mineralization is less as compared to degradation, probably due to generation of stable intermediate during process. Therefore, it is supposed that a long irradiation is compulsory for entire removal of total organic carbon (TOC). Moreover, the mineralization concept is avoiding the generation of undesirable products is the excellent mode to degrade the organic compounds. The TOC is defined as the total quantity of bounded carbons in any organic compound and measured by TOC analyser. The possible mechanism of pollutant mineralization is shown in Figure 2 coupled with photodegradation mechanism.

For example, different degradation products as well as the mineralization products of Lignocaine are shown in Figure 3 as follows [77];
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Figure 3. Different degradation and mineralization products of Lignocaine.

2.2. Nano- and Micromotors

Nanotechnology, an area of research that has progressed at such a quick pace in early decades and offered many approaches for water treatment. In modern era, nano/micromotors have been considered that can convert the energy from several resources into machine-driven force, empowering them to achieve special goals through various mechanisms. These innovative motors are motorized in both cases by using fuel or without fuel sources (acoustics, magnetic field, electric field) have several significant exciting applications [78]. They show more speed, high power, specific control movement, self-mix ability, etc. The removal of contaminant from polluted resources is a significant focus for environmental stability and sustainability [79]. The trend of water purification and its treatment has grown quickly throughout the world because of high demands for pure water resources and novel water superiority regulations. A large variety of approaches are used earlier for removal of pollutants from polluted groundwater, fresh water, sediments wastewater, etc. Different mechanisms employed by nano/micromotors for treatment of water pollutants are graphically shown in Figure 4 and some environmental applications of nano/micromotors are shown in Table 2 with their mechanism.

Traditional treatment processes are inadequate through diffusion and, hence, entail outward agitation to stimulate the wastewater treatment process. Though, nano/micromotors could possibly overwhelmed the diffusion boundary by energetic mixing due to their self-propulsion competences. These self-propelled nano/micromotors expressively stimulate the water treatment efficiency through water decontamination efficiency, merging with materials nano/microstructure i.e., greater surface area and working activities [80–83]. Moreover, nano/micromotors can go in nano/microscale detentions in the presence of a magnetic field, serving as programmed cleaners, where conventional approaches are not actively working. However, most positive concept for nano/micromotors in term of wastewater decontamination depends on fuels as shown in Table 3. There is problem, this condition reduced the working potential of nanomotors in biological applications. Although some photocatalytic, biocatalytic and magnetically driven nano/micromotors have been industrialized, still there are some challenges in order to apply nano/micromotors for water treatment in future.
Table 2. List of nano/micromotors and their applications.

| Motors                        | Working Mechanism                  | Applications                                      | References |
|-------------------------------|------------------------------------|---------------------------------------------------|------------|
| Zn, Al/Pd micromotors        | speed-pH dependence               | pH controlling                                    | [85]       |
| Hydrophobic agglomerates of  | Surface tension induced            | Increased diffusion of pollutants                 | [86]       |
| pollutants                    |                                    |                                                   |            |
| Polymer capsule motors        | Surface tension induced cargo towing|                                                   | [87]       |
| Au/Pt nanomotors             | silver-induced acceleration         | Detection of silver ions                          | [88]       |
| Ag-based Janus MIP microparticles | Molecular imprinted polymer recognition | solid-phase extraction                          | [89]       |
| Au/Pt nanomotors             | DNA hybridization through using Ag nanoparticle | DNA detection                                 | [90]       |
| Bubble-propelled Pt-based    | High fluid transport               | Oxidative detoxification of nerve agents          | [91]       |
| micro engines                 |                                    |                                                   |            |
| Bubble-propelled Pt-based     | Fenton reaction; high diffusion     | Degradation of organic pollutants                | [92]       |
| micro engines                 |                                    |                                                   |            |
| SAM modified Pt micro engines | Hydrophobic interactions with oil droplets | Oil removal                                    | [93]       |
| Ir/SiO₂ Janus motors          | Speed-concentration dependence      | Detection of hydrazine                           | [94]       |
| Pd nanoparticle-containing    | pH dependence                      | pH monitoring                                     | [95]       |
| Microspheres                  |                                    |                                                   |            |

Figure 4. Different pollutant removal mechanisms used by nano/micromotors (adapted with permission from Royal Chemical Society) [84].

For example, different degradation products as well as the mineralization products of Lignocaine are shown in Figure 3 as follows [77];
Table 3. List of nano/micromotors for water decontamination in presence of fuel.

| Type of Nanomotors                                      | Target Pollutants                                      | Operational Mechanism          | Fuel   | References |
|--------------------------------------------------------|-------------------------------------------------------|--------------------------------|--------|------------|
| PEDOT/Pt bilayer nanomotor                             | Organophosphorus nerve Agents                          | Oxidative neutralization       | H\(_2\)O \_2\) | [96] |
| Ag-incorporated zeolite                                | -                                                     | Adsorptive Detoxification      | H\(_2\)O \_2\) | [97] |
| rGO-SiO\(_2\)–Pt Janus magnetic micromotors            | Polybrominated diphenyl ethers (PBDEs) and 5-chloro-2-(2,4-dichlorophene) phenol (triclosan) | Adsorption                     | H\(_2\)O \_2\) | [98] |
| Pt coating Activated carbon-based motors                | Heavy metals (Pb\(^{2+}\)), nitroaromatic explosives, dyes | Adsorption of active carbon    | H\(_2\)O \_2\) | [99] |
| Zero-valent-iron/platinum (ZVI/Pt)                     | Methylene blue                                         | Fenton reaction                | H\(_2\)O \_2\) | [100] |
| CoNi@Pt nanorods                                       | 4-nitrophenol, Methylene Blue, and Rhodoamine B       | Degradation                    | Borohydride | [82] |
| Pd-Ti/Fe/Cr tubular microjets                          | 4-nitrophenol (4-NP)                                   | 4-nitrophenol (4-NP)           | Borohydride | [101] |
| Au NPs/TiO\(_2\)/Pt nanomotor                         | super organic mixture                                  | Photocatalytic Degradation     | H\(_2\)O \_2\) | [102] |
| Polystyrene–Zn–Fe coreshell Microparticles             | Rhodamine B                                            | Fenton reaction                | H\(_2\)O \_2\) | [103] |
| TiO\(_2\)/Au/Mg microspheres                          | Mineralization of the highly persistent organophosphate nerve agents, bis (4-nitrophenyl) phosphate (b-NPP) and methyl paraxon (MP) | Photocatalytic degradation     | -     | [104] |
| Biotin-functionalized Janus silica Micromotor          | Rhodamine B                                            | Charge adsorption              | H\(_2\)O \_2\) | [105] |
| Fe\(^{0}\) Janus nanomotors                            | Azo dyes                                               | Fenton reaction                | Citric acid | [106] |
| CoNi-Bi\(_2\)O\(_3\)/BiOCl-based hybrid Microrobots   | Rhodamine B                                            | Photocatalytic degradation     | UV light | [107] |
| DNA-functionalized Au/Pt Microtubes                    | Hg\(^{2+}\)                                            | Adsorption                     | H\(_2\)O \_2\) | [108] |
| GOx-Ni/Pt                                              | Pb\(^{2+}\)                                            | Adsorption                     | H\(_2\)O \_2\) | [109] |
| 3D printed motors (TSM)                                | Oil droplets                                           | Adsorption                     | -      | [110] |
| Alkanethiols-coated Au/Ni/PEDOT/Pt microsubmarine      | Oil droplets                                           | hydrophobicity upon the oil-nanomotor interaction | H\(_2\)O \_2\) | [111] |
2.2.1. Advantage and Disadvantages of Nano- and Micromotors

Recently, nano/micromotors are used to overcome the environmental issues such as water pollutant treatment and environmental sensing/monitoring. The nano/micromotor are considered as excellent option, because the reactive nano-based materials have potential properties which make it more efficient to convert toxic pollutants into toxic free. Nanomachines offer different advantages as compare to traditional remediation agents. The small machines improve a dimension which based on decontamination approaches, lead to in-situ and ex-situ nano-remediation rules, and have ability to decrease the clear-out time and entire cost [112]. Specifically, the constant movement of nanoscale substances can be utilized for transferring reactive nanomaterials for water purification through polluted samples, for discharging remediation agents to long distances, and for communication of important mixing throughout decontamination processes [113]. Existing technologies are insufficient for fulfilling the demand in term of scaling up, as stated in the treatment of polluted water, therefore more efforts are required. Some issues require to be explained prior to move toward applied application at commercial level. For example, the lifecycle of multi-functional nano/micromotor is restricted to the residual materials in its physique that were consumed in locomotion or oxidation reactions. Another disadvantage is poisoning of Pt layer because the compounds present in wastewater can bond chemically to other surface-active sites of the catalyst, or great viscosity-based wastewater which hinder the movement of micromotors [114]. The introduction of novel development in nano/micromotors will offer countless environmental treatment possibilities to achieve more multifaceted and challenging operations.

2.2.2. Future Perspectives of Nano- and Micromotors

Nano/micromotor are still considered as immature techniques because it still on initial stages but this topic open a new door of research for researcher. As Compared with other traditional wastewater treatment approaches, this subject is still novel and but has a lot of restrictions in extensive and real-world applications. Despite all, current approaches are insufficient to fulfill the current demand in scaling up the technique described in water pollutant treatment, therefore considerable work is still required [115]. Novel materials should link with nano/micro-motors, such as graphene to treat wastewater. These kinds of materials show better performance in wastewater treatment as compared with other materials. Moreover, some new mechanism should functionalize in nanomotor design for better results. Soon, we believe that excellent nanomotor will be planned by associating with other approaches. These predictable new, novel micro/nanomotors would ultimately develop the ecological monitoring and wastewater treatment technologies, from a struggle to advance the class of life.

2.3. Nanomembranes

Nanomembranes are a unique type of membrane formed with different nanofibers which are employed to eliminate unwanted nanoparticles present in aqueous phase. Using this technique, the process takes places at a very high elimination speed with condensed fouling propensity and it also served as a pre-treatment process which is used for reverse osmosis [116]. There are many reported studies on membrane nanotechnology in order to produce multifunction membrane by using different nanomaterial substance in different polymers-based membranes. Water porous membrane for water treatment did nanofiltration, ultrafiltration, reverse osmosis, etc. The membrane contains a porous support with composite layer. Typically, the considerable composite layer is carbon-based material (graphene oxide/CNT) dispersed into polymer matrix for significant practice. This provide promising and significant progresses in fouling resistance and aqueous transport. For example, CNTs hold anti-microbial properties that can minimize fouling, biofilm formation and it can also reduce the chance of mechanical failures [117]. The doping process of nanomaterial (zeolite, alumina, TiO₂, etc.) into polymer ultra-filtration membranes show the formation of amplified membrane on surface of hydrophilicity and fouling resistance [118–120]. The antimicrobial material like silver metal particles are
also doped with a polymer to produce polymeric membrane to prevent attachment of bacteria and inhibit biofilm production on surface of membrane [121,122]. It served to inactivate viruses and it has also ability to prevent the biofouling of membrane [123]. The production and growth of nanomaterial thin film are incorporated into active thin film composite through doping in surface modification. Usually, there are a few major challenges in nanomembrane i.e., membrane clogging and membrane fouling. Therefore, it is a need to overcome this problem. By the addition of super hydrophilic nanoparticles in making a thin film nanocomposite membrane, the prevention from clogging and fouling could be checked. Furthermore, metal oxide nanoparticles (Al$_2$O$_3$, TiO$_2$), antimicrobial nanoparticles (nano silver, CNTs) and aquaporin-based membranes are very useful material to overcome the membrane clogging and fouling issue due to having high hydrophilicity, high porosity, better fouling resistance and a better homogenous nanopore. Generally, nanoparticles affect the selectivity and permeability of a membrane which depends upon the sort, quantity, dimension, etc. of nanoparticles. Moreover, there are many biological membranes present with highly permeable and selective ability [124,125]. Nanomembranes are also used for wastewater treatment due to having several properties that make this material more prolific, these are high uniformity, homogeneity ability, optimization, short time required, easily handled and contain much order of reaction [126]. There are some nano photocatalysts which can be introduced in the nanocomposite membrane to make fit it for the degradation of organic pollutants. For example, TiO$_2$ incorporated nanomembranes and films are effectively used to deactivate different microorganisms and degrade the organic pollutants [127]. The developments and progressive growth of nanotechnology especially in nanomaterial produced several nanostructured catalytic membranes which contain novel properties like improved selectivity, high decomposition rate, and larger foul resistance [128,129]. In order to synthesize these types of nanomaterials, there were many approaches used to produce it with multi-functionality features [130]. The incorporation of nanostructured catalytic materials like iron-catalysed based free radical and enzymatic catalysis within pore membrane showed a constructive progress in this technology. Therefore, it possible to carry out oxidative reactions for removal of pollutants and detoxification of water without use of any toxic chemicals. To prove the efficiency of nanostructured catalytic membrane in industrial/commercial applications, immobilized membrane nanoparticle (ferrihydrite/iron oxide) reaction was carried out with hydrogen peroxide to make free radicals’ ions for removal of chlorinated based organic pollutant in real groundwater. The development of nanostructured materials is still very useful in many other environmental applications [131]. There were several reported studies of metallic nanoparticles immobilization on membrane (e.g., chitosan, cellulose acetate, polysulfones, etc.) for dichlorination, degradation of a toxic substance which contains novel properties such as, hindrance of nanoparticles, high reactivity, absence of agglomeration and surface reduction [132,133]. Palladium acetate and polyetherimide both are used to prepare nanocomposite films and a novel type interaction is present among hydrogen and Pd nanoparticles in order to improve water treatment efficiency [134]. In situ and ex-situ methods are also used to produce nanomaterials within the matrix with precursor film under many conditions [135–137]. This offers many opportunities to produce nanomaterial with tunable properties. Moreover, the developments of nanotechnology are also responsible to produce many significant catalytic membranes with high selectivity, better permeability and high resistance fouling. Modern methods contain hybrid and bottom-up approaches for empowering its multi-functionality characteristics in the field of wastewater treatment [138].

2.3.1. Advantage and Disadvantages of Nanomembrane

The main objective of using membranes in case of drinking water is to separate the toxic particles from water resources. The nanomembrane filters were also used to measure the water safety level [139]. The advantages of nano membrane as compared to traditional approaches for filtration is that; in traditional approaches of filtration, throughout the entire process, calcium and magnesium required another ion to compensate, therefore mostly Na$^+$ ions are served as an exchanger but in case of nanomembrane, there will be no need [139,140]. Nanomembranes limitations are usually reducing
its efficiency compared to other conventional approaches. The first one is fouling of nanomembrane which comes after using the membrane few times. It is the major issue, which make this approach more expensive and inefficient. Fouling problems occur in the nanomembrane because it entirely depends on working conditions, sometime the working conditions are not appropriate such as over temperature, pressure, and optimization is also considered as responsible for membrane fouling [141]. Second major limitation is membrane stability. The nanomembrane could not keep the stability for long period. After sometimes, the stability start reducing its efficiency and it does not give excellent outcomes as earlier. So, there will be a need for changing the nanomembrane to get excellent results, but this will cause several other issues such as high cost, impurity chances during changing process, etc. [142]. The stability is depending on the essential chemical resistance which apply for material cleansing. The disadvantages are less reliability, slow operation process, less selectivity, high maintenance cost and working efficiency reduce with passage of time. There are some common disadvantages that is why it is not extensively explored [143]. Some nanomembranes types are summarized in Table 4 along with their advantage and disadvantage and applications.

2.3.2. Future Perspectives of Nanomembranes

Nanomembranes separate the inorganic ions, organic, nanoparticles viruses-based pollutants from water resources through solution using diffusion and size exclusion. Though these described nanomembranes are proved effectively at the research laboratory level, upscaling to lower cost, but making them ideal for industrial scale is still emerging as a challenge. To cross this barrier toward productive upscaling, the commercialization objective needs a joint collaboration struggle through research institutions and manufacturing companies. The selectivity of nanomembrane should be improved, secondly upgrade the nanomembrane resistivity to avoid membrane fouling. Surface grafting-based polymers like zwitterionic may be a significant candidate for the development of new generation membranes. Surface grafting, though, would not report fouling resistance to inner walls pore [149]. Thereafter, the prime of other appropriate anti-fouling convertors fixed into the membrane matrix that will be vital. It is also very significant to improve the high sensitivity of polyamide membranes to many types of oxidants like ozone and chlorine. Furthermore, the multi-functional membranes fabrication requires a significant attention for better innovation at industrial scale. However, still there are several challenges to be solve for manufacturing production of lower cost and effective nanomembranes for water treatment.

### Table 4. Advantages/disadvantages and applications of nanomembranes.

| Different Type of Nanomembranes | Advantage of Nanomembrane | Disadvantages of Nanomembrane | Application | Reference |
|---------------------------------|--------------------------|-------------------------------|-------------|-----------|
| Nanofiber membranes             | Excellent porosity, tailor-made, bactericidal, good permeate efficiency, | Pore blocking, conceivably discharge of nanofibers | Ultrafiltration, prefiltration, filter cartridge, water handling, separate filtration devices | [144] |
| Nanocomposite membranes         | High hydrophilicity, better water permeability, high fouling resistance, good thermal and mechanical stability | Resistant substance substantial required when oxidizing nanomaterial, used to discharge nanoparticles | Entirely dependent on composites | [145] |
| Aquaporin-based membranes       | Improved ionic selectivity and better permeability | Poor mechanical stability | Less pressure desalination | [146] |
| Self-assembling membranes       | Homogeneous nanopores membranes | Laboratory scale availability only | Ultrafiltration | [147] |
| Nanofiltration membranes        | Charge-based repulsion, comparative less pressure, better selectivity | Membrane blocking | Colour, Reduction of hardness, odour | [148] |
2.4. Nanosorbents

Nanosorbents hold wide properties like high sorption capability that make the nanosorbents more appropriate and powerful for water treatment [150]. These nanosorbents are very rare in commercial form but researcher and experts doing a lot of work on it to produce nanosorbents in larger quantity at commercial level [151]. The most commonly reported nanosorbents are based on carbon (e.g., carbon black, graphite, graphene oxide). Furthermore, metal/metal oxide and polymeric nanosorbents were also exist [152]. The composite of different material like Ag/polyaniline, Ag/carbon, C/TiO₂, etc. carrying huge significant importance in order to reduce the effect of toxicity in the wastewater treatment process. The carboneous material such as CNTs with a cylindrical form nanostructure may present as single-walled and multiwalled nanotubes depending on the method of synthesizes. CNTs hold measurable adsorption sites and due to high surface area, they hold sustainable surfaces. It must be stabilized to prevent from agglomeration that decreases the surface-active sites because CNTs has hydrophobic surface properties. So, it is an efficient material for the pollutants by adsorbing process. Similarly, the polymeric nanoadsorbents like dendrimers are functional for eliminating organic pollutants and heavy metals from wastewater [153]. For example, copper ions were reduced with the help of dendrimer-ultrafiltration system [154]. They simply regenerated by shifting of pH effect and show biocompatibility, biodegradability, and toxic free environment. Furthermore, the removal percent of dyes or others organic pollutants is almost 99% [155]. Another important nanosorbent is zeolites, which have an absorbent structure in which several nanoparticles like copper, silver ions can be implantable [156]. The advantage of zeolites is to control the amount of metals and it also served as anti-microbial agent [157]. Moreover, the magnetic nanosorbents have play vital role in water treatment and a unique tool to remove different organic pollutants from water [158]. Some organic containments are also removed by using magnetic filtration. Magnetic separation nanosorbents are synthesized by ligands coating with magnetic nanoparticles at specific affinity [159]. There were many methods like ion exchange, cleaning agents, magnetic forces, etc. reported to regenerate these nanosorbents. These regenerated nanosorbents have the ability of being cost-effective and more promotions of commercialization. Despite all, the carbon has some health risks. The reported studies demonstrated that toxic effect is depends on morphology of nanoadsorbents, chemical stabilizers and surface modifications [160,161]. So, there is a need to give an attention to synthesize more stable morphology (size and shape) to overcome the toxicity issues as well as health risks. Furthermore, the bioadsorbents have the properties of high biodegradable, good biocompatible and nontoxicity which could be replaceable with chemically synthesized nanosorbents. The graphene oxide is suggestable to scientific community because it is very emerging nanomaterial to use as nanosorbents to remove pollutant and it can give better result than others due to its superior properties. There are some reported nanosorbents and their functions as shown in Table 5.

### Table 5. Most commonly used nanosorbents and their functions.

| Different Nanosorbents          | Treatment Function                                                                 |References |
|--------------------------------|-----------------------------------------------------------------------------------|-----------|
| Carbon-based nanosorbents       | Nickel ions present in water                                                      | [162]     |
| Graphite Oxide                  | Removal of dyes                                                                   | [163]     |
| Regenerable polymeric Nanosorbents | Organic pollutants, inorganic contaminants of wastewaters                  | [164]     |
| Nanoclay                        | Hydrocarbons, Dyes                                                                | [165]     |
| Nano-metal oxides               | Different Heavy metals                                                            | [166]     |
| Nano-Aerogels                   | To remove the uranium from drinking water                                         | [167]     |
| Nano-iron oxides                | To eliminate the hormones and toxic pharmaceuticals material from water          | [168]     |
| Polymer Fibers                  | To remove the arsenic and other toxic metals                                      | [169]     |
Advantages, Disadvantages and Future Perspectives of Nanosorbents

The role of nanomaterials as sorbents in explaining ecological issues such as decontamination of wastewater received a great interest due to having remarkable physiochemical properties. These properties distinguish them in several fields as compare to conventional traditional sorbents. For an ideal sorbent to treat the pollutant very effectively in a short time, it should hold large surface area, excellent rate of adsorption, short time adsorption and equilibrium times. Similar to nanosorbents, nanomaterials got interest because of having nano-size which can hold excellent rate of adsorption with short time. Furthermore, nanosorbents that can be used as a separation medium in water decontamination to eliminate the organic, inorganic-based pollutants from polluted water are nanoparticles [170]. Literature review shows that a lot of efforts are already done for wastewater treatment and used nanomaterials as sorbent for efficient results. Some challenges are required to be addressed entirely for commercialisation purpose of the nano-size sorbents for water decontamination such as production scalability, as well as excellent adsorption measurements, selectivity, stability of material, operational duration of material, etc. However, there is an enormous need for an active approach to treat the wastewater and fabricate some new nanosorbents which could be applied to control toxic ions and compounds from wastewater [171]. The future prospects looking admirable, as scientific community working on advances knowledge and improving the adsorption mechanisms. In the modern world, researchers, consultants and officials are concerned about wastewater pollutant which holds health risks and they all are dedicated to find an effective explanation as concerning the nanomaterials should be used at industrial scale.

3. Self-Toxicity of Nanomaterials

Nowadays, nanomaterials have become most attractive and widely used material for different applications in various fields such as electronics, medicine, agriculture, wastewater treatment plants, energy generations and other sciences. These nanomaterials are doped metal oxides, doped carbon nanotubes (single and double walled), nanosorbents, etc. There were many reports available in literature which show that these nanomaterials served as a leading role in order to remove different pollutants from waste waters [172]. In addition to their importance, utilities and applications in different fields, especially in water treatment process, it is very important to know about their self-toxicity effects. There are studies which show the toxicity effect of few nanomaterials, as shown in Table 6. Moreover, few metal oxides show some toxic character at high and some, even at low concentrations [173,174]. Furthermore, the toxicity of CNTs is depending on different properties like length, surface area, distribution ratio, aggregation degree, initial concentration of material [175]. Furthermore, single walled CNTs are less toxic as compared to double walled [176]. They are associated for pulmonary inflammation, oxidative stress, granuloma in lungs, basic inflammation, apoptosis and fibrosis [177]. Similarly, in case of TiO$_2$, the toxicities of different composition ratio of TiO$_2$ depend upon initial concentration and time. Generally, it is considered as non-toxic even at a higher concentration for 24 h [178]. Currently, the studies by scientific communities on these nanomaterials are ongoing to see the toxic and side effects and try to find out the mechanisms with a focus on explaining the outlines of nanomaterials transport, degradation, elimination, accumulation, etc. Furthermore, nanomaterials can harm body through various sources. Therefore, there is a critical need to find out the effects of nanoparticles on health.
4. Applications of Nanomaterials

There were many opportunities to use engineered/modified nanomaterial for water treatment and many other industrial fields. Currently, nanomaterial attracts more attention of researcher in the field of wastewater treatment. The study trend in the field of nanomaterials is increasing day by day as we can observe through previously reported data. The number of publications in nanomaterial was less than 5% in 2005 but in 2019 number of reported works is more than 80% as shown in Figure 5 [184].

![Figure 5. Publication trends in field of nanomaterial for wastewater treatment.](image)

With emerging several aspects of nanomaterials, the wider environmental water resources effects are also considered. Such attentions might contain models to measure the significant advantages of reduction or inhibition of contaminants from engineering sources. Nanoscience expertise holds excellent potential for constant improvement for environmental protection. The present article has presented more indication to this matter and it has a response to what are the significant environmental impacts of this nanotechnology. For a quick assessment, the summary of nanomaterial applications for treatment of pollutants from water resources are briefly summarized in Table 7 [185].

**Table 6. Observation of self-toxic effect of some common nanomaterials.**

| Nanomaterials                                      | Observations                                                                 | References |
|----------------------------------------------------|-----------------------------------------------------------------------------|------------|
| Gold nanorods doped poly(styrenesulfonate) (PSS) composite | Non-toxic                                                                  | [177]      |
| TiO₂, Al₂O₃/Carbon black Composite                 | More toxic at micron particle sized                                         | [177]      |
| Hexadecylcetyltrimethylammonium bromide (CTAB) doped Au nanorode composite | High toxic at certain Concentration                                          | [178]      |
| Fe₂O₃ and carbon nanotubes Composite               | It showed toxic effects and damage DNA even at lowest concentration         | [179]      |
| Carbon, metal, Al₂O₃ composite                      | Concentration- and time-dependent.                                          | [180]      |
| CdSe Quantum dots doped with polyvinylcarbazole composite | Acute toxicity observed                                                     | [181]      |
| Single and Multi-walled carbon Nanotubes            | Toxicity increases when concentration rises beyond 15 µg/cm.                | [182]      |
| Au/Carbon composite                                 | Non-toxic at lower range.                                                   | [183]      |
| Ag/Carbon composite                                 | Time- and dose dependent but toxic                                          | [179]      |
Table 7. Summary of water treatments by using nanomaterial by different mechanisms [185].

| Nanoparticles (NPs) | Target Analyte | Treatment Mechanism | Limitation | Positive Aspect |
|---------------------|----------------|---------------------|------------|-----------------|
| TiO₂                | Organic Pollutants | Photocatalysis      | Higher operation cost, Tough to recovery, sludge production | Toxic less, Water insolubility, photostability |
| Fe                  | Heavy metals, anions, organic pollutants | Reduction, adsorption | Tough to recovery, sludge production, difficult sludge disposal, Health risk | In situ water remediation, Less cost, harmless to handle |
| Bimetallic NPs      | Dichlorination | Reduction, adsorption | Tough to recovery, sludge Production | Higher reactivity |
| Nanofiltration and nanomembranes | Organic and inorganic substances | Nanofiltration | High cost, membrane Fouling | Low pressure |
| Magnetite NPs       | Heavy metals, organic Compounds | Adsorption | Outside magnetically field needed for Separation | Easy separation, no sludge production |
| Metal-sorbing vesicles | Heavy metals | Adsorption | Re-use option, higher selective uptake profile, better metal affinity | Difficult to maintain stability |
| Micelles            | Organic pollutants | Adsorption | In situ treatment, excellent affinity for hydrophobic | Costly |
| Dendrimers          | Heavy metals, organic Pollutants | Encapsulation | Easy separation, renewable, high binding no sludge production | Costly |
| Nanotube            | Heavy metals, anions, organic pollutants | Adsorption | Dealing with pollution from water, Good mechanical properties, exclusive Electrical properties, Good chemical stability | High cost, lower adsorption process, Tough to recovery, sludge production, Dangerous Health risk |
| Nanoclay            | Heavy metals, anions, organic pollutants | Adsorption | Lower cost, Exclusive structures, long stability, recycle, Higher sorption capacity, Informal recovery, better surface and pore volume | Sludge production |

(1). Nanomaterials are very efficient in removing arsenic from drinking water when titanium nanoparticles and exchange based resin material impregnated with iron hydroxide material. The researcher also studied that titanium served as an adsorbent to remove arsenic from water present in packed bed reactor setting. In some developed countries, iron oxide is used as coated sand to remove arsenic from drinking water [186].

(2). Different nanomaterial like magnetic and carbon nanotubes can be served as sensor components due to having remarkable physical, electrical and chemical properties. Therefore, these sensors may offer opportunity to monitor water quality. Nanomaterial-based sensor is used to detect different pollutants because there have optical properties that make sensor more selective and sensitive to detect the pollutants [187].

(3). Recently, WHO reported that almost 783 million populations are suffering from fresh drinking water. Boschi-Pinto et al. stated that children deaths ratio of nearly 1.87 million is only due to water diseases [188]. Few conventional techniques are not suitable in underdeveloped countries because high investment is required for this project for maintenance expenses, and many other problems. Furthermore, generally people carry their water from another area and then save it for many days because there is no proper supply of drinking water. During collection and transport of water, there are chances of water contaminations. An efficient method of ceramic water filters (CWFs) provides an offer to treat these kinds of water infections (pathogens). Recently, CWFs are equipped by firing and pressing of flammable material and clay with silver nanoparticles [189]. The filter is produced by pressure and then dried air fired in a kiln. Therefore, a ceramic material produces filtered or clean water but by using this process removal is not possible up to high level. Silver doped nanomaterials could be used to get a higher percentage of pathogen’s removal from water due to having antimicrobial properties. Ag solutions are used by brushing on CWF. It was observed that 80% of CWFs industries used Ag nanoparticles doped with some other
materials. The Ag nanoparticles give remarkable results in order to remove different pathogens from drinking waters [190].

(4). Water pollutants are responsible for environmental pollutions. The polymer-based nanomaterial helps in environmental protection. Reported studies show that the purification of water using polymer material could be attained by nanoclay incorporation. The hydrophobicity enhancement helps to promote nanocomposite properties. Applications in contact with moist environments clearly indicate benefits from nanomaterial incorporation of nanoclay particles [191].

(5). The research is on the way to produce nanosorbents for different metals and organic compounds. Nanomaterial can act as sorbents like carbon nanotubes, zeolites and self-assembly layers on mesoporous supports, which control mesoporous ceramics with a sorbent that indicate efficient removal process of metals and anions from drinking water [192].

(6). Some nanomaterial has high antimicrobial activity properties. This type of material includes AgNPs, fullerene, TiO$_2$, CNT based nanocomposite, etc. and they contain several properties like mild oxidant, inertness to water and produce safe by-products [193].

(7). Now a days, many pollutants are present in water resources such as organics-based substances and even they present in trace amount which are very dangerous for human health. Usually, the chlorination and flocculation processes are used for removing water pollutants. There are some drawbacks in these conventional filtrations processes. These kinds of systems show less efficiency to remove pollutants entirely and also produces some sludge in water recourses which also creates big issues in environment pollution [194]. Therefore, to keep safe from sludge nanomembranes, it was employed because it does not allow any solid particle to pass into water and reduce the chances of sludge production in water resources. This reason makes nanomembrane more prominent in market than other methods. Certainly, some improvements are required to make it completely perfect technique.

(8). Metal oxides nanoparticles also play a very good role as catalyst in different oxidation reactions. They show strong catalytic reactivity towards pollutant molecules and change these pollutants into environmentally suitable products [195,196]. Some unique properties are present of these nanomaterials like nano size, high reactivity and greater surface area. Specially, TiO$_2$ photocatalysis plays a vital role in removing different impurities from surface water as shown in Figure 6.

![Figure 6. Schematic illustrating of TiO$_2$ photocatalytic process (Adapted with permission from Jurnal Teknologi) [197].](image-url)
The summary/mechanism of pollutant removal by using TiO$_2$ nanoparticles as nanophotocatalyst is shown in Table 8.

Table 8. Observation of different pollutant removal by TiO$_2$ nanophotocatalyst.

| Nanophotocatalyst | Target Analyte     | Initial Concentration of Pollutant | Remediation Efficiency | Doses of Nanophotocatalyst | References |
|-------------------|--------------------|------------------------------------|------------------------|----------------------------|------------|
| TiO$_2$           | Nitrobenzene       | 50 mg/L                            | 100                    | 0.1M                       | [185]      |
| TiO$_2$           | Methyl orange      | 30 mg/L                            | 100                    | 3 g/L                       | [185]      |
| TiO$_2$           | Rhodamine 6G       | 125 mmol/L                         | 90                     | 0.1%(w/v)                  | [185]      |
| TiO$_2$           | Parathion          | 50 mg/L                            | 70                     | 1000 mg/L                  | [198]      |
| TiO$_2$           | Benzene            | 45 mg/L                            | 72                     | 5 g                         | [199]      |
| TiO$_2$           | Phenol             | -                                  | 100                    | 1.8 g/L                     | [185]      |
| TiO$_2$           | Rhodamine B        | $1.0 \times 10^{-3}$ M             | 97                     | 50 mg/50ml                  | [185]      |
| TiO$_2$           | Toluene            | 45 mg/L                            | 71                     | 5 g                         | [185]      |
| TiO$_2$           | Basic dye          | 20 mg/L                            | 80                     | 1.22 g/L                    | [200]      |
| TiO$_2$           | 4-chlorophenol     | $1.0 \times 10^{-3}$ M             | 99                     | 25 mg/100ml                 | [201]      |
| TiO$_2$           | Procion Red MX-5B  | 10 mg/L                            | 98                     | (2.0mg TiO$_2$ (30%))       | [202]      |

(9). Different types of pollutants such as organic pesticides, organic dyes, pharmaceutical drugs, etc. are photodegraded by many researchers under several conditions such as choice of UV or Visible light, doped nanoparticles or undoped, metal/non-metal doping, etc. According to literature, as shown in Table 9 indicate clearly that modified or doped form of TiO$_2$ can give better results especially in photodegradation of pollutants. Table also demonstrates that the efficiency of doped-TiO$_2$ in visible light showed better results as compared to UV light.

Table 9. Observation of different pollutant removal by Doped-TiO$_2$ nanophotocatalyst.

| Nanophotocatalyst | Target Analyte    | Doping Agent | Remediation Efficiency | Source of Light | References |
|-------------------|-------------------|--------------|------------------------|-----------------|------------|
| TiO$_2$           | Glyphosate        | Mn           | 80                     | Visible         | [134]      |
| TiO$_2$           | Methylene Blue    | Mn           | 75                     | Visible         | [33]       |
| TiO$_2$           | Methylene Orange  | Cu           | 100                    | Visible         | [203]      |
| TiO$_2$           | Methylene Blue    | S, I         | 90                     | Visible         | [204]      |
| TiO$_2$           | Formaldehyde      | N, S         | 65                     | Sunlight        | [204]      |
| TiO$_2$           | Ramazol Brilliant Blue | La | 72                     | Visible         | [204]      |
| TiO$_2$           | Gentian violet    | Mn           | 84                     | Visible         | [194]      |
| TiO$_2$           | Acid Red 88       | Mo           | 77                     | Visible         | [194]      |
| TiO$_2$           | Rhodamine B       | P            | 93                     | Sunlight        | [205]      |
| TiO$_2$           | Methylene Blue    | Fe           | 72                     | UV              | [205]      |
| TiO$_2$           | Methylene Orange  | Fe           | 99                     | UV              | [205]      |

5. Nanomaterial Challenges for Water Treatment

Currently, the emerging nanomaterial possesses some challenges in the field of wastewater treatment [206,207]. Nanomaterial provides several possibilities of treatment of wastewater and they
contain different kinds of substances which are distinct on the basis of the particles morphology. The developments regarding the commercial applications of nanomaterials is too quick and production of nanomaterial is increasing at a global level [58, 208]. Nanomaterials are used for purification of polluted water through different methods such as photocatalytic, adsorption, and nanosorbents [209, 210]. These methods need some modifications to work more effectively. Moreover, understanding of risk pretended by nanotechnology has not improved as quickly as research has giving possibilities to different applications of nanomaterials. The major challenge is the lack of information about the nanomaterial and how nanomaterials are released into environment, how they travel into water, how they start to exist in water [196]. Another challenge is related to human health because these types of material have some adverse effects/toxicological effect. The reported studies show that nanomaterials may cause some health issues but still research is going on. It is not easy to give a conclusion and ongoing research requires some conducting experiments at appropriate concentrations and more about toxicological studies. The membrane process is also effectively used wastewater treatment but there were very few reported studies about this process. The major challenge is the use of the membrane for fouling process and water treatment because after performing work/filtration, their pores may block, and the efficiency starts to decrease. In case of nanosorbents, the reusability is the main drawback, so there is need to synthesize such types of nanomaterials which can efficiently remove the pollutants from wastewater and after that the recovery process of these nanosorbents should be very easy. The United State Environmental Protection Agency (USEPA) found some basic challenges in order to remove nanoparticles using a process of water treatment [210–213]. (a) What is the mechanism of removing nanoparticles from wastewater? (b) What is the effect of nanoparticles on other waste substances during wastewater treatment? (c) How coagulation, carbon adsorption, etc. methods are effective in working. Moreover, water contains some pollutants and after treatment by the above mentioned methods, they degrade or are decomposed. There is a basic need to design an experiment for finding the intermediate products during these processes. Furthermore, constant development in methodology is needed to evaluate nanomaterials with low cost and it should be appropriate for complex nanomaterials.

6. Conclusive Remarks and Future Perspectives

Water distinguishes and makes our planet superior as compared to other planets. Though the worldwide available supply of pure water is high to meet all existing and predictable water demands. There are several areas where the drinking water resources are insufficient to fulfill the basic, economic and domestic developmental needs. In such areas, the insufficient fresh water to fulfill human water need and sanitation requirements is certainly a limit on human health and for other living creatures. Scientific community/research institutes must find a path to eliminate these limitations. Moreover, the world is facing several challenges in doing that, especially given a fluctuating and undefined future environment, a fast-rising population that is driving enlarged community and financial growth, urbanization and globalization. How superlatively overcomes on these challenges which entails exploration in all features of water management. The trend of nanomaterial for water pollutant treatment is rapidly increasing in this modern era due to very horrible conditions of water and demand for fresh water in the whole world. There is an important need for innovative progressive water treatment approaches, in specific to certify a high class of water for drinking purpose, remove micro/macro pollutants and increase industrial production developments through flexibly modifiable water treatment approaches. Nanotechnology has proved great achievement for controlling water purification challenges and makes some future advancement. Nanomaterial approaches like nanosorbents, nanostructured catalytic membranes, etc. are very efficient, less time required, less energy and eco-friendly techniques but all these methods are not cheap, and they are not used yet for commercial purpose to purify the wastewater at a large scale.

Nanomaterials show high efficiency due to having high rate of reaction. However, there are still some weaknesses that must be negotiated. Up to now, no operational digital monitoring techniques
exist that offer consistent real-time measurement facts on the superiority of nanoparticles which are existing in small amounts in H$_2$O [212]. Furthermore, to reduce the health risk, some research institutes and international research communities should prepare proper guidelines to overcome this issue. Another, further mechanical restriction of nano-engineered water approach is that they are infrequently flexible to mass developments, and at present-day, in several cases are not modest with conservative treatment approaches [213]. However, nano-engineered materials provide excessive potential for water revolutions, in specific for decentralized water treatment technologies, point-of-use strategies, and seriously degradable pollutants. Furthermore, there is a great need to synthesize some modified nanomaterials which should be effective, having high efficiency, easy to handle and eco-friendly. It is also necessary to take the cost challenges and commercialization of these technologies for wastewater treatment. The different applications of nanomaterial can provide a tremendous offer in order to supply drinking water to whole world.

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