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RESEARCH PAPER

Reviewing of Using Nanomaterials for Wastewater Treatment

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Abstract
Increasing the pollution rate of water sources is one of the most severe issues that the world faces. This issue has stimulated researchers to investigate different treatment methods such as adsorption, chemical precipitation, membrane filtration, flocculation, ion exchange, flotation, and electrochemical processes. Among them, adsorption has gained broad interest due to its ease of operation, low cost, and high efficiency. The critical factor of the successful adsorption treatment process is finding attractive adsorbents with attractive criteria such as low cost and high adsorption capacity. In the last few decades, nanotechnology has attracted much attention, and numerous nanomaterials have been synthesized for water and wastewater treatment. This work provides a quick overview of nanomaterials, which have been investigated for water remediation as adsorbent and photocatalyst. This work reviewed 120 articles to provide a critical review to determine the limitation of using nanomaterials in water treatment at the commercial scale.

Keywords: Graphene; Nano-sheet; Nanoparticles; Metal oxides; Adsorption.

INTRODUCTION

Treatment of water is an essential process due to the crucial role of water in the life of all creatures. There is a rapid increase in the pollution rate due to the fast industrial development, which increases the amount of wastewater released to water sources. In addition, the rapid increase of the world population is another reason for increasing the pollution rate (Ali and Aboul-Enein, 2004). Expanding the world population causes a massive demand for water for domestic, industrial, and agricultural fields, which increases the wastewater generated from these sectors. There are different pollutants, such as heavy metals, pesticides, dyes, and toxic materials. When these materials are released or reach water resources, the results would be pollutant water that causes vital impacts on all creatures. These pollutants cause a limitation in using water by humans and animals. Thus, the treatment processes are essential to eliminate the negative impact of these pollutants on the life of all creatures and the environment.

Several techniques have been used to treat wastewater. These techniques can be classified into three main categories which are physical, chemical, and biological treatment. Under these

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classifications, several methods were used, such as solvent extraction, oxidation, sedimentation, gravity separation, ion exchange, micro and ultrafiltration, reverse osmosis, precipitation, coagulation, electrolysis, flotation, adsorption, evaporation, distillation, and electrodialysis. Among these methods, adsorption has attracted much attention due to the availability of numerous types of adsorbents, low cost of the process, simple operation procedure, and the ability to use it for different pollutants such as inorganic, soluble/insoluble organic, and biological contaminants.

Despite these advantages, adsorption has certain drawbacks, such as its limitation to compete with other methods at industrial levels. The main reason for this limitation is the lack of excellent adsorbents that provide excellent removal with an extended performance stability to avoid the replacement process and the expected cost and time. In addition, it is impossible to use one adsorbent for all kinds of pollutants, which limits the commercial application of this method. It has been reported that cost-effectiveness comparison of the different treatment methods puts the adsorption process in front of other methods (Santhosh et al., 2016). Despite the drawbacks of the adsorption process, it is considered a promising method that could be adopted widely on the commercial level in the future. Most of the investigations in this field focused on performing the treatment process in a batch mode (Matschullat, 2000). Activated carbon was the most material that has been investigated as an adsorbent due to its high surface area, which increases its adsorption capacity (Mohammed Ali et al., 2022). However, due to its high manufacturing cost, there is a need to find a more cost-effective adsorbent material to replace activated carbon. Several materials have been investigated, such as agriculture wastes, algae, and nanomaterials (Alalwan et al., 2021b; Mohammed Ali et al., 2022).

The rapid development in the nanotechnology field increased its involvement in different applications, covering almost all science and technology sectors (Afluq et al., 2021; Mohammed et al., 2021). Nanomaterials have been synthesized and used as adsorbent material for water and wastewater treatment (Gautam and Chattopadhyaya, 2016). Recently, researchers paid much attention to nano adsorbent materials due to the high promise that they have shown. This promise represents a vital opportunity to develop practical solutions for scaling the adsorption process to be compatible with commercial requirements. The significant number of publications that reviewed or reported experimental results in this field (Al-Furaijia et al., 2021; Kalash et al., 2020a; Singh and Batra, 2018; Xu et al., 2012) indicates the importance of providing new solutions for the water treatment sector. Thus, this review article focuses on the work published in the last ten years and briefly covers the technical applicability of nanomaterials as adsorbents to treat water and wastewater. This work aims to summarize and present the significant findings of different nanomaterials used in the treatment process. This article provides essential insights into this field to enhance the knowledge about this topic.

Nanomaterials as adsorbents for water and wastewater treatment

Nanoparticles have been used in numerous applications in different sectors such as industry, medicine, energy, and the environment (Alalwan and Alminshid, 2020; Alalwan and Alminshid, 2021; Alalwan et al., 2021a; Alminshid et al., 2021). The application of nanoscale materials as adsorbents for pollutants has attracted researchers due to their high active surface with high porosity and small size, which resulted in increased surface area. These advantages increase their adsorption capacity and enable nano adsorbents to capture pollutants with different molecular sizes, hydrophobicity, and speciation attitudes (Amrane et al., 2020). Nano adsorbents have several unique criteria, such as their rapid adsorbent rate, considerable pollutant-binding capacities, and regeneration ability after being exhausted (Yang and Xing, 2007). Due to these criteria also, nano adsorbents show adorable properties, such as catalytic potential and strong reactivity, which distinguish them from conventional materials. In addition, the involves of highly porous nanoparticles in the adsorption of pollutants have gained more attention. As an example, modified silica nanoparticles were used for phenol adsorption from aqueous solutions achieving high removal percentage of 85% at an initial concentration of 10 mg/L of phenol (Kalash et al., 2020b). To facilitate the final separation of nano-adsorbents materials to reduce the health risk, nanomaterials can be used on their own or incorporated with other adsorption material with a bigger size as a base material as will be discussed in the following sections.

Carbon-based nanomaterials

As mentioned before, the most important criteria for adsorbent materials are high surface area, pore-volume, and considerable functionality. Thus, the focus is on developing porous materials such as activated carbon, zeolites, pillared clays, mesoporous oxides, polymers, and metal-organic frameworks. These materials have shown different efficiencies in removing contaminants from the water, air, and soil (Gupta and Bhattacharyya, 2012). Carbon-based adsorbents have attracted much attention due to their high adsorption capacity and thermal stability. Several types of carbon-based adsorbents have been investigated, such as activated carbon, fullerenes, carbon nanotubes, and graphene (Rao et al., 2007). Among them, carbon nanotubes (CNTs) and fullerene have been widely investigated, but their large-scale use is limited due to economic reasons. Thus, lowering the designing cost of these materials is the biggest challenge that faces their adoption for commercial use.

Generally, CNTs consists of cylindrical shape rolled up in a tube-like structure. There are two types of CNTs, which are single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). SWCNTs consist of a single graphene sheet with a roll-up, while MWCNTs consist of multiple graphene roll-up sheets, as shown in **Figure 1** (Xu et al., 2018).

CNTs have higher sorption capability and efficiency than ordinary granular or powder-activated carbon due to their controlled pore size distribution and the higher surface-active sites to volume ratio. The adsorption capacity of CNTs correlated strongly to their surface functional groups and the nature of the adsorbate. Specifically, the presence of acidic surface groups such as carboxylic, phenolic, and lactonic groups enhances the uptake of polar compounds (Wang et al., 2008). On the other hand, nonpolar compounds such as polycyclic aromatic hydrocarbons are attracted more to unfunctionalized CNT (Stafiej and Pyrzynska, 2008). The adsorption mechanism of CNTs usually involves chemical interaction for polar compounds, while physical interaction is dominant for nonpolar compounds. Table 1 shows the significant results reported in the literature for adsorption processes using CNTs.

Graphene is another form of carbon nanomaterial that has attracted considerable attention. In the last decade, there was a noticeable increase in the application of graphene and graphene-based nano adsorbent for ecological treatment due to their attractive criteria, which assist in increasing the efficiency of several environmental processes. Using graphene as a carbon-based nanocomposite depends on different factors such as processability, cost, and environmental implications of each material. Graphene oxides (GO) have attracted more attention than

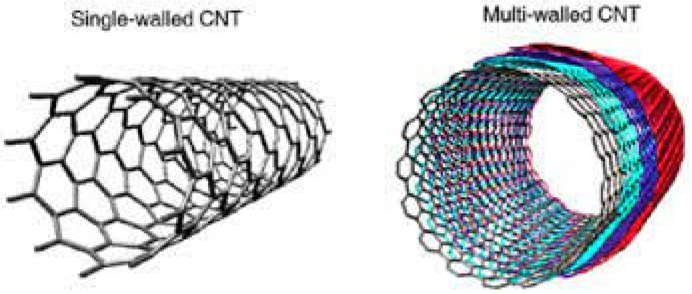


Fig. 1. SWCNTs and MWCNTs shapes (Xu et al., 2018).

Table 1. Significant adsorption results using CNTs as adsorbent materials

No.	Type of CNTs	Adsorbate	Maximum capacity of adsorption (mg/g)	References
1	Polymer coated MWCNTs	Cu^{+2}	189	(Hosseinzadeh et al., 2018)
2	MWCNTs	Co^{+2}	78.94	(Dehghani et al., 2020)
3	Alkali-activated MWCNTs	Methylene blue (MB)	399	(Ma et al., 2012)
4	Untreated MWCNTs	MB	59.7	(Wang et al., 2012)
5	Hydroxylated and pristine MWCNTs	Sulfamethazine	13.31 and 24.78	(Yang et al., 2015)
6	Untreated MWCNTs	Tetracycline (TC)	269.54	(Zhang et al., 2011)
7	MWCNTs	TC	192.7	(Álvarez-Torrellas et al., 2016)
8	CNTs-C@Fe-chitosan composite	TC	104.0	(Álvarez-Torrellas et al., 2016)
9	CNTs	Pb^{+2}	17.44 at pH=7.0	(Stafiej and Pyrzynska, 2008)
10	CNTs (HNO_3)	Pb^{+2}	49.95 at pH=7.0	(Li et al., 2002)
11	SWCNTs	Ni^{+2}	9.22 at pH=7.0	(Lu and Liu, 2006)
12	MWCNTs	Ni^{+2}	7.53 at pH=7.0	(Lu and Liu, 2006)
13	Untreated SWCNTs	Reactive red 120	426.49	(Bazrafshan et al., 2013)
14	Oxidized SWCNTs	Basic red 46	49.45	(Moradi, 2013)
15	SWCNTs	4-Chloro-2-nitrophenol	1.44	(Mehrizad et al., 2012)
16	MWCNTs	4-Chloro-2-nitrophenol	4.42	(Mehrizad et al., 2012)
17	Untreated SWCNTs	Dissolved organic matter (DOM)	26.1 – 20.8	(Lou et al., 2011)
18	KOH activated MWCNTs	Toluene, ethylbenzene, and m-xylene	87.12, 322.05, and 247.83	(Yu et al., 2012)
19	MWCNTs	Methyl orange	52.86	(Zhao et al., 2013)
20	Chitosan/Fe_2O_3/MWCNTs	Methyl orange	66.90	(Zhu et al., 2010)
21	Calcium alginate/MWCNTs	Methyl orange	12.5	(Zhu et al., 2010)

ordinary graphene due to the lower manufacturing cost of GO (Santhosh et al., 2016). Graphene is an ideal adsorbent for water treatment and a promising alternative for CNTs due to several advantages that graphene offers over CNTs. From these advantages, single-layered graphene materials have two basal planes active for uptake, while it is hard for adsorbate to reach the inner walls in CNTs (Sitko et al., 2013b). In addition, the synthesis processes of GO and reduced GO (rGO) are quickly done by chemical exfoliation of graphite without using any catalyst, and no further purification step is needed.

Furthermore, GO has plenty of oxygen-containing functional groups, eliminating the need for acidic treatments (Zhao et al., 2011a). This is an essential criterion that CNTs lacks. Therefore, acidic treatment is mandatory to supply a hydrophilic feature and reactivity to CNTs because those functional groups play crucial roles in the adsorption of metal ions. Besides these essential advantages, graphene-based materials possess common attractive properties such as high surface area and electron-rich environment. GO showed promising efficiency in removing metal ion complexation due to the powerful functional groups on the GO surface. The removal process is done through electrostatic and coordinate approaches (Yang et al., 2010). Several investigations have been done on applying graphene-based materials to remove inorganic species from wastewater (Zhao et al., 2011a). Many of these investigations have determined the ability to use GO as a typical adsorbent for metal ions in aqueous solutions based on the cost, process efficiency, and environmental implication (Sitko et al., 2013a). Specifically, GO propose more realistic potentials compared to ordinary graphene due to GO's lower manufacturing costs. Composites of GO and metal oxides have shown promising efficiency for removing metal ions and organic pollutants from aqueous solutions, as shown in Table 2, which listed some of the significant results reported in the literature. However, there is still a lack in investigating the toxicological effect of GO.

Carbon is also recently involved in manufacturing of some other adsorbents such as MXenes, which are a group of two dimensions (2D) thin layer structure materials bonded to each other. MXenes basic formula is $M_{n+1}X_nT_x$, where M, n, X, and T are a transition metal, number ranges between 1 to 3, carbon or nitrogen, and a functional group, respectively (Sun et al., 2017). The preparation of MXene involves etching the middle layers with acids (Szuplewska et al., 2020). MXenes have received great attention in the last years due to their attractive properties, such as the 2D shape, strong negative charge, and high availability of the activation groups. However, their manufacturing cost is still high compared with other adsorbents (Kadhom et al., 2022).

Metal-oxide based nanomaterials

Several metal oxides in the nanoscale have been addressed as promising adsorbent materials such as the oxides of manganese, aluminum, iron, titanium, magnesium, and cerium (Wang et al., 2020a) due to their high surface area and significant reactivity resulting from their nano-size

Table 2. Significant adsorption results using GO or GO-based materials

No.	Adsorbent	Adsorbate	Maximum capacity of adsorption (mg/g)	Ref.
1	GO-$MnFe_2O_4$	Pb^{+2}	673	(Kumar et al., 2014)
2	GO-EDTA	Pb^{+2}	479	(Madadrang et al., 2012)
3	GO/silica/Fe_3O_4	Pb^{+2} and Cd^{+2}	333.3 and 166.7	(Wang et al., 2013)
4	Reduce GO/$COFe_2O_4$	Pb^{+2}	299.4	(Zhang et al., 2014)
5	SiO_2-GNs	Pb^{+2}	113.6	(Hao et al., 2012)
6	GO/Mn-doped Fe^{+3} oxide	Cd^{+2} and Cu^{+2}	87.2 and 129.7	(Nandi et al., 2013)
7	TiO_2/GO	Pb^{+2}	65.6	(Madadrang et al., 2012)
8	GO/Fe_3O_4/sulfanilic acid	Cu^{+2}	50.7 and 56.8	(Hu et al., 2013)
9	GO/Fe_3O_4/sulfanilic acid	Cd^{+2}	55.4	(Hu et al., 2014)
10	GO/Fe_3O_4	Cu^{+2}, Pb^{+2} and Cd^{+2}	23.1, 38.5 and 4.4	(Hur et al., 2015)
11	GO	Pb^{+2}	35.6	(Lee and Yang, 2012)
12	TiO_2-graphene sponge	Tetracycline	1805	(Zhao et al., 2015)
13	GO	Doxycycline	398.40	(Gao et al., 2012)
14	GO	Tetracycline	313.48	(Gao et al., 2012)
15	GO	Tetracycline	381.77	(Ghadim et al., 2013)
16	Single-layer GO	Ciprofloxacin	379	(Chen et al., 2015)
17	GO sponge	Methylene blue	397	(Liu et al., 2012a)
18	GO	Methylene blue	351	(Bradder et al., 2011)
19	Porous graphene hydrogel	Ciprofloxacin	235.6	(Ma et al., 2015)
20	GO	Oxytetracycline	212.31	(Gao et al., 2012)
21	KOH-activated graphene	Ciprofloxacin	194.6	(Yu et al., 2015)
22	Fe_3O_4/GO hybrids	Methylene blue	167.2	(Xie et al., 2012)
23	GO-α-γ-Fe_2O_3	glyphosate	46.8	(Santos et al., 2019)

Table 3. Adsorption capacities of NMOs for metal removal.

No.	Adsorbent	Adsorbate	Maximum capacity of adsorption (mg/g)	Ref.
1	Goethite (α-FeOOH)	Cu^{+2}	149.25	(Grossl et al., 1994)
2	Hematite (α-Fe_2O_3)	Cu^{+2}	84.46	(Chen and Li, 2010)
3	Maghemite γ-Fe_2O_3	Cu^{+2}	26.8	(Hu et al., 2006)
4	ZnO	Pb^{+2}	6.7	(Ma et al., 2010)
5	CeO_2	Pb^{+2}	9.2	(Cao et al., 2010)
6	TiO_2	Pb^{+2}	401.14	(Engates and Shipley, 2011)
7	Modified Al_2O_3	Pb^{+2} and Cd^{+2}	100 and 83.33	(Afkhami et al., 2010)
8	SiO_2	Cu^{+2}, Ni^{+2}, and Pb^{+2}	6.35, 0.880, and 5.20	(Manyangadze et al., 2020)
9	Fe_3O_4	Cu^{+2} and Pb^{+2}	25.42 and 140.9	(Manyangadze et al., 2020)

(Hua et al., 2012). Recent investigations demonstrate that many nano metal oxides (NMOs) offer attractive adsorption attitudes towards heavy metals in terms of adsorption capacity and selectivity, which helps remove toxic metals efficiently and achieve the prim standards (Deliyanni et al., 2009). NMOs have other advantages, such as the fast adsorption kinetics for different pollutants. On the other hand, there are some limitations on using NMOs, such as their low stability due to the increase in their surface energy resulting from decreasing the size of the particles to the nanoscale. This high surface energy makes NMOs tend to agglomerate due to the interaction forces such as van der Waals (Pradeep, 2009). Consequently, NMOs would partially or even totally lose their elevated capacity and selectivity. Another disadvantage of NMOs is the disability of using them in fixed beds or any other flow-through systems due to several reasons such as their poor mechanical strength, high-pressure drops, and the complexation of their separation from aqueous systems.

To overcome these obstacles, researchers have been created larger size composites by impregnating NMOs into porous supports such as natural materials (including bentonite and sand), activated carbon, and synthetic polymeric hosts (cross-linked ion-exchange resins as an example) (Ndolomingo et al., 2020; Yang et al., 2018). Also, magnetic NMOs attracts researchers due to their ability to remove them from aqueous solutions when applying magnet field on them (Zhang et al., 2019). Combining magnetic NMOs with GO or graphene nanosheets (GNs) provides an efficient solution to the separation issue associated with graphene (Wang, 2017). Also, supporting these NMOs can prevent or lower the agglomeration and restacking of the graphene sheets, which enhances the surface area and increases the adsorption capacity (Yang et al., 2019). In addition, magnetic nanocomposite adsorbents offer considerable isolation from the treatment process for recycling or regeneration (Zhao et al., 2011b). The ability to recycle or regenerate the adsorbents is crucial to enhance the efficiency and the cost effect of any treated process. Table 3 shows some of the significant results reported in the literature on using NMOs as adsorbents. These results show some differences in the adsorption capacities, which might be due to the differences in the process conditions such as pH, adsorbate, and temperature or due to the synthesis conditions that impacted the characters of the NMOs such as the surface area, particle size, and surface chemistry.

Hydrogels (HGs)

Hydrogels have received great attention from the researchers in the wastewater treatment field in the last years. HGs are polymeric networks with very efficient functional groups with strong binding affinity for different pollutants in water. Their tendency to adsorb high water capacity inside its three-dimensional reticulated networks encourages researchers to incorporate it as an intelligent material for water treatment (Sinha and Chakma, 2019).

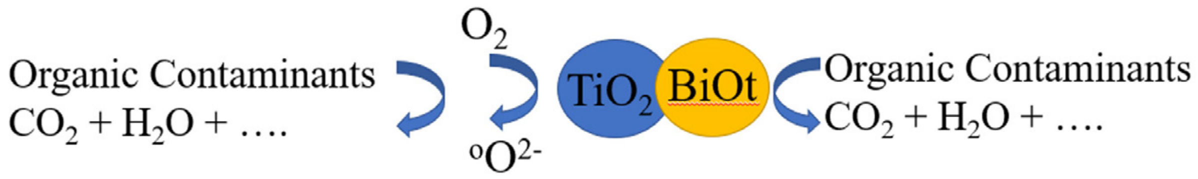


Fig. 2. A schematic diagram explaining the mechanism of treating organic pollutants through a reverse micro-emulsion method using hybrid NPs synthesis of bismuth oxyiodine/TiO_2 (Liu et al., 2012b).

HGs have high efficiency for the adsorption of a broad type of organic and inorganic contaminants, such as metal ions, noxious dyes, and pestilential pharmaceutical wastes (Tang et al., 2018). Encouraging results for the application of HGs for capturing and immobilization of activated sludge, including microbes, were reported (Yu et al., 2018). HGs are fabricated from a series of natural and synthetic monomeric and polymeric units such as starch, cellulose, acrylamide (Zhang et al., 2016), polysaccharides viz. chitosan, alginate (Sahraei and Ghaemy, 2017), rice husk (De France et al., 2017), gums (Ding et al., 2018), cellulose (Gharekhani et al., 2017). Natural polysaccharides based HGs have some more advantages than that synthesized from the synthetic base material such as their availability, bio-renewability, and environment-friendly impact. These gels contain hydrophilic groups, which are hydrated when contacting water resulting in a three-dimensional gel structure (Wan et al., 2016).

Nanomaterials as photocatalysts

In the last decades, much attention was paid to the treatment of toxic organic compounds by photocatalytic degradation method, especially for dyes with TiO_2 nanoparticles (NPs) using UV or visible light as an alternative method for the traditional biological processes which have low efficiency in degrading these toxic compounds (Hoffmann et al., 1995; Hu et al., 2003). In addition to UV-irritation, visible light irritation of TiO_2 NPs has also gained great attention recently (Asahi et al., 2001; Montallana and Vasquez Jr, 2021). Precisely, mesoporous nanocomposite consists of Au/TiO_2 microspheres that can enhance visible light photocatalytic degradation of organic molecules (Rahman et al., 2018). Liu et al. synthesized a bismuth oxyiodine/TiO_2 hybrid NPs with prominent photoinduced initiation under visible light eradiation, where the organic pollutants go through photocatalytic detoxify to CO_2 and H_2O under visible light eradiation as shown in **Figure 2** (Liu et al., 2012b).

Savage N. and Diallo M. S. synthesized TiO_2-SiO_2 nanocomposite inside the pore structure of a carbonating stone, resulting in a self-cleaning structure material as explained in **Figure 3** (Pinho et al., 2013). This nanocomposite showed outstanding performance in transforming organic compounds to CO_2 and H_2O using UV light. Furthermore, the formed stone showed better mechanical performance and durability than conventional TiO_2. Despite the advanced knowledge in this field, more work is required to scale up the TiO_2-based photocatalytic degradation process to the commercial level (Savage and Diallo, 2005). Different design parameters must be determined to scale up the multiphase photocatalytic process. One of the most critical parameters is the regularity in the delivery of light and light intensity inside the photocatalytic reactor due to the limitation of the light penetration depth in treating suspensions, which is approximately two centimeters. In addition, it is imperative, to provide a high surface area for photocatalyst per unit of reactor volume. These aspects require technical developments to scale up the laboratory-tested materials to the pilot-scale and finally to the commercial-scale level. Thus, several aspects should be addressed well, such as installation of the photocatalyst, decreasing of light loss, enhancing reactant-catalyst contact, process temperature, mass transfer, flow pattern, and mixing, reaction kinetics.

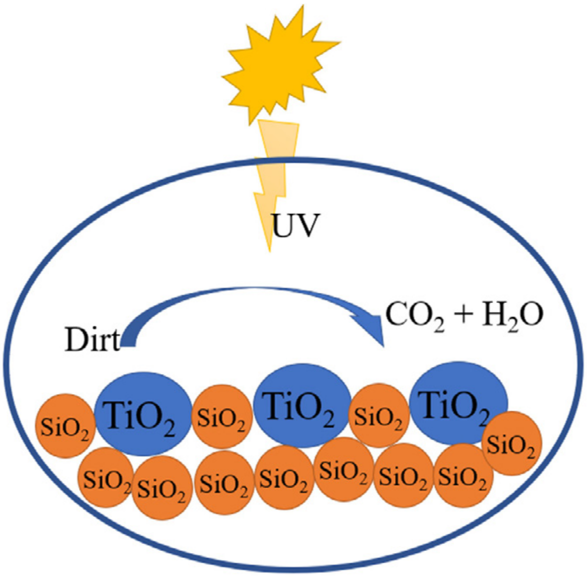


Fig. 3. Schematic diagram explaining the porous structure of carbonate stone covered the TiO_2-SiO_2 nanocomposite synthesized by simple spraying of a sol containing silica oligomers and TiO_2 NPs (Pinho et al., 2013).

The photocatalytic degradation mechanism of dyes was investigated by several researchers, and several proposals were suggested. One of these proposals assumes that the first step in the oxidation process of organic compounds is initiated by the free radicals resulting from the electron-hole (e−/h+) pairs at the photocatalyst surface (Kormann et al., 1991). Another proposal suggests that the first step is the adsorption of the organic compound by the photocatalyst surface followed by the reaction of the organic compound with irritating superficial e−/h+ pairs or OH radicals, which results in the final products (Ollis et al., 1984). A diversity of reaction mechanisms based on both solution-phase and surface adsorbed species leads to various photodegradation kinetics. One of the most remarkable factors in deducting the degradation rates is the adsorption step of the organic compounds (Mamy et al., 2015). Although a promising photocatalytic efficiency on eliminating different organic compounds was reported for semiconductor materials, but their utilization was limited commercially due to some drawbacks such as the low stability of these materials and the low efficiency of the illumination of light. However, group II−VI semiconductors have been known as promising compatible nominees for photocatalysts.

Several researchers have been explored novel materials with high stability and degradation efficiency for different organic compounds under visible light (Li et al., 2011; Yu et al., 2014). Shen et al. reported promising activity for prepared ZnCdS NPs uploaded on a two-dimensional platform of rGO sheets by a one-pot ionic-liquid-assisted hydrothermal method regarding photocatalytic degradation of organic pollutants (Shen et al., 2015). In general, three parameters that play the leading role in providing composites with their high efficiency for the photocatalytic process. These parameters are light irradiation absorption, pollutant adsorption, and charge transportation and separation (Alansi et al., 2018; Kumar et al., 2017). Although utilizing TiO2 NPs in photocatalytic degradation of organic pollutants has been widely studied, the insufficient utilization of solar energy and the need for UV irradiation to activate the process limits its commercial application. Thus, ZnCdS, can provide a better response to visible light than TiO2 NPs due to the higher negative value of its valence band energy, which is lower than that of TiO2 NPs by 1.0 eV. The lower value of the valence band energy resulted in decreasing the bandgap energy, which increased the response to visible light (Hwang et al., 2002). However, due to the unique characteristics of graphene, it would not only enhance the separation and transport of photocarriers but also can result in an elevated conduction band position with a more powerful reductive force.

Different percentages of rGO uploaded to the ZnCdS were used under visible light to evaluate the photocatalytic degradation of methyl orange and Rhodamine B (RhB) in an aqueous solution (Shen et al., 2015). The results showed that the low percentages of the rGO served better than the higher percentage in the photocatalytic degradation of dyes and RhB because increasing the rGO content increases its black color, which lowers the photoactivity due to the limitation of the light penetration through the reaction solution. Generally, three factors have been reported for the promised photocatalytic activity of the rGO–ZnCdS in degrading of organic dye molecules using visible-light excitation. These factors are its enhancement for organic adsorption, its ability to extend photo-responsive range, and the formation of the rGO–ZnCdS hetero system, which has a synergetic impact on its photoactivity (Sudha and Sivakumar, 2015).

Nanofiltration

One of the effective water-treatment methods is filtration, which uses membranes and effectively removes a wide range of pollutants such as heavy metals, organic, and ions. Several membrane processes have been developed and showed remarkable efficiency in water treatment, which emphasize their commercial applications. Among these types, pressure-driven membrane filtration such as ultrafiltration (UF), microfiltration (MF), nanofiltration (NF), and reverse osmosis (RO) have attracted great attention in the previous decades. In the last decades, nanofiltration (NF) was presented as a solution for some drawbacks of the filtration technique (Punia et al., 2021). NF enables molecularly sieving out contaminants from the polluted water. The removal efficiency depends on the pore sizes and charges characteristics of the nanomembrane (Wang et al., 2020b). This process also has some drawbacks, such as the high costs for the production of membrane filters (Al-Furaiji et al., 2020). In the NF process, a pressure between 5 and 20 bar is applied to separate solute particles up to the size of 2 nm from solvent, but it can sometimes exceed up to 40 bar (Punia et al., 2021). NF-membranes characterization relies on the properties of both solute and solvent and the operating conditions of the filtration process. According to nanotechnology, the NF membranes can be classified as presented in **Figure 4**. Although these membranes have significant advantages, the most critical drawback that minimizes the dependence on them in the filtration process is membrane fouling. This problem results from the deposition of a particle or solution on the surface of the membrane. NF considers one of the advanced purification methods, which also include ultrafiltration, advanced oxidation, microfiltration, and reverse osmosis (RO), and **Figure 5** shows the efficiency of these methods in eliminating different pollutants that usually exist in the water.

Polyvinylidene difluoride (PVDF) with MWCNT nanocomposite UF membrane hybrid with photocatalytic reactor was also applied to treat of petroleum refinery wastewater. PVDF nanocomposite UF membrane was fabricated from pristine and oxidized MWCNT. The process involves subjecting the treated wastewater to photocatalytic irritation using UV light in the presence of TiO_2. This process results in the decomposition of more than 90% of the presented organic pollutants by the UV radiation, which is applied for six hours. The next step involves passing the feed through the PVDF/MWCNT nanocomposite UF membrane, which can increase the removal percentage of the organic matter to more than 99% (Munirasu et al., 2016).

Environmental Risk

Generally, the most concern related to using nanomaterials is its release to the environment and the possible risk behind its contacting the water sources, which can cause secondary toxic impacts and the possibility to hurt humans, animals, and other life species (Ghasemzadeh et al., 2014). This problem requires close attention from the scientific community. Ensuring the

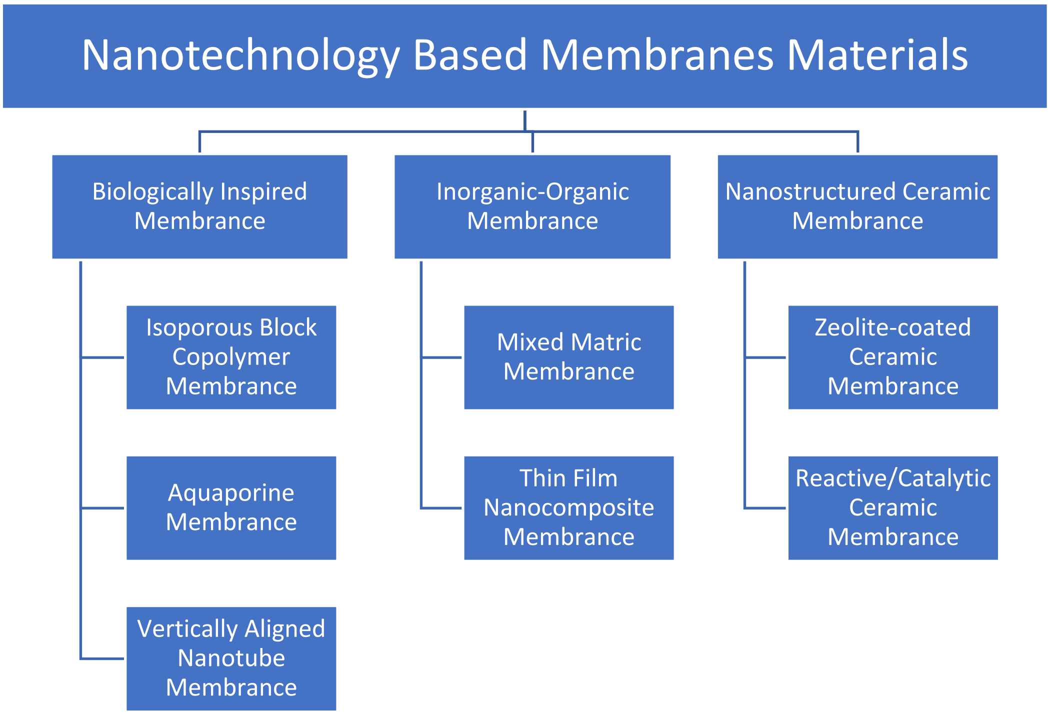
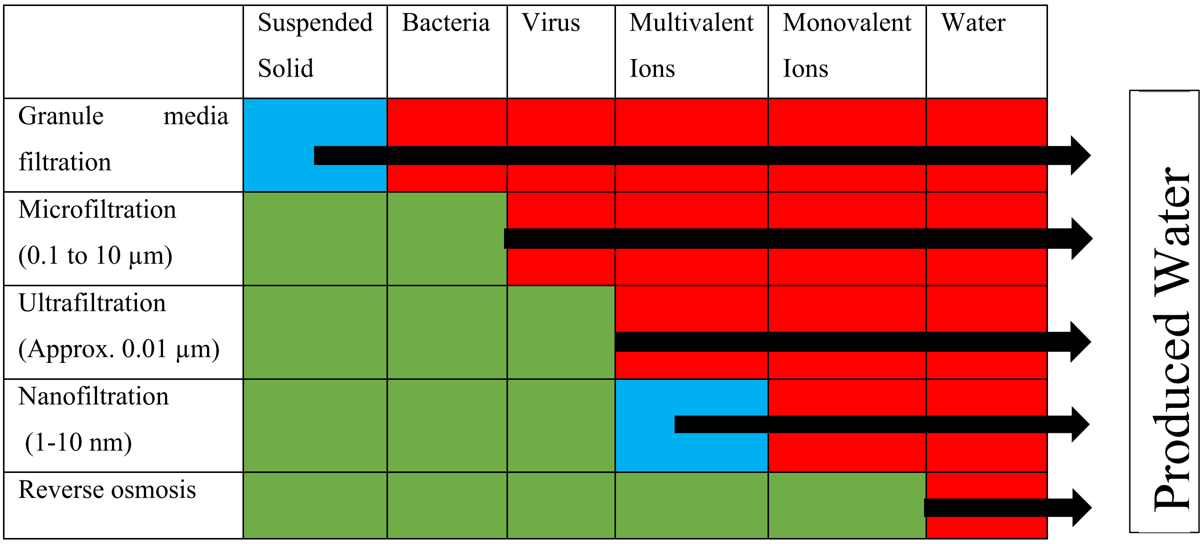


Fig. 4. Categories of nanofiltration membranes (Punia et al., 2021).



	Suspended Solid	Bacteria	Virus	Multivalent Ions	Monovalent Ions	Water
Granule media filtration	🟦	🟥	🟥	🟥	🟥	🟥
Microfiltration (0.1 to 10 μm)	🟩	🟩	🟥	🟥	🟥	🟥
Ultrafiltration (Approx. 0.01 μm)	🟩	🟩	🟩	🟥	🟥	🟥
Nanofiltration (1-10 nm)	🟩	🟩	🟩	🟦	🟥	🟥
Reverse osmosis	🟩	🟩	🟩	🟩	🟩	🟥

Fig. 5. Treatment efficiency of different filtration methods. Blue color (partial removal), red color (allowed to pass), green color (complete removal)(Punia et al., 2021).

safety of the use of nanomaterials and their potential health impact are severe challenges for the emergence of these promised materials. In addition, there should be an identifying for the toxicity thresholds of nanomaterials and determining the possibility of applying the presently used biomarkers of hurtful impacts in investigating environmental nanotoxicity. Therefore, many researchers have been investigated the practicality of applying natural nanomaterials as adsorbents. For example, an allophone is a premium adsorbent for several components such as copper, 17β- estradiol, and surface-modified smectite adsorbs naphthalene (Yuan, 2004). All these minerals, which exist in the natural soil in nano-size, are of geological and pedological nature.

Current Challenges and Future Perspectives

There is a critical necessity for the providing of efficient water technologies to guarantee an excellent quality of drinking water. Scaling up the laboratory-tested systems to the commercial level requires more efforts to supply flexible and adaptable water treatment systems. Nanomaterials can provide unique advantages when compared with other water technologies, such as their capability to combine several characteristics, forming multifunctional materials such as nanocomposite and membranes that enable both the particle retention and elimination of pollutants. In addition, nanomaterials display outstanding performance due to their valuable properties, such as a high surface area. However, some limitations prevent the successful applications of nanomaterials. For example, functionalizing materials with NPs has a risk potential, as NPs might be released to the environment, as discussed before. Thus, to reduce the health risk, different laws and regulations have been established. One of the technical severe drawbacks of nano-engineered water technologies is that they are rarely applied for industrial scale due to the poor competitivity with standard treatment technologies in terms of cost (Nasrollahzadeh et al., 2021). However, earth-abundant nano-engineered materials supply excellent possibilities to develop better and safer candidates shortly, especially for the heavily degradable pollutants (Nasrollahzadeh et al., 2021). Biogenic NPs have high potentials due to the ingrained greenness and sustainability of the manufacturing processes and their great activity in the eliminating of environmental pollutants (Gautam et al., 2019). The improvement of developed analytical and imaging methods has enabled different pathways for the evaluation and determining of nanosized objects in this field.

CONCLUSIONS

In this article, involving nanomaterials in the adsorption process for (waste) water treatment is reviewed. Adsorption can effectively contribute to environmental remediation. This process has gained considerable interest from researchers and even commercially. This review shows that a variety of nanomaterials has been investigated for the adsorption of inorganic and, or organic pollutants. Several nanomaterials show promising efficiency in removing contaminants, which making them a potential alternative to standard remediation technologies. However, there are still some drawbacks that limit marketing these materials. These drawbacks are the cost-effectiveness of the process, environmental concerns, and technical challenges such as scaling up to the industrial level and system setup. In addition, there are some other challenges related to the size of these materials, where the separation of nano adsorbents from aqueous solutions is a serious issue. Also, the availability of large quantities of nano adsorbents with low costs for water treatment destinations can be a severe issue for commercial uses. Furthermore, preventing the release of used nanomaterials to the environment is a serious challenge because they accumulate for long periods. Despite these drawbacks, nano adsorbents could supply high potential in (waste)water treatment and environmental remediation soon.

LIST OF ABBREVIATION

Carbon nanotubes	CNTs	Nano metal oxides	NMOs
Graphene oxides	GO	Polyvinylidene difluoride	PVDF
Graphene nanosheets	GNs	Reduced graphene oxides	rGO
Hydrogels	HGs	Reverse osmosis	RO

microfiltration	MF	Rhodamine B	RhB
Multi-walled carbon anotubes	MWCNTs	Single-walled carbon nanotubes	SWCNTs
Nanofiltration	NF	Two dimensions	2D
Nanoparticles	NPs	Ultrafiltration	UF

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CONFLICT OF INTEREST

The authors declare that there is not any conflict of interests regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/ or falsification, double publication and/or submission, and redundancy has been completely observed by the authors.

LIFE SCIENCE REPORTING

No life science threat was practiced in this research.

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