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REVIEW ARTICLE

An overview of nanomaterials for industrial wastewater treatment

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Abstract−Industrial wastewater is a universal environmental issue. Numerous organic pollutants, heavy metals, and non-disintegrating materials are present at extreme concentrations. Presently, removing these pollutants from industrial wastewater in an effective way has become a momentous issue. Efficient purification procedures are needed to remove those pollutants before disposal. In this direction, wastewater treatment has been one of the nanomaterial applications. Additionally, nanomaterials are innovationally effective for purifying water by using low-budget nanoadsorbents and nanofiltration. This review article highlights the use of nanomaterials for the removal of different polluting materials from industrial wastewater with a special focus on metal and metal oxide nanomaterials (NMs), carbon-based nanomaterials (CNMs) and nanofiber/nanocomposite membranes. The goal is to offer a recent overview and references in the area of emergent nanomaterials used for removing toxic pollutants from real industrial wastewater for researchers and industrializers.

Keywords: Industrial Wastewater, Pollutants, Nanomaterials, Nanoadsorbents, Nanofiber Membranes, Nanocomposite Membranes

INTRODUCTION

Wastewater is the water containing surplus substances that unfavorably affect its quality, making it unsuitable for use. Wastewater is produced from numerous sources as in residential areas, commercial areas, industrial properties, agriculture lands etc. Composition of wastewater differs broadly and it is highly dependent on the source it is generated from. Common constituents of wastewater are inorganic substances like solutes, heavy metals, metal ions, ammonia alongside with gases, complex organic compounds such as excreta, protein, natural organic matter, plants material, food, nitrate, and several other contaminants in ground water, surface water, and/or industrial water. When untreated those components may pose a hazard to the environment and living beings, and so, it is pivotal to treat wastewater before disposal. Many biological, physical, and chemical treatment processes are exploited to handle wastewater [1]. The common materials and treatment technologies like activated carbon, oxidation, reverse osmosis (RO) membranes [2] and activated sludge [3] are not adequate to get rid of complex and intricate polluted water that contains pharmaceuticals, surfactants, various industrial additives, and abundant chemicals. The decades-old water treatment processes cannot adequately address the removal of toxic chemicals, organic materials and microorganisms found in raw water. Currently, researchers broadly study nanotechnology, as it provides potential advantages that include low cost, reuse and high proficiency in removing and recovering the pollutants. Many nanomaterials like carbon nanotubes (CNTs), nanomembranes, zeolites and dendrimers are aiding in the improvement of more competent treatment pathways amongst the enhanced aqua methods [4].

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Nanotechnology facets can be utilized to address the many complications of water quality to warrant environmental stability by industrial wastewater treatments systems. Most industries produce wet wastes, even though new tendencies in the developed countries aim to reduce these productions or recycle the wastes inside the production procedure. Nevertheless, numerous industry processes release wastewaters. Overall, nanomaterials are materials of which the structural elements are sized (at the least in one dimension) between 1 and 100 nm [5]. Properties, like mechanical, electrical, optical, and magnetic properties, are remarkably different from those of conventional materials due to their sizes. Different nanomaterials have the features of catalysis, adsorption, and high reactivity. In the past years, nanomaterials have been researched, developed and successfully used in many applications, such as catalysis [6], medicine [7], sensing [8], and biology [9]. Particularly, nanomaterials applications in water and wastewater treatment have drawn global concern. Nanomaterials possess superior adsorption capacities, reactivity, and their high mobility in solution [10]. Numerous types of nanomaterials can successfully remove heavy metal ions [11], organic pollutants [12], inorganic anions [13], and bacteria [14]. On the base of several studies, nanomaterials promise great applications in industrial wastewater treatment. In addition, zero-valent metals, metal oxides, carbon nanotubes (CNTs) nanoparticles and graphene-based nanomaterials were used widely for wastewater treatment application as overviewed in Fig. 1.

This review covers the types of nanomaterials used for different pollutants in real industrial wastewater. The appropriateness of metals, metal oxides-based nanomaterials (Ag, Fe, Ti, Zn), carbon-based nanomaterials (CNMs), and membranes nanomaterials is examined. The advantages and restrictions of the type of nanomaterials and its functionality are evaluated. Finally, extents and restrictions of these nanomaterials are also considered while investigating the types of metal ions that are harmful.

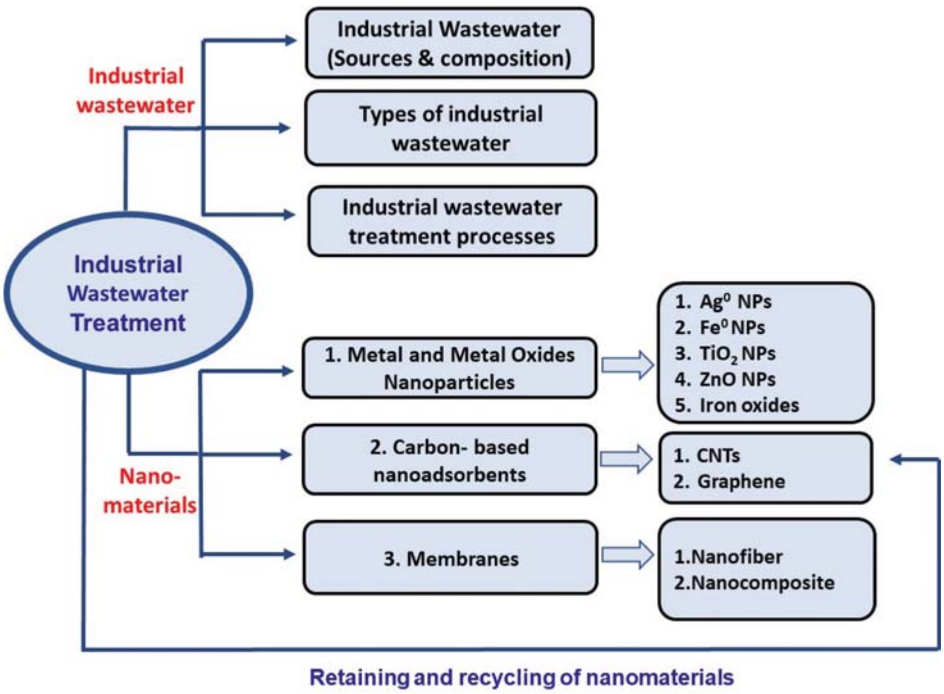

Fig. 1. An overview of the review structure.

INDUSTRIAL WASTEWATER: SOURCES AND COMPOSITIONS

Industrial wastewaters are liquids resulting from human activities relatable to raw-material management and manufacturing. Industrial wastewater acts as one of many grave pollutions contaminating the water environment. Tremendous quantities of industrial wastewater were released into lakes, seashores and rivers in recent years. The result of such action has caused grave pollution complications in the water environment and given rise to negative outcomes to the eco-system and human's life. The consequences of the industrial wastewater spill on the human population and environment prove to be tragic in most cases [15,16]. Variable compositions exist in industrial wastewaters counting on the processed substances and therefore the industry kind. Many of these wastewaters are organically exceedingly strong, largely inorganic, easily biodegradable, or potentially inhibitory. Thus, the total dissolved solids (TSS), biological oxygen demand (BOD) and chemical oxygen demand (COD) values could be very high.

There are several kinds of industrial wastewater; each industrial sector produces its own precise blend of contaminants. Similar to the varied characters of industrial wastewater, the processing of industrial wastewater has to be planned specifically for the particular type of liquid produced. The metal working industries release heavy metals and their compounds, and the electroplating industry is a significant cause of pollution. Photo processing workshops produce silver compounds, while printing plants discharge dyes and inks. The pulp and paper industry depends mostly on chlorine substances and hence, its effluents contain chloride compounds and dioxins. The petrochemicals industry releases plenty of phenols and oils. Food processing plant effluents are full of suspended solids and organic matters. Mostly, industrial wastewater is often dichotic into two categories: inorganic wastewater and organic wastewater. Table 1 shows different water pollutants released from the industrial sector.

Inorganic industrial wastewater mainly exists in the coal and steel industry, the non-metallic minerals industry, and in commercial ventures and manufactures for metals surface processing (iron pickling works and electroplating plants). Commonly, wastewater and solid substances and oils are produced, and they contain extremely toxic solutes. These include blast-furnace gas-washing wastewater inclusive of cyanide, metal processing industry wastewater with acids or alkaline solutions within (mostly non-ferrous metals and often cyanide or chromate), wastewater emanating from the gas purification of aluminum works, which contains fluoride. Non-metallic minerals, which come in small and average sizes, along with metal processing plants are located in a specific way so that they release their wastewater into municipal wastewater systems and their effluents should be treated before liberation, according to local regulations [19,20].

Organic industrial wastewater includes waste flow that comes from those chemical industries and chemicals act on large-scale, which mostly exploit substances for chemical reactions. The liquids include organic substances with variable properties and origins [21]. The following industries and plants issue the majority of organic industrial wastewaters:

- Factories manufacturing pharmaceuticals, cosmetics, glue and adhesives, organic dyestuff, synthetic detergents, soaps, pesticides and herbicides.
- Leather and tanneries factories.
- Textile factories.
- Paper and cellulose manufacturing plants.
- Factories related to oil-refining industry.

Table 1. Major water pollutants released from industrial sector [17,18]

Substance	Released to wastewater from
Acetic acid	Acetate rayon, beet root manufacturing
Acids	Chem. Manufactures, mines, textiles manufacture
Alkalis	Cotton and straw kiering, wool scouring
Cadmium	Plating
Chromium	Plating, chtome tanning, alum anodizing
Copper	Copper plating, copper pickling
Cyanides	Gas manufacture, plating, metal cleaning
Fluorides	Scrubbing of flue gases, glass etching
Hydrocarbons, mineral oils, phenols and chromium	Petrochemical and rubber factories
Nickel	Plating
Phenols, heavy metals, and cyanide	Gas and coke manufacture, chemicals plants
Starch	Food processing, textile industries
Sulfides, sulfates and chromium	Textile industries, tanneries, gas manufacture
Tartaric acid	Dyeing, leather, chemicals manufacture
Zinc	Galvanizing zinc plating, rubber process
Free chlorine	Paper mills, textile bleaching
Oil, metals, acids, phenols and cyanide	Iron and steel industry
Chlorinated organic compounds	Pulp and paper industry
Fluorine	Non-ferrous metals
Organic chemicals	Microelectronics
Metals, acids and salts	Mining industries

- Metal processing industry.

The steel industry is considered an essential and vital industry presently and in the future. Steel industries produce large volumes of wastewater that contains many dissolved, undisclosed substances and chemicals in the sludge as well as wastewater. Producing iron out of its ores implicates potent reduction reactions in blast furnaces. Cooling waters, of necessity, are soiled with cyanide and ammonium hydroxide. Wastewaters contain acidified rinse waters and waste acid mix. In spite of many plants operating in acid recovery plants where the mineral acid is boiled away from the iron salts, a large volume of highly acid ferrous sulfate or ferrous chloride remains undisposed [22].

The production of paper and wood-pulping products creates a troubling amount of contaminators related to chemical oxygen demand (COD), biochemical oxygen demand (BOD), suspended solids (SS), color, and noxiousness when unprocessed liquids are released into effluent waters. The resulting liquid harms aquatic organisms and possesses intense mutagenic impacts and physiological impairment [23-25].

The textile industry also significantly contributes to water pollution in converting manufactured and natural threads into fabrics and other products. When manufacturing most textiles, wet chemical procedures are mandatory to rightfully purify, prepare, color or finalize the product. That accounts for the formation of wastewater, and its contamination load emanates not only from removing impurities from the raw materials themselves, but also from the remaining chemical reagents used for processing [26,27]. Primary contaminators in textile wastewaters are highly suspended solids, chemical oxygen demand, heat, color, acidity, and other soluble substances [28]. The contamination of textile wastewater derives from dyeing and finishing operations as depicted in Table 2.

Table 2. Specific pollutants from textile wet processing [31]. Reproduced with permission from Life Science Global publisher

Process	Various physicochemicals
Desizing	Enzymes, Starch, Waxes
Bleaching	H_2O_2, Sodium silicate, Organic stabilizer, Surfactant
Mercerizing	NaOH, Cotton Wax
Dyeing	Dyes, Salts, Surfactant, Urea, Soda ash
Printing	Urea, Dyes, Pigments, Binder, Soda ash, Thickener
Finishing	Resins, Formaldehyde, PVA, Waxes, Hydrocarbon

INDUSTRIAL WASTEWATER TREATMENT PROCESSES

Industrial wastewater treatment technologies are generally classified into chemical, physical, and biological processes. The most commonly adopted technologies may be classified according to their position in the plant: (i) pretreatments; (ii) primary treatments; (ii) secondary and tertiary treatment; (v) refinement treatments; and (v) disinfection.

Generally, primary treatments are size-based separations using physical methods such as sedimentation/filtration for basic cleanup. The secondary treatment mainly involves physicochemical methods and/or biological methods and is capable of removing 85-95% of BOD/COD and TSS from the wastewaters. Tertiary treatment involves the final polishing of the effluent by removing toxic/harmful pollutants to desired levels; more than 99% removal can be achieved

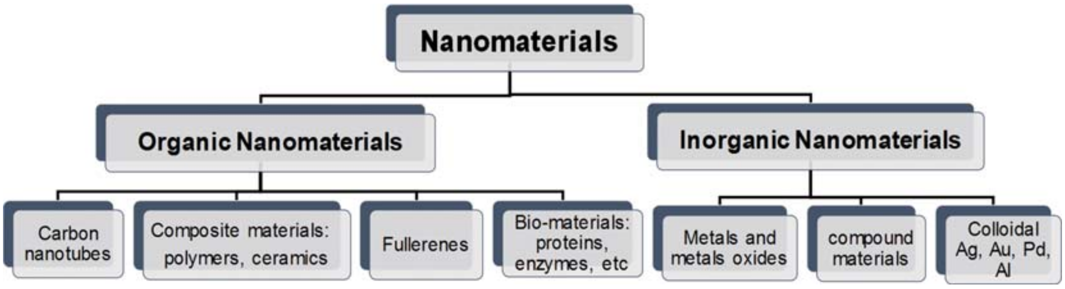

Fig. 2. Types of nanomaterials.

on completion of tertiary treatment. The primary processes produce wastewaters that are not suitable for discharge or for recycling and reuse, the main objective being to produce water quality suitable for treatment involved in secondary and tertiary separations. The primary processes mainly have a mandate for protecting processes and materials that are to be used in secondary/tertiary treatments in order to avoid process failure. A prominent example of this is pH modifications/ filtration/clarification before sending the stream for membrane separations/adsorption/ion exchange. The separation processes that are typically considered in primary treatment involve size-based separation, by and large, involving physical driving force for effecting separation. They mainly comprise screening, sedimentation, thickening, precipitations, centrifugation, cyclone separations, and filtration [29]. Among the most important pretreatments, homogenization/equalization is aimed to equalize and homogenize the inlet wastewater especially when industrial production processes are discontinuous and variable with respect to intake pollutants.

In secondary and tertiary treatment stages, more advanced separation processes are used with huge variation in the nature of process and equipment. These processes include evaporation, distillation, absorption, extraction, adsorption, ion exchange, crystallization, cavitation, biological processes, and membrane separations. The separation processes employed here can be classified based on driving force such as thermal driving force (distillation, evaporation, pervaporation) and pressure-driven processes such as membrane separation-microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and RO or electrical forces such as electrodialysis [30]. Physicochemical methods are the most important class of separation processes that play a vital role in the field of wastewater treatment [31]. These mainly include processes that exploit both physical and chemical reactions/interactions for effecting desired separation. This important class includes a wide variety of processes, such as coagulation/flocculation, extractions, reactive separations, oxidations, and cavitation. Separation processes such as adsorption and ion exchange also come into physicochemical methods of treatment employing both surface forces and chemical/electrostatic attraction. Coagulation, adsorption, ion exchange, and some of membrane separations (ion exchange membranes) belong to the class of charge-based separations where separation is largely affected by neutralizing the charges and is specifically applicable for the removal of charged bodies/ions from the solution. Depending on the nature of the effluent, one or more separation processes are employed for meeting end objectives of discharge/water recycling/reuse.

NANOMATERIALS FOR INDUSTRIAL WASTEWATER TREATMENT

Nanomaterials are normally customary materials with enhanced properties and recently developed, high-performance materials. Moreover, they may be of all material types (e.g., metals, polymers, ceramics), they are inclusive of semiconductors, nanoengineered materials, and biomaterials. The majority of old-style techniques like adsorption, extraction, and chemical oxidation are, in general, effectual for wastewater treatment but are extremely costly. In that sense, advanced nanomaterials may play a leading role [32]. Different types of nanomaterials like those that nanoadsorbents, nanocomposite and metal nanoparticles with active surface area, which can used in wide applications are summarized in Fig. 2.

1. Metal and Metal Oxide Nanoparticles

Metal nanoparticles are investigated to overcome significant heavy metals like lead arsenic, cadmium, mercury, copper, chromium, and nickel. They have shown great ability to overcome activated carbon [33]. Metal nanoparticles can be produced by comparatively low-budget preparation methods. Having high adsorption capacity, lower cost, easy separation and regeneration give them advantageous from technological and economical point of view.

On the other hand, metal oxide nanoparticles like iron oxide and titanium dioxide are efficient, uncostly adsorbents for various heavy metals. Their adsorption capacity is primarily contingent on the interaction between adsorbate ions and the oxygen in metal oxides [67]. In addition, it is a process of two-steps; first quick adhering of metal ions on the outside surface of the adsorbent and the rate-limiting internal particle penetration along the porous walls comes after [68]. Their nanoscale matching part possesses excellent adsorption capability and faster kinetics because of their higher surface area, lower distance of internal particle diffusion and the massive counts of reactive sites on the surface. Some forms of iron oxide nanoparticles, like nanomaghemite and nanomagnetite, have superparamagnetic properties besides their high adsorption capacity. These nanoparticles could be directly applied as adsorbents or as core-shell materials where the shell propose the desirable role and the core magnetically separates the contaminant.

1-1. Silver Nanoparticles

Silver nanoparticles (Ag NPs) are exceedingly toxicant to microorganisms, therefore possess intense antibacterial effects at odds with a wide assortment of microorganisms, involving viruses [35], bacteria [34], and fungi [36]. Silver nanoparticles have been broadly applied as a great antimicrobial agent to sanitize water. The mech-

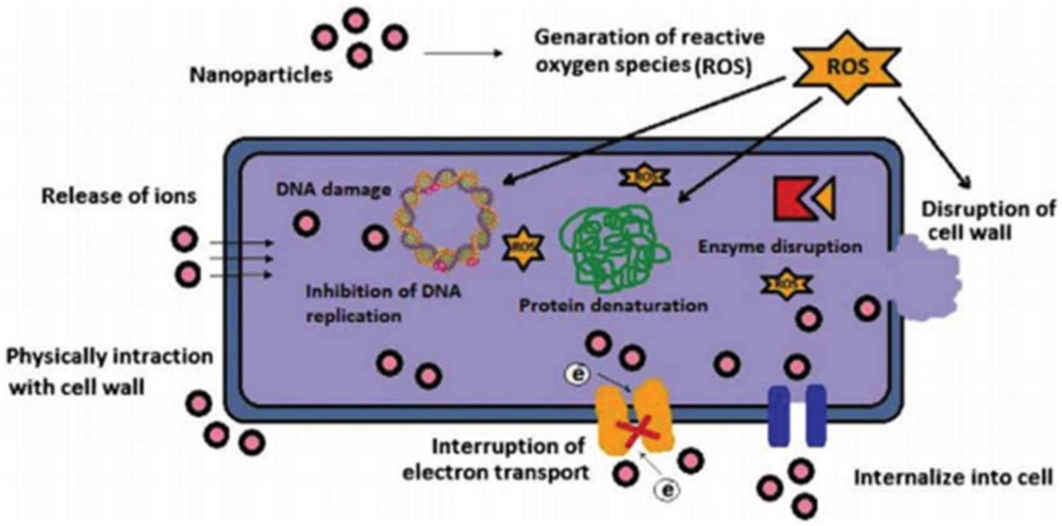

Fig. 3. Various mechanisms of antimicrobial activity of the metal nanoparticles [37]. Copyright permission from IOP Publishing.

anism of the antimicrobial effects of Ag NPs is obviously unknown and is up for debate. In recent years, several theories have been put forward. Fig. 3 shows different proposed pathways of antimicrobial activity of the metal nanoparticles.

Ag NPs have been recounted as a bacterial cell wall sticker and go deeply inside it afterwards, thus leading to structural alterations of the cell membrane and accordingly increasing its permeability [38]. Besides, free radicals can be generated when Ag NPs are attached to bacteria. They have the ability to get rid of the cell membrane and are considered of the cell's death [38]. Over and above, since DNA is comprised of plentiful sulfur and phosphorus elements, Ag NPs can interact with it and hence, destroy it. This is another clarification to explain the death of cells owing to Ag NPs [39]. Moreover, the dissolution of Ag NPs releases antimicrobial Ag+ ions that can attach to the thiol groups of different vital enzymes, deactivate them, and disrupt ordinary functions in the cell [40]. Thanks to the advancement of nanotechnology, Ag NPs were applied successfully in water and the disinfection of wastewater those previous years. Direct exploitation of Ag NPs could be the cause to many escalations, namely, their ability to agglomerate in aqueous media that slowly decreases their efficiency on the long run application [41]. Attached Ag NPs to filter materials have been viewed optimistically regarding water disinfection because of their high antibacterial activity and cost-effectiveness [42]. Furthermore, Ag NPs sheets obtained by reduction of silver nitrate showed antibacterial qualities towards suspensions of Enterococcus facials, Escherichia coli, and in activated bacteria during filtration through the sheet. Moreover, the percentage of lost silver in the Ag NPs sheets was less than the standards for silver in drinkable water submitted by Environmental Protection Agency (EPA) and World Health Organization (WHO) [43]. Therefore, regarding bacteria-contaminated water, paper filtration precipitated with Ag NPs could be an efficient emergency water treatment. Besides, AgNPs synthesized by chemical reduction got incorporated into poly ether sulfone (PES) microfiltration membranes. The activity of microorganisms nearby the membranes was announced as notably constrained. The PES-AgNPs membranes exhibited strong antimicrobial properties and hold great potential in application for water treatment [44].

In the past two decades, Ag NPs on ceramic materials/membranes have garnered significant attention owing to their biofouling and disinfection reduction for water treatment in households [45]. For instance, the addition of AgNPs to ceramic filters constructed with clay and sawdust has turned out to be able to improve the removal efficiency of Escherichia coli. It was also found that higher porosity filters accomplished greater bacteria removal than lower porosity filters. [46]. Beyond that, colloidal Ag NPs have been combined with cylindrical ceramic filters, which were made out of clay-rich soil with water, grog, and flour, in different quantities and techniques (dipping and painting). It was proved that colloidal AgNPs improved the filter performance and the filters can remove Escherichia coli in the rate between 97.8% and 100% [47]. Recently, AgNPs attached to ceramic membranes have been successfully predicted by Derjaguin Landau-Verwey-Overbeek (DLVO) approximation methods [48]. Extensive studies on Ag NPs will enhance their applications in different environmental fields.

1-2. Iron Nanoparticles

In recent years, numerous zero-valent metal nanoparticles, namely Fe, Zn, Al, and Ni, in water contamination treatment have attracted wide research interest. Due to the extremely-high reductive capability, nano-zero-valent Al is thermodynamically active with water present, favoring the existence of oxides/hydroxides above the surface, encumbering (entirely) the transferring of electrons from the surface of the metal to the pollutants [49]. Contrasted with Fe, Ni's typical reduction potential has less negativity, hence, low reduction capability. With a temperate typical reduction potential, nano-zero-valent Fe or Zn possesses great potential to perform as reducing agents relative to many redox-labile pollutants. Despite a weaker reduction ability, Fe owns several colossal advantages than Zn does regarding applications in water contamination treatment, not excluding excellent adsorption properties, precipitation and oxidation (with the help of dissolved oxygen), and low cost. Therefore, amongst the zero-valent metal nanoparticles, zerovalent iron nanoparticles have been the most extensively studied to overcome different metal ions waste [50,51].

Because of the exceedingly diminutive size and large specific surface area, nZVI has great adsorption qualities and stable reducing ability [52]. These traits contribute most to its superior performance in removing the pollutants. Under anaerobic conditions, as shown in Eqs. (1) and (2), Fe^0 can be oxidized by H_2O or H^+ and generates Fe^{2+} and H_2, which are also potential reducing agents for contaminants. In the oxidation-reduction reaction between nZVI and contaminants, Fe^{2+} will be oxidized to Fe^{3+}, which can form $Fe(OH)_3$ with the increase of pH. As a standard and efficient flocculant, Fe $(OH)_3$ eases removing pollutants, for instance, Cr(VI) [53]. What is more, ZVI may reduce and oxidize variable organic compounds in the audience of dissolved oxygen (DO) since ZVI transfers two electrons to O_2 to produce H_2O_2 (Eq. (3)). The resultant H_2O_2 can be reduced to H_2O by ZVI (Eq. (4)). Moreover, the combination of H_2O_2 and Fe^{2+} (known as Fenton reaction) can obtain hydroxyl radicals ($HO^{\cdot}$) that possess unfluctuating oxidizing ability to a wide range of organic compounds (Eq. (5)) [54]:

$$Fe^0+2H_2O \rightarrow Fe^{2+}+H_2+2OH^- \quad (1)$$

$$Fe^0+2H^+ \rightarrow Fe^{2+}+H_2 \quad (2)$$

$$Fe^0+O_2+2H^+ \rightarrow Fe^{2+}+H_2O_2 \quad (3)$$

$$Fe^0+H_2O_2+2H^+ \rightarrow Fe^{2+}+2H_2O \quad (4)$$

$$Fe^{2+}+H_2O_2 \rightarrow Fe^{3+}+HO\cdot+OH^- \quad (5)$$

With the effects of reduction, oxidation, adsorption, and precipitation, (with the help of DO), nZVI has been applied successfully in the elimination of a large number of contaminants, including halogenated organic compounds [55], nitroaromatic compounds [56], organic dyes [57], phenols [58], heavy metals [59], inorganic anions like phosphates [60] and nitrates [61], metalloids [62], and radio elements [63]. More than that, studies about the benefits and drawbacks modifications application of nZVI in water and wastewater treatment are not restricted to water or laboratory tests and have been set in motion. In previous years, nZVI has been, as well, exploited in soil remediation [64] and already achieved pilot-scale and full-scale applications at real water-contaminated locations. [65]. Common modification approaches principally subsume doping with other metals, surface coating, supported conjugation, emulsification, and encapsulation in matrix [66].

1-2-1. A Case Study: Smelting Wastewater Treatment

Iron nanomaterials have exhibited excellent activity for the removal of pollutants from industrial wastewater [69]. For example, wastewater resulting from smelting non-ferrous metal industry is highly noxious because of the presence of diverse number of heavy metal ions especially arsenic (As) with high concentrations (up to 1,000 mg/L). A pilot scale study was carried out for the treatment of smelting wastewater using zero-valent iron nanoparticles (nZVI) [70]. The process comprised two successive nZVI treatment units where each unit had a reactor, a clarifier and a recirculation pump for nZVI. The nanoparticles and smelting wastewater were mixed in the reactor and the pilot experiment was conducted with wastewater flow rate of 400 L/h. About 35,000 liters of wastewater was treated using 75 kg nZVI for removing 17.9 kg arsenic and other metals (Cu, Zn, Ni, Cd, Cr and Pb) were also removed concurrently. The high removal capacity of iron nanoparticles (239 mg-As/g-Fe) was attributed to its large surface area and the catalytic effect of copper in the wastewater. The compound $Fe_3(AsO_4)_2{\cdot}8H_2O$ was found in the pilot reactor and the batch tests, which refers to the vital role of ferrous ion (Fe^{++}) precipitation during the process. This precipitation was also supported by the pH increase and low content of ferrous ions during reaction. The simultaneous removal of other heavy metals showed the multiple functions of nZVI. The removal of Ni, Pb and Cr ions was the combined effects of reduction and/or adsorption while Zn and Cd ions were secluded via adsorption and/or co-precipitation.

In a conclusion, the authors showed by their pilot experiment that nZVI was a promising material for smelting wastewater treatment and the process could be scalable and applicable to a broader range of wastewater containing pollutants, which are acquiescent to nZVI sorption and reduction. The achievement of this pilot study authorized the construction of a fully scaled wastewater treatment plant in which the same nZVI process was used.

1-3. TiO_2 Nanoparticles

Photocatalytic degradation has drawn great attention as an emergent and promising technology since 1972. Recently, photocatalytic degradation technology was applied successfully for the contaminant degradation in wastewater. When light and catalyst are present, contaminants can be gradually oxidized into low molecular weight intermediate products and eventually converted to CO_2, H_2O, and anions such as Cl^-, NO^{3-} and PO_4^{3-}. Most common photocatalysts are metal oxide or sulfide semiconductors, among which TiO_2 has been widely researched. Owing to its excellent photocatalytic activity, photostability, chemical and biological stability and fair price [71], TiO_2 is the most exceptional photocatalyst to date. Having large band gap energy (3.2 eV), TiO_2 necessitates ultraviolet (UV) excitation to maintain charge separation inside the particles. When irradiated with UV, TiO_2 NPs release reactive oxygen species (ROS) able to destroy contaminants completely and quickly. Fig. 2 presents the proposed mechanism of TiO_2 photocatalytic process. Due to its little selectivity, TiO_2 NPs are suitable for degrading all kinds of contaminants, such as chlorinated organic compounds [72], polycyclic aromatic hydrocarbons [73], dyes [74], phenols [75], pesticides [76], arsenic [77], cyanide [78], and heavy metals [79]. What is more, hydroxyl radicals generated under UV irradiation (λ<400 nm) enable TiO_2 NPs to damage the function and structure of various cells [80].

TiO_2 NPs have the ability to kill various microorganisms, like bacteria, fungi, algae, protozoa, and viruses [81]. However, TiO_2 NPs also have some shortcomings.

Several reports indicate the use of bare or modified TiO_2 for the degradation and/or mineralization of bio-recalcitrant compounds (pesticides, pharmaceuticals, personal care products, phenol and derivatives) [82-84]. However, despite numerous research efforts, there are very few examples for the large-scale development of these systems. Two of the major challenges are: to modify TiO_2 in order to make it active under solar light radiation [85,86] and the development of efficient supported materials.

Their high band gap energy makes them require UV excitation, and the photocatalytic properties under visible light are relatively

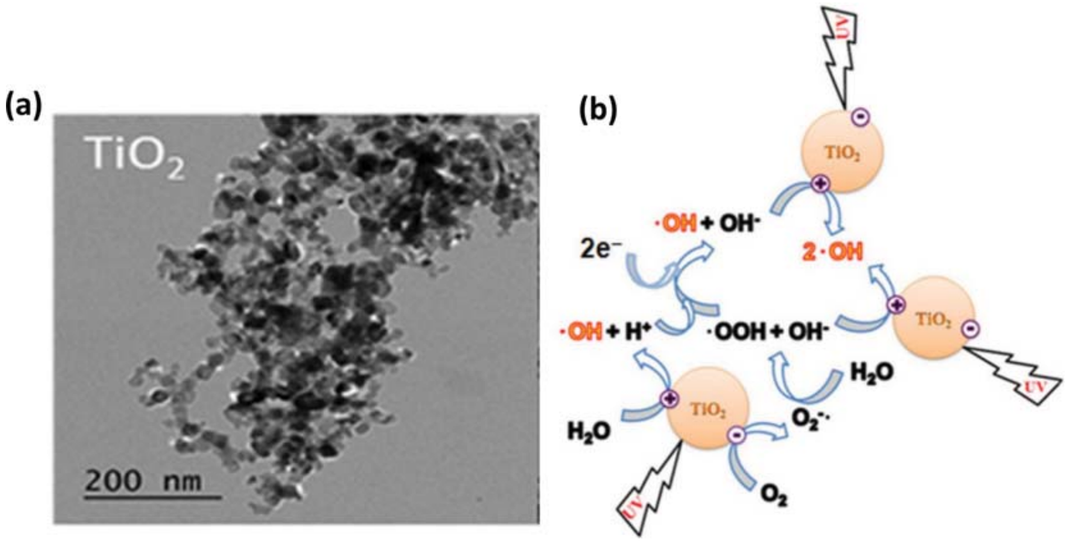

Fig. 4. TEM image of TiO_2 (a) and its proposed mechanism generation of hydroxyl radicals (b) [80,81]. Reprinted with permission from MPDI as well as RSC publishers.

inconspicuous. Therefore, researches have been made for improving its photocatalytic activity under illumination with visible and UV light. Moreover, doping TiO_2 NPs with nonmetal elements like N, F, S, and C, can narrow the band gap remarkably, improve absorption in the visible region, and the dye degradation when irradiated with visible light, particularly solar light [86].

Pedroza-Herrera et al., prepared TiO_2 nanoparticles doped with Cu for the detoxification of hospital and industrial wastewater. The nanoparticles had an excellent activity for removing pathogenic microorganisms from industrial discharges. The authors used a process of two-steps: sol gel then microwave hydrothermal treatment [87]. The incorporation of Cu at relatively low doping levels into the TiO_2 array decreased the bandgap to 2.86 eV. A reasonable photocatalytic activity for diclofenac pollutant degradation and removing dissolved organic matter in an industrial effluent was distinguished. It was revealed that the removal efficiency of these nanoparticles increases with the amount of copper dopant. For example, after 7 hours of illumination, diclofenac degradation efficiencies of 21.41, 28.95 and 33.26% were observed for Cu-TiO_2 (1.0, 1.5 and 2.0%), respectively.

Restrictions of TiO_2 for applications in industrial wastewater treatment are principally ascribable to its small particle size, which can lead to expensive filtering treatment [88]. However, advancement has been formed to address this issue using innovative nanocomposites containing TiO_2 or titanate with polymers, metals and humic acid. Another worry is the toxicity of TiO_2 based nanomaterials reported by many studies [89]. Besides, the production method of TiO_2 NPs is quite difficult. What is more, it is not easy to recover TiO_2 NPs from the treated wastewater, particularly if they are in suspension. In the past few years, extra efforts have been made to conquer this problem. Among them, the conjugation of the photocatalysis of TiO_2 NPs with membrane technology, which showed great promise for conquering the recovery problem of TiO_2 NPs [90].

1-4. ZnO Nanoparticles

Apart from TiO_2 NPs, ZnO NPs have arisen as another efficient candidate in wastewater treatment thanks to their exceptional features, in particular varied band gap in the region of near-UV spectra, high oxidation capability, and excellent photocatalytic properties. ZnO NPs are environment-friendly as they are consistent with organisms [91], which makes them suitable for the treatment of wastewater. In addition, the photocatalytic ability of ZnO NPs is just like that of TiO_2 NPs due to the similarity in their band gap energies [92]. Yet, ZnO NPs are of lower cost than TiO_2 NPs and can absorb light at different regions of solar spectra [92,93]. Besides, the application of ZnO NPs is restrained using photocorrosion, which causes quick recombination of the generated photo charges lowering the photocatalytic efficiency [94]. To advance the efficiency of ZnO NPs photocatalytic activity, doping with metal is a common approach.

Many types of metal dopants have been tested, comprising anionic dopants, cationic dopants, rare-earth dopants, and codopants [95]. Besides, many studies have shown that coupling with other semiconductors, such as CeO_2 [96], SnO_2 [97], TiO_2 [98], graphene oxide (GO) [99], and reduced graphene oxide (RGO) [100], is an attainable approach that enhances the ZnO NPs photodegradation efficiency.

There is inadequate literature on the use of ZnO as an adsorbent to remove pollutants from wastewater solutions. Other studies have used ZnO to load onto supports in an effort to create a hybrid adsorbent. Kikuchi et al. published an extensive analysis on the effect of ZnO loading onto activated carbon [101]. There have been reports of coating the surface of ZnO with humic acid to remove phenanthrene, but no mention of its applicability for heavy metals removal was made [102].

Generally, a few restrictions to using metal oxides nanomaterials as adsorbents are present. Reducing metal oxides to nanosizes can increase surface area, but this increase can also cause instability [103]. Because of being mentally ill, they get more likely to agglomerate due to van der Waals forces and other interactions. Once these interactions occur, they lose high capacity, selectivity and develop poor mechanical strength. To evade these limitations, metal oxides

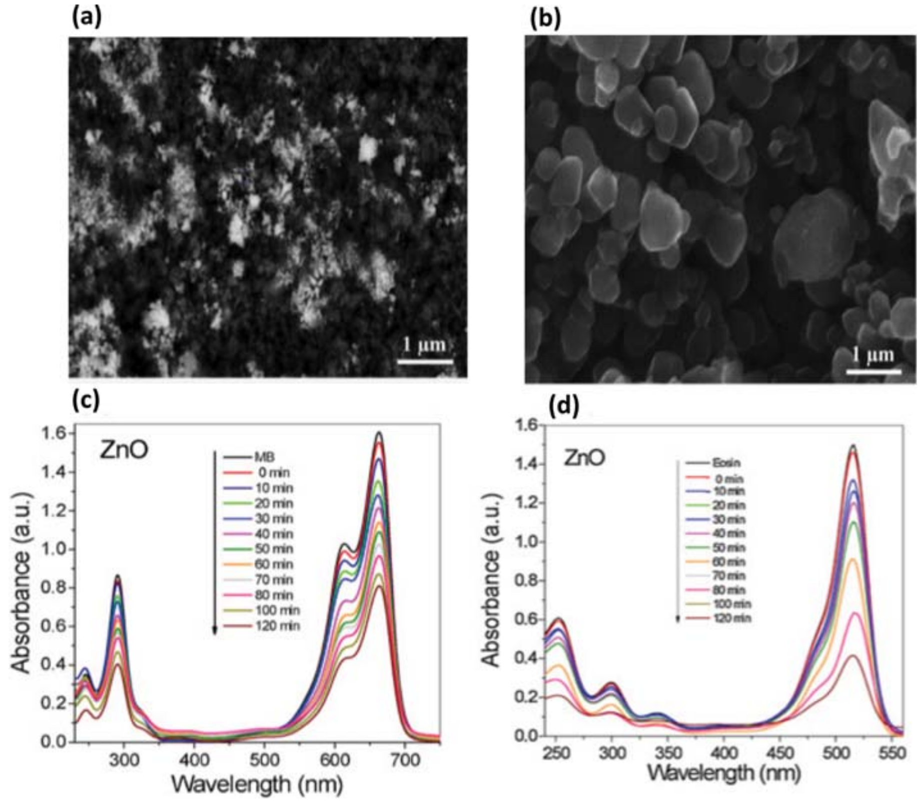

Fig. 5. (a) and (b) SEM images Characterization of ZnO nanoparticles and (c) and (d) absorption spectra of photodegradation for methylene blue and eosin dyes over ZnO nanoparticles [94]. Reprinted with permission from Elsevier publisher.

are characteristically incorporated into supports or other bulk adsorbents [103].

1-5. Iron Oxide Nanomaterials

Recently, using iron oxides nanoparticles for heavy metals removal of has drawn a great interest owing to their availability and simplicity. Magnetic magnetite (Fe_3O_4) and magnetic maghemite (γ-Fe_2O_4) and nonmagnetic hematite (α-Fe_2O_3) are frequently used as nanoadsorbents. Mostly, due to the small size of nanoadsorbent materials, their separation and recovery from the treated water are challenging issues. Thus, some researchers have excellently used these materials as sorbent materials for removing various heavy metals from wastewater systems [104,105]. Various varieties of iron oxides suchlike goethite (FeO(OH)), amorphous and crystalline ferric oxide are applied to get rid of metal ions like copper [105] and arsenic [106], from wastewater.

Adsorption efficiency increased and other metals ions interference decreased by functionalization of iron oxides nanoparticles by adding different ligands for controlling their adsorption features. Ethylene diamine tetra acetic acid (EDTA), hepta (ethylene glycol) (PEG-SH), and meso-2,3-dimercaptosuccinic acid (DMSA) are some examples of the used ligands [107,109]. Polymers such as copolymer sofacrylic acid and crotonic acid can also be used for the same purpose [108]. In addition, a polymer shell has been found capable of preventing particle agglomeration as well as improving the dispersion stability of the nanostructures [98]. Polymer molecules could also serve as binders for the metal ions, thus become their "carrier" from treated water [109]. Hematite (α-Fe_2O_3) has been regarded as a stable cheap material in different applications as sensors, catalysis, and environment [110]. Furthermore, nanohematite has also been validated as effectual adsorbent able to remove heavy metal ions existing in contaminated tap water. The flower-like α-Fe_2O_3 could effectively prevent further aggregation, and the enhanced surface area with different space sand pores provided several active sites interacting to contaminants. Moreover, the highest adsorption capacities of this prepared α-Fe_2O_3 for As (V) and Cr (VI) were extremely higher than those of many previously described nanomaterials [110].

Metal oxide nanoparticles can be renewed easily either if the pH of the solution or the adsorption capacity of it is changed [111]. However, adsorption capacity reduction after regeneration of the nanoparticles has, as well, been described [113]. Mainly, low budget methods can be employed for producing metal-based nanoparticles. Metal-based nanoadsorbents are economically and technologically beneficial because of their good adsorption capacity, cheap price, easy regeneration and separation.

Iron oxide restrictions include poor recovery (hematite) and the size of the particle can be a factor in its overall performance [112]. In the case of magnetic nanoparticles, if they are too small (<12 nm) magnetic separations require large external magnetic fields to overcome contrary forces, which can lead to costly separators [114]. Researches did not discuss the possibilities of scaling up the synthesis of iron oxide nanomaterials in order to show their real application for pollutants' removal from industrial wastewaters. Nevertheless, iron oxide is plentiful, relatively non-toxic and cost-effective.

2. Carbon Based Nanoadsorbents

2-1. Carbon Nanotubes

Carbon nanotubes (CNTs) have extremely more efficient adsorption capacity than activated carbon to numerous organic pollutants. This extraordinary capacity for adsorption originates principally from the huge surface area and the various interactions of CNTs with contaminants. The effective surface area available for adsorption on particular CNTs exists in their outward surfaces [115]. In solution, CNTs form loosened packs or aggregations owing to their graphitic surface hydrophobic character, which reduces the efficient surface area. Yet, CNTs aggregates have interstitial spaces and channels that are considered high sorption areas for organic molecules [116]. Activated carbon shows similar specific surface area as CNTs, but its micropores are inaccessible to massive molecules like some pharmaceuticals [117]. Thus, CNTs possess extremely efficient adsorption capacity for several massive organic molecules due to larger bundles pores and additional available sorption sites.

Activated carbon's major defect is its lower adsorption capacity for molecules of polar organic compounds having low molecular weight. CNTs efficiently adsorb numerous substances owing to the variable pollutant-CNT interacts that include hydrophobic effect, π-π interactions, covalent bonds, H-bonding, and electrostatic forces [115]. CNTs surface rich in p electron allows p-p interactions with organic molecules containing double bonds between carbons, as in polar aromatic molecules [118,119]. Organic compounds containing carboxylic, hydroxyl, and amino groups also form H-bonding with the CNTs surface, which provides electrons [120]. Electrostatic forces ease adsorbing some antibiotic compounds at appropriate pH values [117]. Oxidized CNTs efficiently adsorb heavy metal ions better than activated carbon mostly through electrostatic attraction forces and formation of bonds [121-123]; hence, surface oxidation remarkably boosts its adsorption capacity. The adsorption capacity and surface area of some CNTs used for metal ions removal are given in Table 3.

Overall, CNTs are not exactly a genuine alternative for activated carbon as an adsorbent. Rather, they might have exceptional utilization in removing disobedient contaminants or pre-concentrate minor organic toxins for investigative determinations as their surface chemistry can be tuned targeting precise compounds. These approaches comprise very small materials amounts and hence are considered economical.

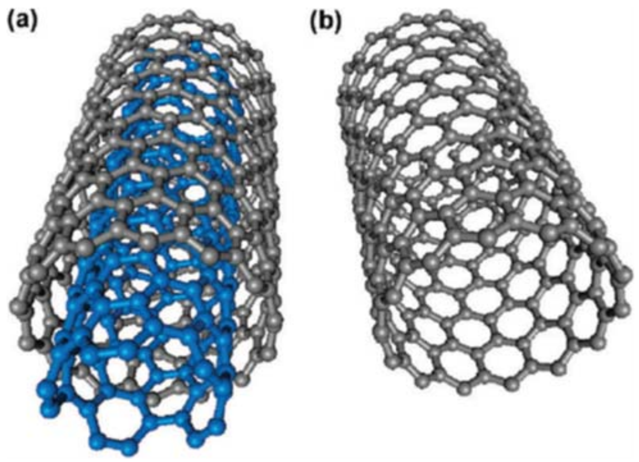

Fig. 6. Structure representation of (a) MWCNTs and (b) SWCNTs [121] Represented with permission from American Chemical Society.

Table 3. Adsorption capacities and surface area of CNTs [123]. Copyright permission from American Chemical Society Publisher

CNTs (m^2/g)	Adsorption capacity (mg/g)	Surface area
As grown	1.10	82.20
H_2O_2 oxidized	2.60	130.0
HNO_3 oxidized	5.10	84.30
$KMnO_4$ oxidized	11.00	128.0
NaOCl oxidized	47.40	94.90

Metal ions adsorption by CNTs can be readily reversed by lowering pH of the solution. The recovery rate of metals is generally above 90% and often close to 100% at pH lower than 2 [123,124]. In addition, the adsorption proficiency often stays stable even after many regeneration processes. Adsorption capacity of SWNT and MWNT towards Zn^{2+} decreased below 25% after 10 cycles of regeneration/reuse, while, that of active carbon was reduced by 50% after one regeneration cycle as stated by Lu and his coworkers [123,125].

2-1-1. A Case Study: Electroplating Wastewater Treatment

Recently, Bankole and team used carbon nanotubes (CNTs) and polyhydroxylbutyrate functionalized carbon nanotubes (PHB-CNTs) to remove heavy metals (As, Pb, Cr, Cd, Ni, Cu, Fe, and Zn) from industrial electroplating wastewater [126]. They found that heavy metals' removal efficiency for PHB-CNTs was higher than CNTs in regard to the high surface area and more functional groups of PHB-CNTs. Temkin isotherm and pseudo-second models explained the adsorption equilibrium and kinetic data of the heavy metals' removal from the electroplating wastewater. They found the adsorption treatment is an endothermically spontaneous process and the controlling mechanisms were ion exchange and electrostatic force mechanism. In addition, CNTs and PHB-CNTs nanomaterials had exceptional and high simultaneous multi-adsorption capacities of heavy metal ions from industrial electroplating wastewater. Likewise, PHB-CNTs was used, for the first time, as an adsorbent having low toxicity, effortless production, and availability. The authors observed that adsorption behavior of both CNTs and PHB-CNTs was controlled by their surface area, water holding capacity and attached functionality. In conclusion, the treated adsorbate matches the water quality standard for re-use, either for industrial or agricultural activities.

2-2. Graphene Based Materials

Investigation has concentrated on a carbon allotrope that is graphene. For the past ten years, a huge increase in the role of graphene and graphene-based materials for environmental purposes has arisen, due their exceptional features, which aim to new potentials on numerous environmental process performances. The choice of using graphene as a carbon-based nanocomposite is dependent on the process cost, capability, and environmental effects of every material. Economic issue and environmental influences of graphene-based materials are considered significant factors in the developing of graphene-based applications. Compared to CNTs, the appli-

Table 4. Removal of important wastewater pollutants by nanoparticles

Nanoparticle	Pollutant	Removal capacity	Ref.
Zero-valent Iron	As(III)	3.5 mg/g	[137]
Titanium dioxide	As(V) and As(III)	As(V) 95 μM/g and As(III) 50 μM/g	[138]
Magnetite Fe_3O_4	As(V) and As(III)		[139]
Zero-valent iron	As(V)		[140]
TiO_2	Cd(II), Pb(II)	244.13 μM/g, 401.14 mg/g	[141,142]
Fe_3O_4 and γ-Fe_2O_3	Co(II)		[143]
Maghemite	Cr(VI)		[144]
δ-FeOOH coated maghemite γ-Fe_2O_3	Cr(VI)		[145]
Fe_3O_4	Hg(II)	125.0 mg/g	[146]
ZnO	Pb(II)	6.7 mg/g	[147]
Goethite (α-FeOOH)	Cu(II)	149.25	[148]
Hematite (a-Fe_2O_3)	Cu(II)	25 84.46	[149]
TiO_2	Se(II)		[150]
Maghemite (γ-Fe_2O_3)	Cr(VI), Cu(II) and Ni (II)	Cu: 26.8 mg/g	[151]
CNTs	Pb (II)	17.44 mg/g, 1.406 mmol/g	[152,153]
CNTs	Cu (II)	1.219 mmol/g	[153]
CNTs	Hg(II)	1.068 mmol/g	[153]
TiO_2	Red 195 azo	87.0 mg/g	[154]
Fe_3O_4	Orange G and acid green	1883 and 1471 mg/g	[155]
Fe_3O_4	Methylene blue, neutral red, and methyl orange	1-2 mg/g	[156]
Fe_3O_4	Methylene blue (MB) and cresol red (CR), Crystal violet	6-35 mg/g, 166.67	[157,158]
TiO_2	N719 dye	65.2-76.6 mg/g	[159]
Zn-Fe_2O_4	Congo red	16.58 mg/g	[160]
γ-Fe_2O_3	Acridine orange	59 mg/g	[161]

cation of graphene-based materials as adsorbents for removing inorganic species from wastewater may offer many merits [129]. Single-layered graphene materials possess two basic planes available for adsorbing pollutants [127-129]. In contrast, the inner walls in CNTs are not approachable by the adsorbates [127].

Many studies have used GO as a model adsorbent for remediating metal ions in wastewater [130-132]. Existence of oxygen groups in graphene oxide structure can offer a good interaction with metal ions, which was confirmed through comparing the Pb(II) adsorption performance of virgin and oxidized graphene sheets [133]. The removal of some important pollutants from wastewater by different nanoparticles is summarized in Table 5.

Table 5. Efficiency of carbon-based nanomaterials for contaminant removal from dairy industrial wastewater

Pollutant	Adsorbent	% Removal	Reference
COD	CNTs	81	165
TN*	CNTs	93	165
COD	GO	84	164
TN	GO	90	164
TP**	GO	80	164
Turbidity	GO	94	164

*TN: total nitrogen; **TP: total phosphate

The destiny, alteration, and toxicology impact of graphene-based materials to the environment have been broadly surveyed in the literature [134-136]. Yet, importance of their environmental impacts must be stressed. Detailed toxicology assessments and life-cycle investigates have to be done to distinguish the contours of graphene-based nanomaterials to apply their properties while diminishing the associated noxious effects. One large, crucial challenge is the successful reduction of GO to graphene material for restoring its intriguing properties. This GO reduction certainly looks as a most promising way for large scale obtaining graphene economically.

2-2-1. A Case Study: Dairy Wastewater Treatment

Wastewater from dairy industries causes substantial pollution of natural water environments. Wastewater generally comes from the dilution of milk or dairy products in addition to detergent materials and cloth fibers used in cleaning that takes place in the wastewater. Dairy wastewater is slightly alkaline, having unpleasant odors, bitter taste, and hard deposits when disposed without treatments. It may result in unfavorable effects on fish growth, reproduction and immunity in water bodies, harmful effect on beneficial microorganism's and plant growth [162,163]. Falahati and his coworkers [164] dealt with the dairy wastewater treatment by graphene oxide nanosheets, in which application of in situ sludge magnetic impregnation" (ISSMI) has been studied for sludge separation after adsorption process. The dairy wastewater was taken from Dairy Company in Tehran, Iran and the effect of operational parameters was studied, including adsorbent dose, pH, and contact time on the removal of total nitrogen (TN), total phosphorus (TP), COD, and turbidity. To increase the interaction between the magnetic nanoparticles and graphene oxide, modification of magnetic nanoparticle surface with amine functional group was performed. The authors confirmed the properly prepared GO and magnetic nanoparticles via SEM, FT-IR, CHNS, and VSM analysis. Some of the noteworthy features of the proposed treatment process were the high adsorption rate, high adsorption capacity, and high sludge separation rate. By increasing GO dose TN, TP, COD, and turbidity plummeted, and at adsorbent dose of 320 mg L^{-1}, the removal efficiencies of 90%, 80%, 84%, and 94% were observed for TN, TP, COD, and turbidity, respectively. The best absorption capacity of the adsorbent was 730 mg g^{-1} for TN, 600 mg g^{-1} for TP, 26,000 mg g^{-1} for COD, and 5,500 mg g^{-1} for turbidity. Freundlich and Temkin isotherms were highly fitting with lower errors than Langmuir. Since TN, TP, and COD are mostly particulates in dairy wastewater, they are trapped between GO nanosheets aggregate and distributed heterogeneously on the adsorbent surface. Consequently, the adsorption does not occur as monolayer on the surface of GO, thus following the Freundlich model, and the kinetics was found following the pseudo-second-order model. Regarding the short contact time, feasibility of absorption process, and elimination of sludge-related expenses, this process can appropriately substitute biological processes for nitrogen, phosphorus, COD, and turbidity removal from dairy wastewater.

3. Membranes and Membrane Processes

The key idea that wastewater treatment contingent on is to overcome the unwanted species from water. Membranes physically hindering such constituents depend on their size, permitting the use of eccentric water sources. They supply significant degree of automation, need small areas and reagents utilization [165]. The intrinsic exchange between membrane selectivity and permeability is the prime obstacle of the membrane technics. The high-energy expenses are a crucial difficulty to the full use of pressure compelled membrane processes. Membrane fouling increases the energy consumption and lessens the lifetime of membranes whose material is highly controlling the performance. Blending functional nanomaterials into membrane structures highly rectifies the permeability, antifouling, mechanical properties and thermal stability, along with better acts for toxins elimination and self-cleansing.

3-1. Nanofiber Membranes

Electrospinning method is competent for making ultra-fine fibers. It can utilize numerous materials suchlike ceramics, polymers, and metals [166,167]. These made nanofibers possess high porosity and specific surface area as mats having intricate pore structures. Arrangement of the electrospun nanofibers, composition, diameter, and secondary phases, can be readily controlled for precise applications [167]. Nanofibers can remove micro-particulates from aqueous sources with a good rate and no considerable soiling [168]. Accordingly, they can be utilized for pretreatments preceding filtration or reverse osmosis (RO) processes. Adding functional nanomaterials as dopants to the solutions during the spinning give rise to implanted nanofiber fabrication [169,170]. The extraordinary and adjustable characteristics of electrospun nanofibers makes them a perfect platform for making multifunctional membrane filters by merging or inserting materials like TiO_2 on the nanofibers. As example, by integrating ceramic nanomaterials or specific catching agents on the nanofiber scaffold, nanofiber membranes can be premeditated to remove heavy metals and organic pollutants throughout filtration.

Copper smelters may release high concentrations of Cd, one of the most mobile and toxic among the trace elements, into nearby waterways [171]. It is not possible to achieve complete removal of some sorts of pollutants, as metals, by conventional treatment methods. Affinity membranes can successfully play a big role in removing heavy metal ions in the future. Polymer nanofibers functionalized with hydrated alumina/alumina hydroxide and iron oxides would be used for affinity membranes fabrication for wastewater industry applications. This polymer nanofiber membrane performs as a carrier of the reactive nanomaterial attracting toxic heavy metal ions, such as As, Cr, and Pb, by adsorption mechanism.

Compared with heavy metal pollutants, the overall water quality is much more sensitive to organic pollutants. Again, affinity membranes provide an alternative approach for removing organic molecules from industrial wastewater. For example, β-cyclodextrin is a cyclic oligosaccharide comprised of seven glucose units. It has a stereo-specific toroidal structure with a hydrophobic interior and hydrophilic exterior that can capture hydrophobic organic molecules from water by forming an inclusion complex. β-Cyclodextrin has been introduced into a poly(methyl methacrylate) nanofiber membrane using a physical mixing method to develop an affinity membrane for organic waste removal [172].

3-2. Nanocomposite Membranes

Membrane nanotechnology has concerned creating multifunction by adding nanomaterials into polymeric or inorganic membranes. Nanomaterials used for such applications comprise hydrophilic metal oxide nanoparticles (like Al_2O_3, TiO_2, and zeolite), antimicrobial nanoparticles (like nano-Ag and CNTs), and photocatalytic nanomaterials (like bi-metallic nanoparticles, TiO_2). Adding metal oxide nanoparticles like alumina, silica, zeolite and TiO_2 to polymeric ultrafiltration membranes has shown an increment in the hydrophilicity of the membrane surface, its permeability, or antifouling character [173-176]. Furthermore, an enhancement in different mechanical and thermal features of polymeric membranes

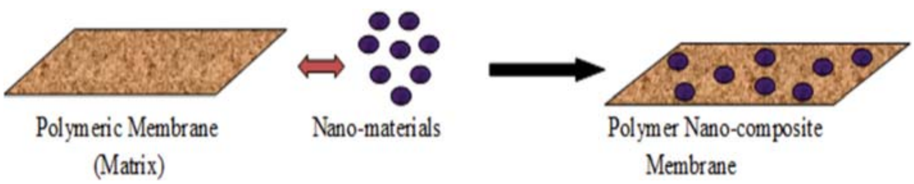

Fig. 7. Representation of polymer nano-composite membrane [177]. Reprinted with copyright permission from OMICS publisher.

Table 6. Efficiency of nanomembranes for contaminant removal from some industrial wastewater

Contaminant	Removal efficiency	Reference
Remazol fiber reactive dyes from cottage textile industry	≥80%	184
Dairy effluents	75-95%	185
Removal of COD, NH_3-N, NO_3-N, and PO_4-P from hospital wastewater	COD (92%), NH_3-N (88%), NO_3-N (80%), PO_4-P (68%)	186
COD, Paracetamol and Nebivolol compounds from complex industrial wastewater	COD (97%), Paracetamol and Nebivolol compounds (100%)	187
Reactive dye Black 5 removal from textile effluent	99%	188
TSS, TDS, oil, grease, COD, BOD from oil wastewater	TSS (100%), TDS (44%), oil (99%), Grease (80%), BOD (76%)	189
Wastewater oil content from Petroleum refinery wastewater	69%	190
Heavy metals and iron from Petrochemical wastewater	70 & 75%	191
COD, BOD_5, TSS, VSS, and Turbidity from petroleum refinery wastewater	COD (82%) BOD_5 (89%), TSS (98%), VSS (99%), Turbidity	192
COD of refinery wastewater	44%	193
COD of petroleum wastewater	93%	194

has been obtained by adding these nanoparticles materials [175,177].

Nanomaterials having antimicrobial activities like nano-Ag and CNTs are capable of decreasing membrane biofouling. Polymeric membranes doped with nano-Ag inhibit bacterial adherence and biofouling [178] of the membrane surface besides deactivating viruses [179]. Nevertheless, its lasting effectiveness to membrane biofouling has not been announced yet. CNTs deactivate bacteria upon contacting directly [180]. As CNTs are water insoluble and not eaten, no replacement is needed [181].

Membranes incorporated with photocatalytic nanoparticle merge physical separation function and the high reactivity of a catalyst towards degrading contaminants. Considerable effort has been dedicated for developing photocatalytic membranes consisting of nano photocatalysts as nano-TiO_2 or modified nano-TiO_2 as well as nano-zero-valent iron (nZVI) [182,183,187].

RETAINING AND REUSE OF NANOMATERIALS

Regenerating and reusing nanoadsorbent materials from an aqueous solution is highly difficult and might create environmental problems, as the adsorbed compounds need to develop sample pretreatment and separation technologies. Petrik et al. [195] claimed that nonporous carbonaceous and nanostructured adsorbent materials can be regenerated using mechanical force or thermal or electromagnetic energy using simple pressure or centrifugation, which renews the adsorption efficiency to minimum 70-90%, and higher dependent on the adsorbent weight. As an alternative, ballistic electrons emitted from the nonporous carbonaceous and nanostructured adsorbent material using microwave irradiation can also destroy the adsorbed compound.

The retaining and reuse of nanomaterials through filtration membrane is a key feature of nanotechnology-enabled device design to permit unceasing chemical use due to both cost and public health concerns. Furthermore, ceramic membranes are more advantageous than polymeric membranes in photocatalytic applications, as they highly resist UV [196] and chemical oxidants. Nanomaterials also can be restrained on various resins and membranes so further separation can be avoided. More research is required to advance simple, low-budget methods to immobilize nanomaterials without affecting their performance. However, the potential liberation is expected to be largely dependent on the immobilization technique and the separation process employed. For nanomaterials, which release metal ions, their dissolution should be cautiously controlled (via coating or optimizing shape and size). The detection of nanomaterial liberation is a major technical hindrance for risk evaluation and still challenging, especially for retaining and reutilization nanomaterials to rectify the process cost [197,198]. For comprehensive applications of nanomaterials in treating wastewater, duet of investigative requirements is required. Upcoming studies in compliance with real conditions are desirable to assess the use and efficiency of different nanomaterials.

CRITICAL COMPARISONS

The treatment of industrial wastewater is complex and often needs multiple sequential treatment steps that form the 'treatment train.' Though distillation of contaminated water is guaranteed to remove all but volatile contaminants, this treatment option can be prohibitively expensive [199]. Furthermore, not all industrial water requires such extreme treatment. For example, to be internally reused in the Oil & Gas industry, the water produced does not need to be completely desalinated as long as specific contaminants are removed [200]. In addition, many existing treatment processes are inefficient and have operating challenges. For example, oil in wastewater may delaminate membranes, change their separation capabilities and inhibit the functionality of different adsorbers, requiring an oil/water separation step before further treatment is possible; microorganisms escaping pretreatment will foul the surfaces of desalination membranes, but unquenched disinfectants in pretreated water can oxidize the desalination membranes or destroy them; sparingly soluble minerals in impaired water will deposit damaging scale on membranes, limiting water recovery during desalination; and residual iron and organic matter can poison ion-exchange resins and other adsorbers, requiring oxidation or adsorption before the water can be further treated. Furthermore, certain technologies have intrinsically limited capabilities; reverse osmosis membranes are limited by osmotic and hydraulic pressure, as well as by mineral precipitation; adsorbers are limited to specific compounds having specific functional groups or structures; and most ion exchange surfaces are specific to specific chemicals [201]. Biological treatments are mainly limited to biodegradable compounds, being sometimes obstructed by the presence of toxic materials in effluents such as complex halogenated organic compounds [202]. Physicochemical methods have also some drawbacks: most of them are relatively expensive and may pose some undesired environmental consequences. As an example, the application of filtration or adsorption processes may result in producing a highly concentrated sludge, thus transferring the toxic environmental contaminants from one phase to another.

In general, there are some barriers for introducing a new technology in the industry, mainly because of the high capital costs and strict environmental regulations which require the technology to be well proven in terms of its efficiency before commercialization. Literature shows that nanotechnology has many advantages over conventional technologies, including the possibility to decrease the size of the reactors and also to amend the treatment efficiency [203]. Nanomaterials offer a unique array of properties that are difficult to obtain using traditional chemicals or bulk materials. Instead of adding bulk chemicals to the entire flow stream, the localized surface reactions allow treatment at targeted locations, greatly enhancing treatment efficiency. Example applications include, among many others, localized reactions that can achieve disinfection at surfaces to prevent biofouling by adding nanosilver or graphitic materials [204,205] disinfection based upon nanomaterial shapes, heating for thermal distillation or oxidation/regeneration of organic pollutants on surfaces, selective sorption of trace organic or inorganic pollutants [206-209]. Many nanomaterials have catalytic properties, and nanotechnology enables the use of both low-cost catalysts such as titanium dioxide activated by light; as well as higher value catalysts such as palladium, platinum, or gold activated by hydrogen peroxide to degrade oxo-anions or chlorinated organics [210-213]. The large surface area offered by nanostructures has already been incorporated into many sorbents such as granular activated carbon for organics removal or granular ferric oxides for arsenic removal, but these materials are traditionally produced in "top-down" processes that involve synthesizing micron to millimeter sized materials and crushing them into pellet-sized media for use in packed bed treatment systems. Nanotechnology allows for "bottom-up" design of sorbents, where morphology, pore sizes and surface composition can be controlled, and then materials can be used directly or agglomerated into pellet-sized media. Specific surface area may not be the key factor for adsorption within the nanorange; instead, available surface area based on the number of reactive sites is a more important characteristic, as shown for selenium ion sorption to nano-hematite [209]. The prior example of agglomerated nano-TiO_2 media for arsenic removal is one example. Thus, the difference between "top-down" and "bottom-up" preparation is one important feature of nanomaterials. In some cases, the economics of manufacturing bottom-up products has limited acceptance of some wastewater treatment products, but the nanomaterials synthesis revolution is moving from custom design to bulk scale manufacturing.

PERSPECTIVE AND FUTURE PLANS

Currently, there is no question of the efficiency of utilization of nanomaterials in industrial wastewater treatment, but they have number of serious disadvantages since they might release into the environment during treatment processes; they can aggregate for long time causing serious risks. In this regard, a pressing need for more research to reduce the environment toxicity is required. Among various metal oxide nanoparticles, TiO_2 for example is widely used and has some major limitations and some harmful effects on environment and human health, thus generating difficulty to develop sustainable removal of environmental pollutants. In this regard, new research initiatives should be explored to counter these challenges and many researches have been ongoing to beat these obstacles. Some studies have already developed new way to decrease the band gap to use solar energy efficiently. Moreover, further work is required to develop the cost-effective methods for the nanomaterial's synthesis and for successful field application to find the efficiency of the materials.

The need of the market is to limit the procedure costs regarding the environmentally friendly nature of the mentioned nanomaterials. For this use, significant emphasis will be devoted to green technology, using low-cost materials (agricultural wastes or byproducts). There are already many works in this field, which are expected to be further improved. The leading disadvantage of the already published studies is that their use is still in the laboratory scale without pilot studies. Limited attempts for detailed economic and market analyses are available [214]. The main future goal of the market is to move the treatment process to a pilot or industrial scale, which would call for an important financial and technological effort. In this regard, universities can play an active role through a more official approach to technology transfer and protection of copyrights [215].

CONCLUSIONS

Nanomaterials possess a number of unique physicochemical features. These features make them very attractive for wastewater treatment: (i) higher surface areas compared with conventional particles; (ii) capability of being functionalized with diverse chemical groups acting to enhance their affinity toward a specific compound; and (iii) use as high selectivity recyclable legions for detrimental elements or ions in effluents. Obviously, the adsorption mechanism and kinetics of various adsorbents depend on the adsorbed materials and the physicochemical investigational parameters as pH of the solution, original concentration of the dye or metal, adsorbent's dosage, and the system temperature. Hence, besides availability and cost, these factors should be considered while evaluating the adsorption capacity of different adsorbents. This review showed that the discussed nanomaterials are favorable adsorbents that can be employed to efficiently remove contaminants, either dyes or metals, from industrial wastewaters.

Commonly, adding diverse categories of NPs (ZnO, Ag, Cu, GO,

TiO_2, graphene, Al_2O_3, and iron oxides) into membranes modifies their hydrophilic characters, thus diminishing the fouling feature. Additionally, some important properties of the polymers are improved likewise. Various chemical modifications for nanocomposite membranes lead to encouraging results for the precise removal of heavy metals. Finally, advancement of new nanocomposite membranes has shown great success in treating wastewater, owing to their antifouling and antibacterial characters, in an effort to rectify their lifetime and elimination efficacy. Yet, nanomaterial applications for industrial wastewater treatment have some major limitations and some harmful effects on environment and human health, thus creating difficulty for developing sustainable removal of environmental pollutants. Hence, new research initiatives should be explored to counter these challenges and overcome these obstacles.

CONFLICTS OF INTEREST

No conflict of interest to be declared.

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