Nanomaterials and Their Role in Removing Contaminants from Wastewater—A Critical Review

Violeta-Carolina Niculescu, Marius Gheorghe Miricioiu, and Roxana-Elena Ionete

Abstract Removal of contaminants from wastewater has become an important research area because the amount of available drinking water in the world continues to decline due to rising demand and/or long periods of drought. Furthermore, the chemical and petrochemical industry generates a wide variety of highly toxic residues. Treatment of wastewater is a controversial field in terms of environment protection. In this chapter, several nanomaterials, which impart their unique properties, will be discussed. Among nanomaterials, carbon nanotubes (CNTs) are a form of carbon allotrope with a graphite-like structure, displaying various adsorption characteristics, as a result of the diameter, internal geometry, physical and chemical properties or the obtaining method. Contaminants removal using CNTs needs further research, only limited studies being available and more practical applications are needed to confirm the results. Several other adsorbent nanomaterials have been reported in literature. Among them, mesoporous materials have large surface areas and narrow pore size distribution, ranging from 20 to 100 Å, being suitable for liquid phase reactions because they favor the diffusion of the reactants to the active site. The adsorbents can be very effective for adsorption of several types of contaminants, such as heavy metals and different types of dyes. Recently, advanced research targeted the wastewater treatment by using nano catalysts, nano photocatalysts or membranes. The purpose of this chapter was to accomplish a comprehensive overview on the use of nanomaterials in wastewater treatment. The renewed interest in the environment pollution has led to the development of effective models describing the performances of these technologies.

Keywords Adsorption · Catalysis · Nanomaterial · Wastewater

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1 Introduction

Safe drinking water and sanitation facilities are essential for human health and well-being, but also a basic necessity for crops and animals. Since water is the key of the body's metabolic processes, once contaminated with toxic compounds, it can cause serious diseases such as cholera, diarrhea, dysentery, hepatitis and typhoid. Up to 1 million people die every year due to diarrhea caused by drinking water or poor hygiene [1]. Due to rapid urbanization and climate change, it will become a challenge to consume water with proper quality, for general needs and even for agriculture. In 2017, according to World Health Organization, 1400 million people use water sources located 30 min away from them, 206 million takes more than 30 min to collect water, 435 million uses groundwater and 144 million uses untreated water from surface sources [1]. Therefore, to achieve high quality standards, wastewater treatment must be performed.

A combination of several factors lead to water pollution, such as the discharge of effluents from various sources (industrial, domestic), intensive use of pesticides in agricultural activities, and poor isolation of landfills. [2]. According to the European Environment Agency, the main contaminants present in soil due to commercial and industrial activities are heavy metals (31%), mineral oil (20%), polycyclic aromatic hydrocarbons (16%), aromatic hydrocarbons (13%), chlorinated hydrocarbons (13%) and others (7%) [3, 4]. The identification of appropriate technological advances and gaps that map with the contaminants removal from wastewater, must be a priority for correctly informing the scientists regarding the application of the best standards, resulting the safe use of water. Nevertheless, only a fraction of the wastewater streams are collected and appropriately treated by various methods (Fig. 1), i.e. primary (settling treatment), secondary (biological methods for reduction of organic compounds) and tertiary (stringent methods for reduction of nutrients) [5]. In Serbia, for example, 48% of the population collects sewage, but does not treat it before evacuation, while at the opposite pole, in Netherlands, 99% of the population applies strict treatments.

During the last decades, several unconventional and conventional technologies were applied for wastewater treatment, taking into account the pollution types, sources and levels. One of the classical technologies, intensively applied, is based on sand filters. Its main advantage consists in the complex filtration, resulting in the removal of solids, such as chemical (e.g. nitrite, nitrate, heavy metals and pesticides) and biological contaminants [6]. Two types of sand filters were used, namely slow and rapid sand filter introduced in various tank designs, depending on the water demands. The filtration rate for the rapid filter is up to 50 times greater than in case of slow filter, due to the particles size, which were significantly higher, ~up to 11 times. Another conventional technology used for many years for wastewater treatment is based on the use of biological activated carbon (BAC) filter, consisting of activated carbon covered by a biofilm [6]. The purification mechanism involves both adsorption and biodegradation [7]. A different filter used only for wastewater treatment, through its aeration configuration, is the biological aerated filter (BAF) [8, 9]. Also,

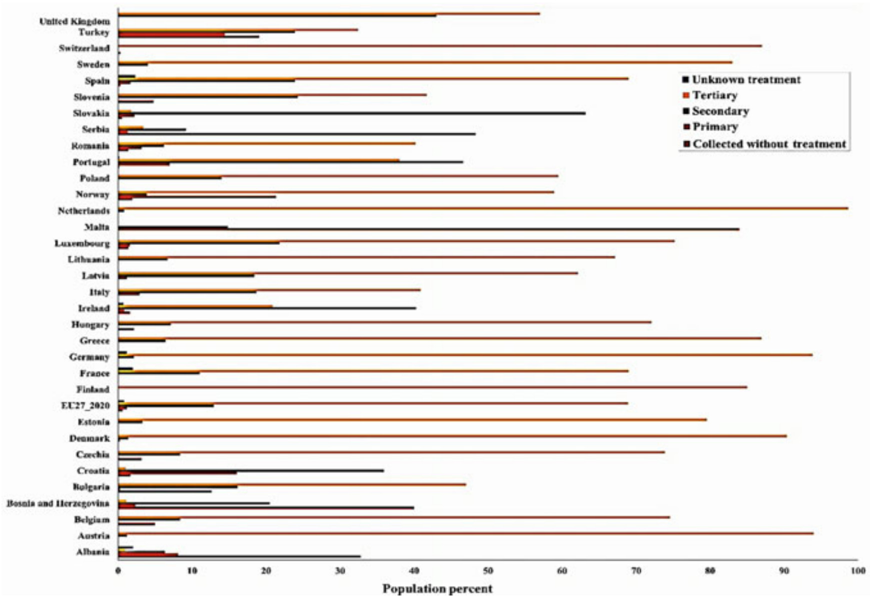

Fig. 1 Collected urban wastewater and types of the treatments

membrane filtration and chemical treatments by using chlorination, UV irradiation and permanganate oxidation have been and are still used, but, in some cases, these treatments do not reach the required standards for wastewater [10–13]. Nowadays, new highly efficient treatments with low-cost operation and environmentally friendly composition are used for human and environment.

In order to have an overview of the efficiency of removing contaminants, including metals, the treatment processes (Fig. 2) were structured in four main categories (nanofiltration, adsorption, reverse osmosis and ion exchange) [14]. It has been observed that conventional adsorption technology has the highest tendency to remove As and Hg, but lower efficiency for Ni removal. Reverse osmosis has a higher efficiency for removing Ni and Zn.

An important aspect of these technologies is the fabrication and operation cost. Taking into consideration the higher cost per treated water volume but lower operation cost, the nanofiltration remains a promising solution for water treatments, being intensively studied in order to obtain cheaper materials with higher efficiency and environmentally friendly properties [14]. The interest in using nanomaterials for wastewater treatment arises from their superior characteristics, such as high surface area, high surface free energy, tunable pores or reactive sites [15]. Therefore, various nanomaterials have been used in different wastewater treatment methods, involving adsorption, photocatalysis or membranes.

The aim of this chapter is to accomplish a comprehensive overview of results obtained in the past years on the use of nanomaterials in wastewater treatment. The renewed interest in the environment pollution has led to the development of

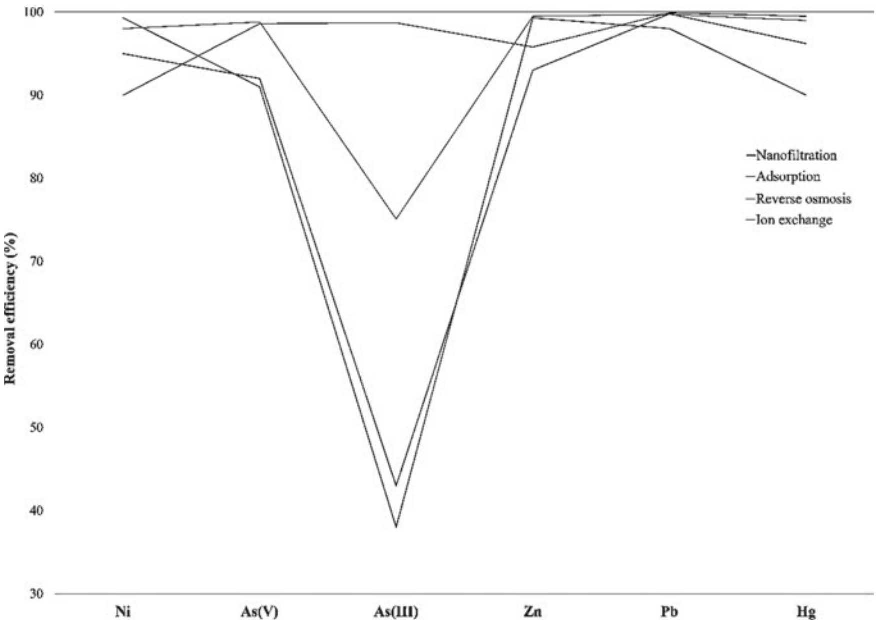

Fig. 2 Technologies efficiency for wastewater treatment

effective models, which equally well describe the performances of these technologies. For wastewater treatment, the nanomaterials can be considered easily adaptable approaches, but some concerns need to be addressed: their limitations, advantages, disadvantages and future perspectives. Moreover, their health risk must be evaluated by the research communities, being responsible for generating suitable regulation to surpass this concern.

2 Nanotechnology for Wastewater Treatment

The necessity of clean water is increasing worldwide due to the freshwater diminishing resources, caused by population increase, extended droughts, climate changes and strict water quality regulation [15, 16]. Nanotechnology has proved to be one of the most suitable methods for wastewater treatment. It can appropriately mitigate many of the water quality problems by using various functional nanoparticles and/or nanofibers [17]. Nanotechnology uses "materials with any external dimension in the nanoscale (around 1–100 nm) or having internal structure or surface structure in the nanoscale" (Fig. 3) [18, 19].

Nanomaterials have significantly improved physical, chemical and biological characteristics resulted from their structure and high surface area [21, 22]. These unique properties (Table 1) were studied for implementation in wastewater treatment

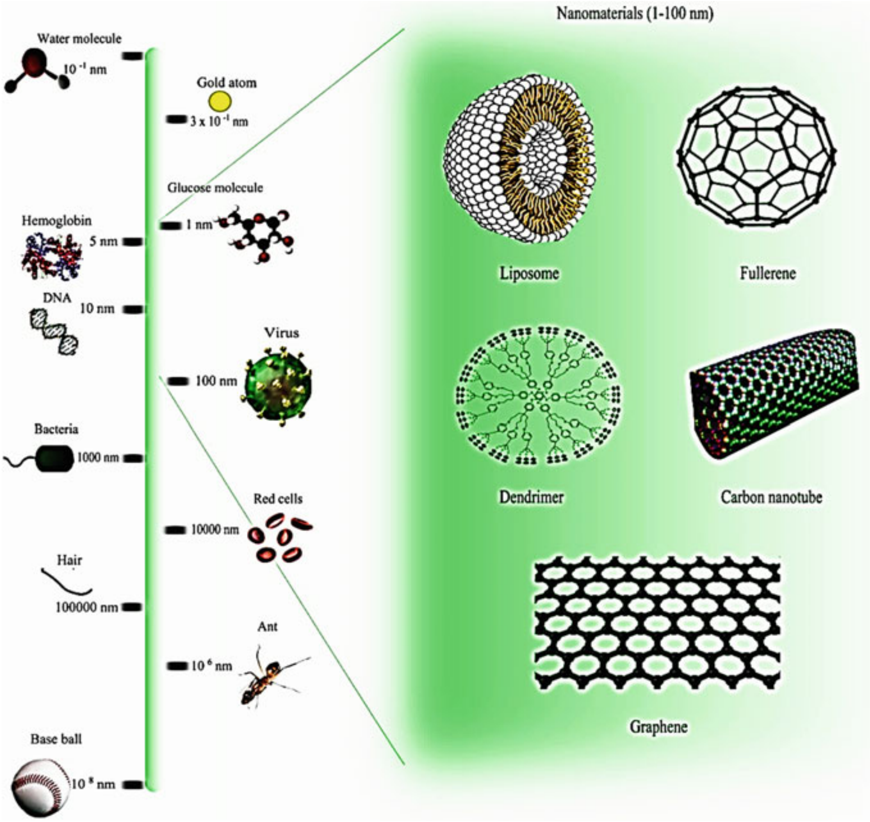

Fig. 3 A size comparison of nanoparticle with other larger-sized materials [20]

Table 1 Potential applications of nanomaterials in wastewater treatment

Treatment method	Nanomaterial	Nanomaterial improved characteristics
Adsorption	Carbon nanotubes, metal oxides, nanofibers, metal-organic frameworks	High specific surface area, selective adsorption sites, tunable pores, easy reuse, etc.
Photocatalysis	Nano-TiO_2, silica derivates	High stability and selectivity, low toxicity and costs, etc.
Membranes	Zeolitic, polymeric, mixed matrix membranes	High permeability and selectivity, hydrophilicity, low toxicity, mechanical and chemical stability, etc.

[23].

The high surface area-to-volume proportion of nanomaterials improves the reactivity against environmental contaminants. In the context of wastewater treatment and remediation, nanotechnology can supply both water quality and quantity, with low-costs and real-time measurements [24, 25]. Energy preservation results in cost savings due to the nanomaterials small sizes, but the total usage cost of the nanotechnology must be compared with other commercial techniques [26]. The development of various nanomaterials like nano adsorbents, nano catalysts, zeolites or nanostructured membranes resulted in toxic metals removal or organic and inorganic compounds.

2.1 Adsorption

Generally, the adsorption of emerging contaminants on the surface of nanomaterials is mainly influenced by the physical structure and chemical properties of the material, such as the pore structure, specific surface area or surface functional groups.

2.1.1 Carbon Nanotubes

Carbon nanotubes (CNTs) are allotropes of carbon with a graphite-like structure, exhibiting various adsorption properties as a result of the chirality, internal geometry and diameter, or synthesis method [27–33]. Carbon nanotubes are single-walled nanotubes (SWNT), having an internal diameter of about 1 nm [34, 35] and multi-walled nanotubes (MWNT), formed by a number of concentric tubes or laminated graphene layers [35–37]. Multi-walled carbon nanotubes can be obtained from single-walled CNTs by using supplementary chemical processing methods, in order to improve the contact area by several times and the amount of active sites for adsorption [38]. Table 2 gives an overview of the applications where CNTs have been used for the removal of emerging contaminants from water.

Specific surface area has an important influence on the adsorption performance of CNTs and it mainly depends on the presence of single- or multi-walled structures. For example, when SWNT were used, tetracycline was removed from wastewater with a 92% efficiency, while MWNT removed only 16% [44]. The adsorption coefficient (K_d) values of SWCNTs, MWCNTs were almost 1500 and 1100 respectively [44]. The sorption data of tetracycline on MWCNTs were evaluated using the Langmuir model, the maximum adsorption capacity being 269.5 mg/g and the efficiency 99.8% [42].

There are only few studies that compare the behavior of single- and multi-walled carbon nanotubes, the majority revealing better performance for the single-walled carbon nanotubes. Also, contradictory results were obtained by using the same carbon nanotubes for removal the same contaminant [45, 46]. For example, the removal of sulfamethoxazole from aqueous solutions was tested under various conditions [45,

Table 2 Adsorption of some emerging contaminants on carbon nanotubes

Nanomaterial	Contaminant	Treatment conditions	Maximum adsorption – q_m (mg/g)/coefficient – k_f ($mmol^{-1-n}L^n kg^{-1}$)	References
MWCNT	Norfloxacin	T = 30 °C; pH = 7	$q_m = 89$	[39]
MWCNT	Sulfamethoxxazole	pH = 7	$q_m = 46$	[40]
MWCNT	Sulfamethoxxazole	pH = 6	$k_f = 510$	[41]
MWCNT	Tetracycline	T = 20 °C	$q_m = 270$	[42]
MWCNT	Sulfonamides	T = 25 °C	$k_f = 352–2815$	[43]
MWCNT	Chloramphenicol	T = 25 °C	$k_f = 570–618$	[43]
MWCNT	Non-antibiotic pharmaceuticals	T = 25 °C	$k_f = 318–1521$	[43]
MWCNT	Tetracycline	pH = 5	$k_f = 240$	[29, 44]
KOH-activated MWCNT	Sulfamethoxxazole	pH = 6	$k_f = 2300$	[29, 44]
KOH-activated MWCNT	Tetracycline	pH = 6	$k_f = 800$	[29, 44]
SWCNT	Tetracycline	pH = 5	$k_f = 1150$	[29, 44]
KOH-activated MWCNT	Sulfamethoxxazole	pH = 6	$k_f = 5200$	[29, 44]
KOH-activated MWCNT	Tetracycline	pH = 6	$k_f = 1400$	[29, 44]

46]. Some authors reported that, from the multiple factors that can be varied, such as pH, adsorbent dosage or adsorbate concentration, the effect of pH affects adsorption capacity most strongly [45]. Others reported that, in the same conditions, the adsorption capacity was mostly influenced by adsorbent quantity or initial concentration of the adsorbate [46].

The adsorption capacity of CNTs can be improved by functionalizing them with other reactive nanomaterials, which is an area of ongoing investigation. For example, zero valent iron (nZVI) was immobilized on the surface of the CNTs to remove the diazo dye Direct Red 23 from aqueous solution [47]. The emerging contaminants removal by adsorption on CNTs still needs further research, only limited studies being available and more experimental proof being needed in order to sustain the reported trends.

2.1.2 Metal-Organic Framework (MOF) Nanomaterials

The adsorption properties of some MOFs are summarized in Table 3. Zeolitic imidazole framework (ZIF)-magnetic graphene oxide exhibited high adsorption efficiency

Table 3 Adsorption of some emerging contaminants on MOFs

Nanomaterial	Contaminant	Treatment conditions	Maximum adsorption – q_m (mg/g)	References
Cr(III) terephtalat-MIL101	Dimetridazole	T = 25 °C; pH = 6	$q_m = 185$	[48]
Cr(III) terephtalat-MIL101	Metronidazole	T = 25 °C; pH = 6	$q_m = 188$	[48]
Cr(III) terephtalat-MIL101	Naproxen	T = 25 °C; pH = 7	$q_m = 156$	[49]
Cr(III) terephtalat-MIL101	Ketoprofen	T = 25 °C; pH = 7	$q_m = 80$	[49]
Zeolitic imidazole framework-magnetic graphene oxide	Benzotriazole	T = 40 °C	$q_m = 300$	[50]
Zeolitic imidazole framework-8	1H-benzotriazole	T = 30 °C	$q_m = 299$	[51]
Zeolitic imidazole framework-8	5-tolyltriazole	T = 30 °C	$q_m = 397$	[51]
Metal organic framework-porous carbon	Ibuprofen	T = 25 °C; pH = 5	$q_m = 320$	[52]
Metal organic framework-porous carbon	Diclofenac solution	T = 25 °C; pH = 5	$q_m = 400$	[52]

against benzotriazole (300 mg/g) [50]. The ZIF-8 adsorption capacity for 1H–benzotriazole and 5-tolyltriazole was better evaluated by pseudo-second-order kinetics, fitting the Langmuir adsorption model with an adsorption capacity of 298.5 and 396.8 mg/g, respectively [51].

Various mechanisms were proposed for MOFs adsorption of pollutants from wastewater, such as Lewis acid–base interactions, electrostatic interactions, π–π interactions or H-bonding [50]. For example, it was reported that the adsorption of nitroimidazole antibiotics on MOFs was achieved by H-bonding between the $–NO_2$ group from nitroimidazole and $–NH_2$ from the modified MOFs [48]. One of the most important parameters that influence MOFs adsorption capacity is the pH. The 1H–benzotriazole and 5-tolyltriazole adsorption on ZIF-8 slightly decreased with the pH increasing [51]. The ZIFs negatively charged with magnetic reduced graphene oxide displayed rather stable adsorption for benzotriazole at pH varying between 4 and 9 [50]. Once the pH increased to 10, adsorption decreased due to the inhibition of electrostatic adsorption by the negatively-charged species graphene oxide [50].

Another MOF, MIL-101, was used for the saccharin adsorption from wastewater, displaying stable adsorption capacity at pH ranging from 3 to 7, which was attributed to the electrostatic interaction of positively charged MOF with negatively charged deprotonated form of saccharin and the stable H-bonding between the NH_2

function on urea-MIL-101 and saccharin anion [53]. Two MOFs composites, MIL-101/chitosan (MIL-101/CS) and MIL-101/sodium alginate (MIL-101/SA) were used for the adsorption of benzoic acid (BEN), IBP, and ketoprofen (KET), exhibiting similar variation of the pH-dependent adsorption, reaching a maximum adsorption at pH around 4, due to the influence of pKa-dependent electrostatic interaction [54]. Urea-modified MIL-101 manifested a decrease in the adsorption capacity one the pH was increased, as a result of the electrostatic interaction between the positive surface charge on MIL-101 and the negatively charged oxygen from the -NO_2 group of the nitroimidazole antibiotics [48].

2.1.3 Mesoporous Silica

Mesoporous silica materials (such as SBA-3, SBA-15, MCM-41 or MCM-48) gained intensive interest as potential adsorbents over the last years, due to their high surface area, tunable, ordered and uniform pores, high pore volume, thermal and mechanical stability and option for functionalization [55, 56]. As a consequence, they have been applied as adsorbents for organic dyes [57–59], heavy metals from wastewater [60, 61], polycyclic aromatic hydrocarbons [62], as well as other organic contaminants [63]. The adsorption capacity of several mesoporous silica materials for various dyes is summarized in Table 4.

As noted, SBA-15 manifested a significantly higher adsorption efficiency than MCM-48, due to its larger pore size (5.27 nm vs. 3.0 nm), allowing dye molecules to easily diffuse from SBA-15 surface to pores [58, 67]. Furthermore, the mesoporous silica adsorption capacity is dependent on the functional group, initially having a negative surface charge due to the Si−OH groups. In this respect, in order to improve the adsorption processes, the mesoporous silica surface was functionalized with groups suitable for adsorption of specific compounds. Various functionalized mesoporous silica materials were used for adsorbing dyes (Table 4). For example, mesoporous silica functionalized with amino or carboxylic groups have been used for adsorption of acidic and basic dyes, with good selectivity and rapid adsorption rate due to the high surface area and to the strong electrostatic interactions [68, 69]. The adsorption of Remazol Red dye by MCM-41-NH_2 reached an efficiency of 98.2%, higher than that obtained using Fe(III)/Cr(III) hydroxide (9%) or various carbon-based adsorbents [68, 69]. Mesoporous silica materials can be easily protonated in water, resulting in charging their surface which can interact with other ions in solution. As a consequence, mesoporous silica could be applied as efficient adsorbents for the removal of various organic contaminants [73].

Also, in the case of using mesoporous silica as adsorbent, the pH controls the amplitude of the electrostatic charges shared by the ionized contaminants molecules. In general, low pH will increase the rate removal of an anionic dye, while that of a cation dye will decrease [74–76]. For example, the removal of cationic methylene blue dye using 3-aminopropyl triethoxysilane-mesoporous silica was increased once the pH increased, a maximum adsorption capacity (66 mg/g) being achieved at pH equal to 7 [77]. The capacity of dimethyldecylamine-mesoporous silica for removing

Table 4 Adsorption of various dyes by functionalized or not mesoporous silica

Nanomaterial/textural properties (surface area – m^2/g; pore diameter-nm)		Functional group	Contaminant	Removal efficiency (R%)/Equilibrium adsorption-Q_e (mmol/q)	References
SBA	1435	–	Orange G—anionic dye	79/0.35	[64]
	1005; 21.6	Ethylenediamine Aminopropyl penta-ethylene-hexamine	Acid Blue 113—anionic dye	83.6/–	[65]
	1290; 6.8		Acid Green 28—anionic dye	95.9/–	[65]
	659; 5.2	–	Methylene Blue—cationic dye	99.1/0.15	[58]
	659; 5.2	–	Janus Green B—cationic dye	– /0.13	[58]
	707; 1.9	Hyperbranched-polyglycerol	Methylene Blue—cationic dye	– /<0.5	[66]
MCM	1149; 3.0	–	Methylene Blue—cationic dye	– /0.04	[67]
	1222; 5.6	–	Methylene Blue—cationic dye	– /0.07	[67]
	1647; 3.8	–	Methylene Blue—cationic dye	– /0.14	[67]
	215; 1.8	– NH_2	Remazol Red—anionic dye	99.1/–	[68]
	774; 2.5	– NH_2	Acid Blue 25—anionic dye	– /0.60	[69]

(continued)

Table 4 (continued)

Nanomaterial/textural properties (surface area – m^2/g; pore diameter-nm)		Functional group	Contaminant	Removal efficiency (R%)/Equilibrium adsorption-Q_e (mmol/q)	References
	754; 2.5	– COOH	Methylene Blue—cationic dye	– /0.30	[69]
Other mesoporous silica	285; 19.0	Dimethyldecylamine	Dark Yellow GG—anionic dye	– /1.71	[70]
	285; 19.0	– NH_2	Red Violet X-2R—anionic dye	– /0.90	[71]
	313	– NH_2	Acid Black 1—anionic	83.0/–	[72]
	516; 4.6	Dimethyldecylamine	Dark Yellow GG—anionic dye	– /1.96	[71]
	516; 4.6	Dimethyldecylamine	Red Violet X-2R—anionic dye	– /1.96	[71]

sulphonated azo dye from wastewater (0.3 mg/g) was slowly increased by decreasing the pH under 4. A higher pH conducted to the adsorption capacity decrease, probably due to the deprotonation of the surface groups and to the protonation of the acidic functional groups of the dye, resulting an electrostatic repulsion between the mesoporous silica and the adsorbate [70]. The maximum adsorption capacities of the acidic dyes were reported in solutions with a pH varying from 2 to 6, while for the cationic dyes, the optimum pH varied between 7 and 11 [78].

Heavy metal ions (Pb, Zn, Cd or Cr) are known as emerging contaminants in a water source. Their direct or indirect release as a by-product from different industries in wastewater stream is a part of water pollution. Ni-SBA-15 and Ni-MCM-41 obtained through co-condensation were used as adsorbents for removing Ni^{+2} from wastewater with an adsorption rate and capacity up to 95% [79]. Determination of Pb^{+2} traces in wastewater was achieved using mesoporous silica functionalized with Pb(II) [80]. The bifunctional modified Al^{+3}/Ti^{+4}-MCM-41 was used to remove Cd^{+2} ions from wastewater [81]. Additionally, the M41S and SBA series were preferred for removal of Cr(VI) from wastewater, due to their unique pore structure [82]. Functionalization of SBA-15 and MCM-41 with amino groups conducted to effective removal of heavy metals such as $Pb^{+2,}$ Cd^{+2}, Cu^{+2}, Ni^{+2} and Cr^{+2}, reaching high adsorption rate (around 99%) [83]. Also, SBA-15 functionalized with two types of functional groups, propyl-trimethylammonium and propyl-ammonium were obtained for nitrates removal from wastewater [84]. The adsorption capacity was influenced by the nature of the functional group and, also, by the synthesis method. It can be concluded that the selectivity and capacity of metal ions adsorption are affected by mesoporous silica obtaining method, functional groups and pH [85].

2.2 Photocatalysis

An advanced oxidation process for removing trace contaminants is the photocatalytic oxidation. The most studied photocatalysts consist of either metal oxides (such as TiO_2 and ZnO) or carbon nanotubes and graphene oxides combined with metal oxides (such as TiO_2, Cu_2O Co_3O_4 and $ZnFe_2O_4$). TiO_2 nanoparticles are used effectively for the photocatalysis of wastewater pollutants like benzenes, polychlorinated biphenyls (PCBs) or chlorinated alkanes [86]. Also, the microcystins were removed from wastewater by photocatalysis using TiO_2 nanoparticles in a "falling film" reactor [87].

Organic contaminants can be efficiently removed by doping TiO_2 with noble metals, due to the hydroxyl radical appearance [88]. For example, nano-TiO_2 doped with noble metal were applied in the methylene blue removal in the visible-light domain [89]. Al_2O_3 was deposited onto nanoporous TiO_2 and it was effectively used for the total organic removal from wastewater [90]. Similarly, significant results were obtained with photocatalysts derived from mesoporous silica, for example combining TiO_2/Al-MCM-41 and TiO_2/Al-SBA-15 for the of phenolic compounds removal from wastewater [91]. Carbon nanotubes were applied as reinforced photocatalytic

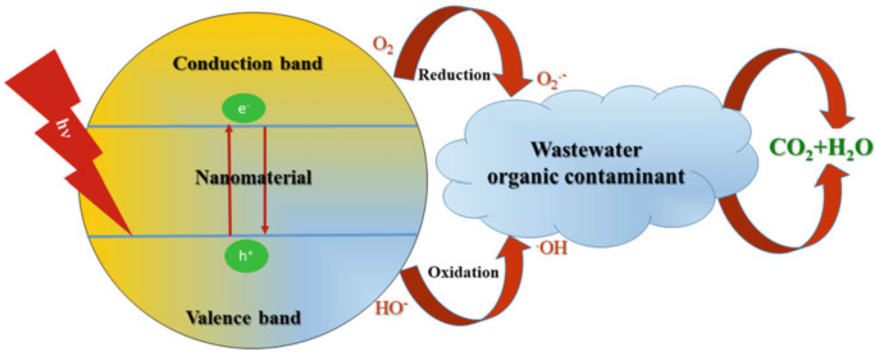

Fig. 4 Representation of photocatalytic mechanism

composite materials along with TiO_2 or ZnO, in order to improve their total surface area, defects or electrical conductivity, affecting the overall photocatalytic activity [92]. A mechanism of action for enhancing photocatalytic activity proposed the involvement of band gap or energy gap defined as energy intervals (no electrons exist) between the valence and conduction bands (Fig. 4).

The valence band consists in the highest energy state with electrons, whereas the conduction band is the lowest energy band without electrons [93]. Photons raised from various light sources can be exposed to a nanocatalyst, the vibration band electrons being excited and moving to the conduction band. In this manner a vacancy or hole appears in the vibration band. The holes react with water molecules or hydroxyl groups, resulting in hydroxyl radicals (·OH) that directly oxidize the pollutants on the carbon nanotubes surface. On the other hand, the excited electrons moved to conduction band form hydroxyl radicals, which interact with oxygen molecules, resulting superoxide radical ions (O_2 −·) that rapidly attacks and oxidizes the target contaminant.

The photocatalysis can be influenced by various parameters, such as light radiation, the type and nature of semiconductor, temperature, pH, as well as contaminant concentration [94]. Although photocatalysis efficiency is increased when UV light is used, various nanomaterials had been tested using visible light for photodegradation of pharmaceuticals and organic dyes [95]. The pH can affect the band edge position, and the surface charge of the nanocatalyst particles. In photocatalysis, the effect of pH is correlated with the catalyst surface charge, as well as with the ionic form of the substrate [96]. The photocatalysis can be improved if an oxidant is added to the reaction. This is captured on the catalyst surface, reducing the hole-electron recombination and promoting the formation of hydroxyl ions. For example, in the photocatalytic oxidation of sulfamethoxazole, hydrogen peroxide was used as oxidant agent which can absorb light, thus resulting the charge separation [97]. Regardless of the light type, introduction of photocatalysts in wastewater treatment can conduct to a decrease in energy requirement.

2.3 Membranes

Membranes act as physical barriers allowing various ions and molecules to pass through. Generally, the pressure-driven membrane process includes reverse osmosis (RO), nanofiltration (NF), microfiltration (MF) and ultrafiltration (UF). The membranes can be obtained with various shapes such as hallow fiber, tubular and spiral, with various separation efficacy.

2.3.1 Zeolite Membranes

Precise nanoscale crystal of 2D zeolites and obtaining of zeolite nanosheets with appropriate mechanical stability received great attention in the last years. Briefly, zeolite membranes are obtained using similar methods as for graphene and MOF nanosheets [98]. Various studies have been achieved in order to obtain a well dispersed suspension of nanosheets via exfoliation method, but their morphology and structure and were affected. Due to these disadvantages, only few studies achieved the rational design and obtaining of 2D membranes, based on pristine 2D zeolite nanosheets. For example, zeolite nanosheets with uniform thickness (≅3.5 nm) were prepared [99]. However, in order to produce well-characterized membrane microstructures, the focus should remain on the preferred orientation, designed interfaces and grain boundary control, with emphasis on reproducibility and stability under multicomponent contaminants mixtures. This can be accomplished by incorporating 2D zeolite nanosheets in an appropriate polymer matrix resulting mixed matrix membranes (MMMs).

Zeolite membranes were used as a substitute to polymeric membranes for desalination of complex wastewaters containing organic solvents or radioactive compounds, as well as in the situation when high temperature operation is required [100]. A preparation method of hydroxysodalite nano porous zeolite membranes on mullite support was reported and the membranes were used in desalination by pervaporation technique, studying the effect of various operation conditions such as feed pressure, temperature or rate on water flow. It was concluded that increased pressure, feed rate and temperature linearly influenced the wastewater flow.

2.3.2 Mixed Matrix Membranes (MMMs)

The aim of developing these membranes was to combine the advantageous properties of the two types of polymeric and ceramic membranes and increasing the overall process efficiency. Apart from the wastewater treatment, the MMMs have revolutionized other areas where separation or purification is important, such as gas separation [101]. Several researchers defined four types of MMMs, based on the membrane structure and filler location in the membrane structure (Fig. 5), namely conventional

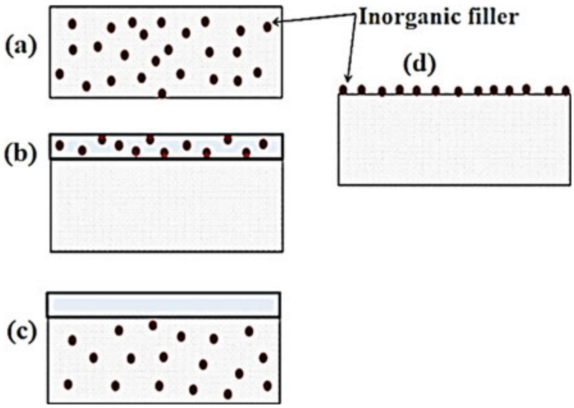

Fig. 5 Illustration of MMMs types: **a** conventional nanocomposite, **b** thin film nanocomposite, **c** TFC with nanocomposite substrate, **d** surface located nanocomposite

nanocomposite, thin film nanocomposite, thin film composite with nanocomposite substrate, and surface located nanocomposite [102].

Various MMMs contain inorganic fillers which attach to the support materials by covalent bonds, hydrogen bonds or van der Waals forces. These inorganic fillers can be obtained through sol gel, photothermal synthesis, thermal plasma synthesis, inert gas condensation, flame synthesis, low-temperature reactive synthesis, pulsed laser ablation, spark, mechanical alloying/milling, electrodeposition and so on [103]. Inorganic fillers contribute to obtain the MMMs desired properties. In the water treatment, these fillers have been incorporated for various purposes: disinfection [104], selectivity improvement [103] or to surpass membrane fouling [105]. Examples of inorganic fillers can be zeolite [106], TiO_2 [107], silica [108] or carbon nanotubes [109]. Figure 6 offers an illustration of various inorganic fillers for MMMs used in water treatment [110].

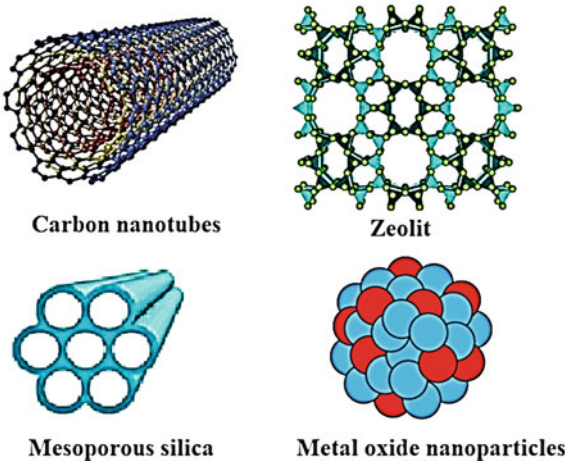

Fig. 6 Different types of inorganic fillers used for MMMs

Carbon nanotubes are currently considered as vital for water treatment, especially for desalination, being able to significantly decrease the cost and energy consumption [109]. MMMs can be obtained also by introducing organic fillers such as cyclodextrin, polypyrrole, polyaniline or chitosan beads into substrate matrix, mainly through blending or phase inversion [111, 112]. The advantage of organic fillers consists in having functional groups that makes them more suitable than the inorganic ones.

A nanocomposite membrane was obtained by blending polyaniline nanofibers in polysulfone polymer, resulting a membrane with good permeability and antifouling characteristic, resulting the water flow increasing up to 1.6 times [112]. Polyaniline nanospheres and oligomers were also introduced into polysulfone matrix, increasing the water flow from 1.7 to 4 times higher than the neat polymeric membranes [113].

The β-cyclodextrin polyurethane was mixed into polysulfone matrix for removal of Cd^{+2} contaminants from water [111]. The permeability of the obtained membranes increased up to 489 Lm^2/h, due to the appearance of wider pores on the surface, higher hydrophilicity and better pores inter-connectivity. The disadvantage was that β-cyclodextrin reduced the membrane strength due to the macro-voids appeared in the structure, resulting a lower mechanic stability [111].

Recent development was achieved by using hybrid fillers to obtain MMMs. Such membranes consist in two different fillers introduced in a continuous phase to accomplish a targeted purpose or to improve the overall process efficiency. For example, the combination of Fe(II)-Fe(III) oxide and polyaniline was introduced into polyethersulfone matrix, resulting a removal of 85% for Cu(II) from wastewater [114]. An antifouling MMM was prepared by Fe_2O_3 nanoparticles and multiwalled carbon nanotube inclusion into polyvinyldene fluoride, speeding the degradation of contaminants such as cyclohexanoic and humic acid [115]. The Fe_2O_3 nanoparticles improved the membrane hydrophilicity but caused the decrease of surface porosity. Reduced graphene oxide/polythiophene (rGO/PTh) were immersed into polyether sulfone matrix, designing an antifouling membrane with high permeability [116]. Despite the observed advantages of hybrid fillers, they could also affect the membrane efficiency, pore blockage being frequently observed [114].

3 Prospective of Nanomaterials Application in Wastewater Treatment

The key issue of nanotechnology introduction in wastewater treatment consists in the possibility of finding nanomaterials in high quantities at low costs. Scaling up these materials at industrial level remains a major milestone in nanotechnology application for wastewater treatment. Also, the nanomaterials characteristics (for example, high surface areas, size, shape or dimensions), their interaction with other contaminants than the targeted ones or with living beings are not fully elucidated and further research needs to be achieved. Environmental fate and toxicity of nanomaterials towards humans are still not fully explored.

The nanomaterials stability (oxidative, photochemical, biological or hydrolytic) in environment needs to be studied. Up to now, it was demonstrated that carbon nanotubes or TiO_2 nanoparticles are very toxic for humans. Many nanomaterials have carcinogenic effect and obstruct the normal cellular roles of lungs or immune system. In order to use nanomaterials in wastewater treatment systems, efficient methods need to be developed, being able to prevent the nanomaterials passing through the treated. Also, cost-benefit evaluation needs to be approached in order to evaluate the nanotechnology application for wastewater treatment.

The nanostructured membranes can be used for the degradation of various organic and inorganic contaminants. To improve their performances, it will be necessary a better understanding of the nanocomposites membranes formation. In this respect, the priority concern in the real field wastewater treatment must be directed towards the pattern of the nanoparticles within the matrix, as well as toward the changes in their structures and properties.

Mixed matrix membranes are claimed to be efficient in terms of efficiency, permeability and selectivity; however, some difficulties were identified, restricting their wider applications. The drawbacks include the discovery of compatible nanoparticles, complexity of the synthesis, high cost, morphology control, as well as structural defects. Furthermore, the introduction of inorganic particles into an organic membrane for wastewater treatment presents a potential hazard to environment and human health, a milestone that must be addressed in the near future. Despite this, it is considered that MMMs have great potential, their successful and competitive application requiring a combined effort to solve the identified drawbacks in order to compete with the classical purification technologies. This chapter aimed to provide a systematic review and a critical bibliometric analysis on nanomaterials and techniques (such as adsorption, photocatalysis or membrane technology) that can be applied for the removal of various classes of contaminants from wastewater.

4 Conclusions

This study intended to emphasize the use of nanomaterials for removing pollutants from wastewater by adsorption, catalysis or membrane processes. While many studies approached the endocrine disrupting chemicals removal, it also must be mentioned the increased interest in pharmaceuticals and personal care products. Both the adsorption and catalysis processes showed great potential for removing pollutants from wastewater. For the adsorption technology, carbon nanotubes and mesoporous silica have attracted an increased interest, the proposed mechanisms including hydrophobic effect, hydrogen bonding, covalent bonding, π-π interactions or electrostatic interaction. In the last years, metal organic frameworks nanomaterials were studied for removing pollutants from wastewater. Among the nanomaterials used for photocatalysis, TiO_2 was, by far, the most studied. Membrane technology has efficiently replaced conventional water treatment. The idea of hybrid or mixed matrix membranes has risen, combining characteristics of polymeric and ceramic membranes by introducing inorganic particles as fillers in an organic polymer matrix, improving the efficiency, permeability and selectivity.

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