Environmental Chemistry Letters (2020) 18:1169–1191
https://doi.org/10.1007/s10311-020-01001-0

REVIEW

Carbon-based nanomaterials for remediation of organic and inorganic pollutants from wastewater. A review

N. Madima[1] · S. B. Mishra[1] · I. Inamuddin[2] · A. K. Mishra[1]

Received: 21 January 2020 / Accepted: 2 April 2020 / Published online: 15 April 2020

Abstract

The deterioration of water quality by pollutants is a major health issue. Actual remediation methods are limited, and, as a consequence, there is a need for new remediation technologies. In particular, nanomaterials of unique properties have been recently developed for remediation. Here, we review mechanisms and applications of carbon-based nanomaterials for the adsorption and photocatalytic removal of organic and inorganic pollutants in wastewaters. Nanomaterials allow enhanced adsorption due to strong interactions between pollutants and adsorption sites. In photocatalysis, enhanced efficiency is attributed to the improved light harvesting and reduced recombination of photo-induced electrons and holes.

Keywords Adsorption · Photocatalysis · Carbon nanotubes · Graphene-based · Graphitic carbon nitrate · Inorganic pollutants · Organic pollutants · Remediation

Introduction

An increase in the world's population together with the rapid growth of factories and industries has led to the energy crisis and environmental pollution. Environmental pollution has become a critical issue across the globe, threatening both industrialized and developing countries. Amongst the world's top environmental concerns, water pollution is a major threat to the human race and aquatic life. Water is one of the most abundant natural resources on Earth, covering about 70% of the Earth's surface, but only less than 3% of water is available and safe for human consumption (Grey et al. 2013; Adeleye et al. 2016). According to the study carried out by the World Health Organization (WHO), about 1.1 billion people worldwide are living without adequate water supply (Organization World Health (WHO) 2001; WHO 2017). The major concern in supplying freshwater lies in the contamination of water resources by a variety of organic and inorganic pollutants (Anderson et al. 2006; Gopinath and Kadirvelu 2018).

Inorganic pollutants include nutrients, sediments, heavy metals, and industrial waste (Zhang et al. 2020). Most of the inorganic pollutants exist naturally within the environment, but due to the increase in anthropogenic activities such as mining, industrial, and agricultural activities, their concentration within the environment has increased (Holt 2000). Most of the inorganic pollutants are non-biodegradable, and their accumulation into the human body can lead to serious diseases (Lu and Astruc 2018). Meanwhile, organic pollutants such as pesticides, pharmaceuticals waste, dyes, and many other forms of industrial waste that arise from the discharge of sewage, surface water runoff, agricultural activities, and industrial discharges cause significant environmental issues due to their persistence and bio-accumulation (Smith and Rodrigues 2015). Therefore, the pollution of water by inorganic and organic pollutants has become the most significant environmental problem threatening human life throughout the world (Feng et al. 2018). In light of this, attention to specific methods and technologies for their remediation is desired.

From the past decade, various conventional methods such as oxidation, precipitation, solvent extraction, distillation, bio-remediation, filtration, reverse osmosis, adsorption, coagulation, membrane technology, photocatalysis, etc., have been widely used for the remediation of both organic

✉ A. K. Mishra
mishrak@unisa.ac.za

[1] Nanotechnology and Water Sustainability Research Unit, College of Science, Engineering and Technology, University of South Africa, Florida Campus, Johannesburg, South Africa

[2] Department of Chemistry, Faculty of Science, King Abdulaziz University, Jeddah 21589, Saudi Arabia

and inorganic pollutants in wastewater (Anjum et al. 2016; Thines et al. 2017; Wang et al. 2018; Feng et al. 2019; Shi et al. 2019). Nevertheless, some of those methods have limitations such as high operational cost, production of a high amount of sludge which results in the generation of secondary pollutants, and economically not viable (Gunatilake 2015; Oguz 2017; Boikanyo et al. 2018; Crini and Lichtfouse 2020). Among the above-mentioned conventional methods, nano-based technology like adsorption, and photocatalysis has received tremendous attention due to their higher removal efficiency, lower operational cost, simplicity in design, and environmentally friendly (Santhosh et al. 2016; Sadegh et al. 2017; Thines et al. 2017; Wang et al. 2018; Shi et al. 2019).

Nano-based technology involves the manipulation of nanomaterials at atomic levels. NMs have at least one of their dimensions in the range of 1–100 nm and are characterized by unique physical and chemical properties such as large surface area, specific affinity, and surface activity. With increasing interest in the field of nano-based technology, carbon-based nanomaterials and their derivatives have emerged. Carbon-based nanomaterials have obtained significant attention in the field of wastewater remediation due to their interesting properties discussed in "Carbon-based nanomaterials" section (Ali et al. 2012; Smith and Rodrigues 2015; Thines et al. 2017; Lu and Astruc 2018). In light of this, this review highlights the deep insight of carbon-based nanomaterials and their potential applications in wastewater remediation. The emphasis on their roles in adsorption and photocatalysis removal of organic and inorganic pollutants is discussed. The upcoming section gives general information on various types of carbon-based nanomaterials.

Carbon-based nanomaterials

Carbon-based nanomaterials have received tremendous attention in the field of water and wastewater remediation (Shan et al. 2017). These nanomaterials are receiving much attention by researchers due to their unique properties such as small size, high surface area to volume ratio, high reactivity, high thermal and chemical stability, vast availability, and catalytic potential at the nanoscale (Madhura et al. 2019). The large surface area gives more active sites for interaction of the material with different chemical species from wastewater. They exist in various allotropic forms such as graphite, diamond, graphitic carbon nitrate, fullerenes, carbon nanotubes, graphene, etc., as shown in Fig. 1 (Jayaraman et al. 2018). Due to their unique properties, these carbon-based nanomaterials have made a greater contribution to the generation of clean, renewable, and viable forms of energy from light-based water splitting and pollutant removal. In

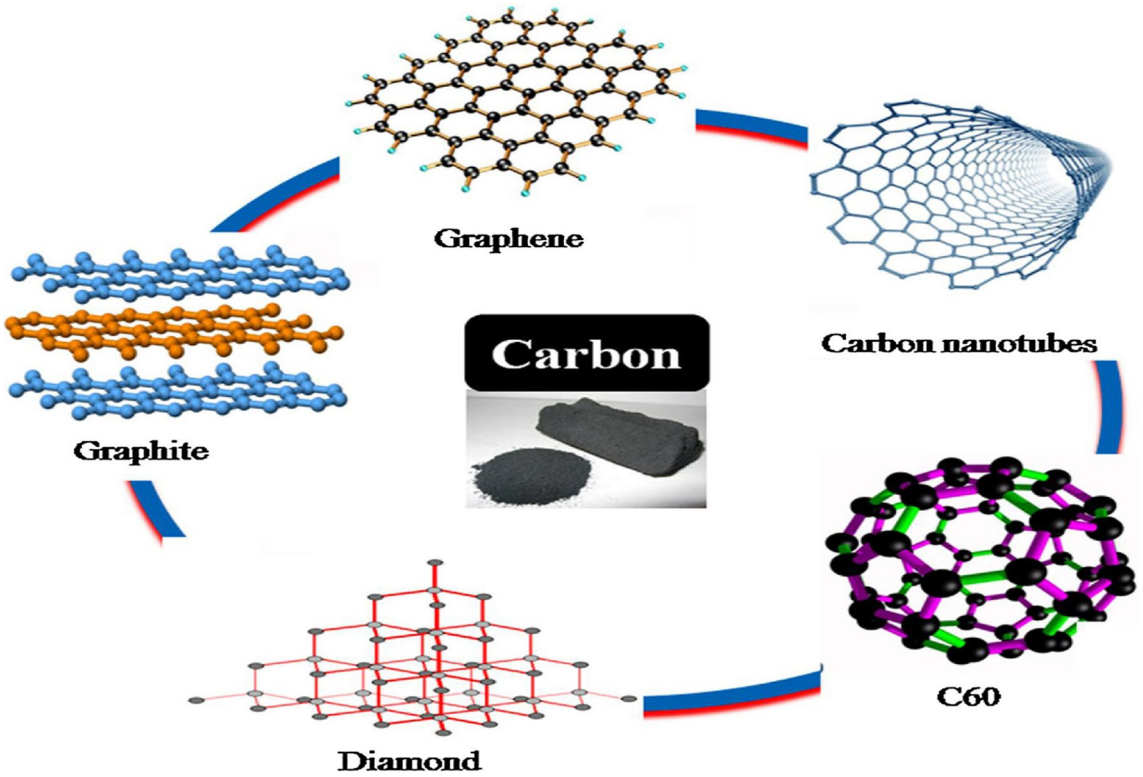

Fig. 1 Allotropic forms of carbon-based nanomaterials. Reproduced with permission from Jayaraman et al. (2018). Copyright 2018, Elsevier

this review, carbon nanotubes (CNTs), graphitic carbon nitrate (g-C_3N_4), graphene, and their derivatives are discussed with respect to their properties toward remediation of organic and inorganic pollutants in wastewater and some previously reported studies are given.

Carbon nanotubes

Carbon nanotubes are cylindrical carbon molecules rolled up in a tube-like structure (Cha et al. 2013). They are divided into two groups, i.e., single-walled carbon nanotube (SWCNT) and multi-walled carbon nanotube (MWCNT) depending on the number of carbon layers as shown in Fig. 2 (Ihsanullah et al. 2016). Single-walled carbon nanotubes are made up of single layer of carbon atoms, while multi-walled carbon nanotubes are made up of several layers of carbon atoms.

Carbon nanotubes have been widely used in the field of wastewater remediation as adsorbents, sensors, membranes, and catalysts owing to their unique properties such as large specific area, high porosity, hallow structure, light-weight, layered structure, and also their strong interaction with pollutants (Cha et al. 2013; Shan et al. 2017; Das et al. 2018). Varieties of toxic pollutants have been removed from wastewater using carbon nanotubes due to those interesting properties (Sarkar et al. 2018).

In addition, carbon nanotubes can also be coupled with other carbon-based materials to increase their effectiveness in removing a wide range of pollutants in wastewater. Although carbon nanotubes have been widely used in the field of wastewater remediation, this carbon-based nanomaterials lack the optimum performance due to the presence of impurities that could be carbonaceous species and residues utilized during preparation. The presence of those impurities results in the alteration of their surface properties by blocking the active sites for the interaction of this nanomaterial with pollutants (Thines et al. 2017). However, most of the studies have shown that the alteration can be prevented by functionalizing carbon nanotubes in the presence of acid and alkali solution which also results in the additional of the new functional group on the surface of carbon nanotubes which can be of particular interest in removing pollutants (Mubarak et al. 2017; Thines et al. 2017). The presence of new functional groups onto the surface of carbon nanotubes together with the nature of adsorbent is of particular interest in measuring the adsorption capacity of this carbon-based nanomaterial. This carbon-based nanomaterial has successfully proved to be an outstanding adsorbent for the removal of pollutants from wastewater, leading to a clean environment due to their exceptional adsorption capability and excellent regeneration and recovery abilities.

Graphene-based nanomaterials

Graphene, as one of the advanced carbon nano-materials, has received tremendous attention since its discovery in 2004 as a two-dimensional (2D) monolayer carbon nanomaterial consisting of sp^2-hybridized carbon atoms arranged in a hexagonal crystalline structure. They have gained significant attention as novel materials for environmental applications due to their high specific surface area (theoretically ~ 2630 m^2/g), high thermal conductivity (~ 5000 W m^{-1} K^{-1}), and rapid heterogeneous electron transfer (Perreault et al. 2015; Xu and Wang 2017; Jilani et al. 2018). In addition, their outstanding mechanical strength and some exceptional performance (such as abundant functional groups, high negative charge density, and extremely hydrophilic properties) make them exceptional nanomaterials in wastewater remediation (Pumera 2010; Wang et al. 2013; Qiu et al. 2018).

These nanomaterials are classified as graphene, graphene oxide, and reduced graphene oxide as shown in Fig. 3.

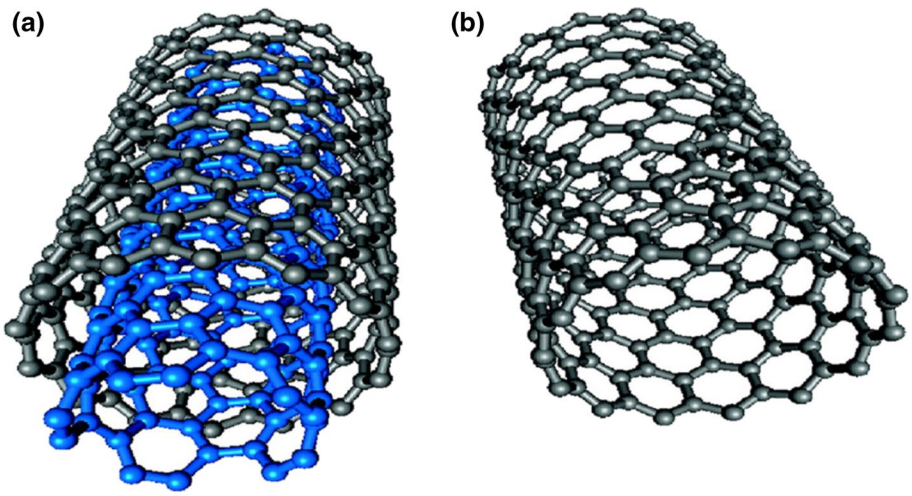

Fig. 2 Multi-wall carbon nanotubes (**a**) and single-wall carbon nanotubes (**b**), representing number of layers in each type of carbon nanotubes. Reproduced with permission from Ihsanullah et al. (2016). Copyright 2016, Elsevier

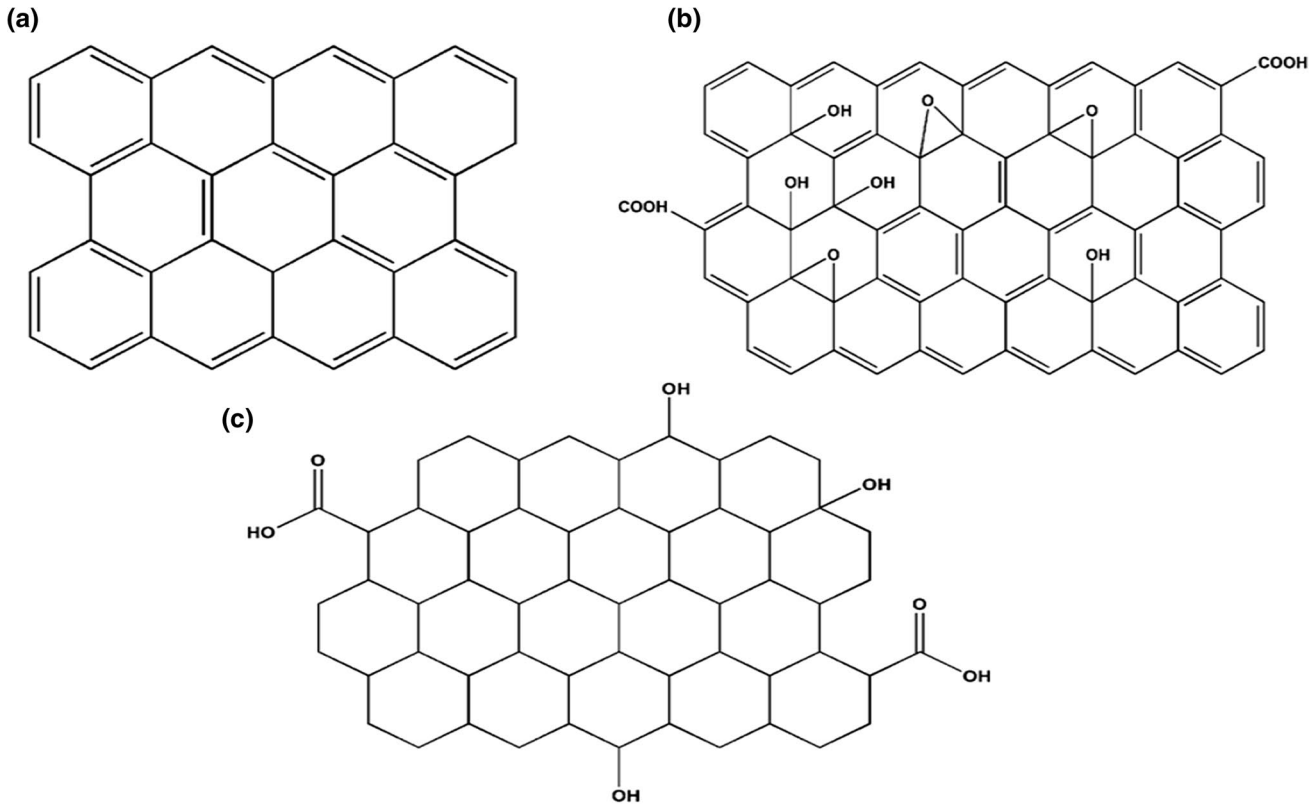

Fig. 3 Graphene-based nanomaterials: graphene sheets (**a**), graphene oxide (**b**), and reduced graphene oxide (**c**). Graphene oxide is obtained through functionalization of graphene using Hummer method and its chemical reduction yield reduced graphene oxide

Graphene (G) and reduced graphene oxide (RGO) are easily obtained through the reduction in graphene oxide (GO) using a simple chemical exfoliation method. In addition, graphene can also be functionalized into graphene oxide through Hummers method which shows a high density of oxygen functional groups (i.e., carboxyl, hydroxyl, carbonyl, and epoxy) in the carbon lattice which is of particular interest in removing a wide range of pollutants in wastewater (Perreault et al. 2015). This graphene oxide can be synthesized from simple and low-cost methods such as chemical oxidation of graphite to graphene oxide followed by exfoliation in ultrasonication (Lü et al. 2012). Due to its hydrophilic nature, high specific surface area, and high functional group density, it can be used as adsorbent and as a catalyst for the removal of organic and inorganic pollutants in wastewater (Perreault et al. 2015).

Application of graphene-based nanomaterials in the field of wastewater remediation is currently hindered by poor reusability and separation, which can be overcome through surface modification and hybridization ((Jun et al. 2018). In addition, this material is usually coupled with other nanomaterials for suitable applications due to its zero bandgap and susceptible to the oxidation reaction. When coupled with other nanomaterials, it can enhance the photocatalytic activities of other nanomaterials by acting as an electron acceptor and transporter (Kumar et al. 2017).

Graphitic carbon nitrate

Graphitic carbon nitrate (g-C_3N_4) is considered the most stable allotrope of five carbon nitride, i.e., α-C_3N_4, β-C_3N_4, g-C_3N_4, cubic-C_3N_4, and pseudocubic-C_3N_4 at ambient conditions with a stacked 2D structure (Sun et al. 2016). It has received much attention due to its unique properties such as metal-free composition, extraordinary chemical stability, non-toxic, graphite-like 2D structure, visible light response with medium energy bandgap (~ 2.7 eV), and tunable electronic structure (Yang et al. 2013). This polymeric semiconductor material consists of two low-cost earth-abundant elements (carbon and nitrogen) as shown in Fig. 4 and can easily be prepared from cheap feedstocks like urea, thiourea, melamine, dicyandiamide, and cyanamide, through thermal condensation (Zhao et al. 2015; Zhang et al. 2019). Its unique properties make it a promising candidate for solar energy conversion and environmental remediation (Wen et al. 2017). This nanomaterial has widely used in the field of photocatalysis due to its medium energy bandgap. However, its industrial application is still limited by poor

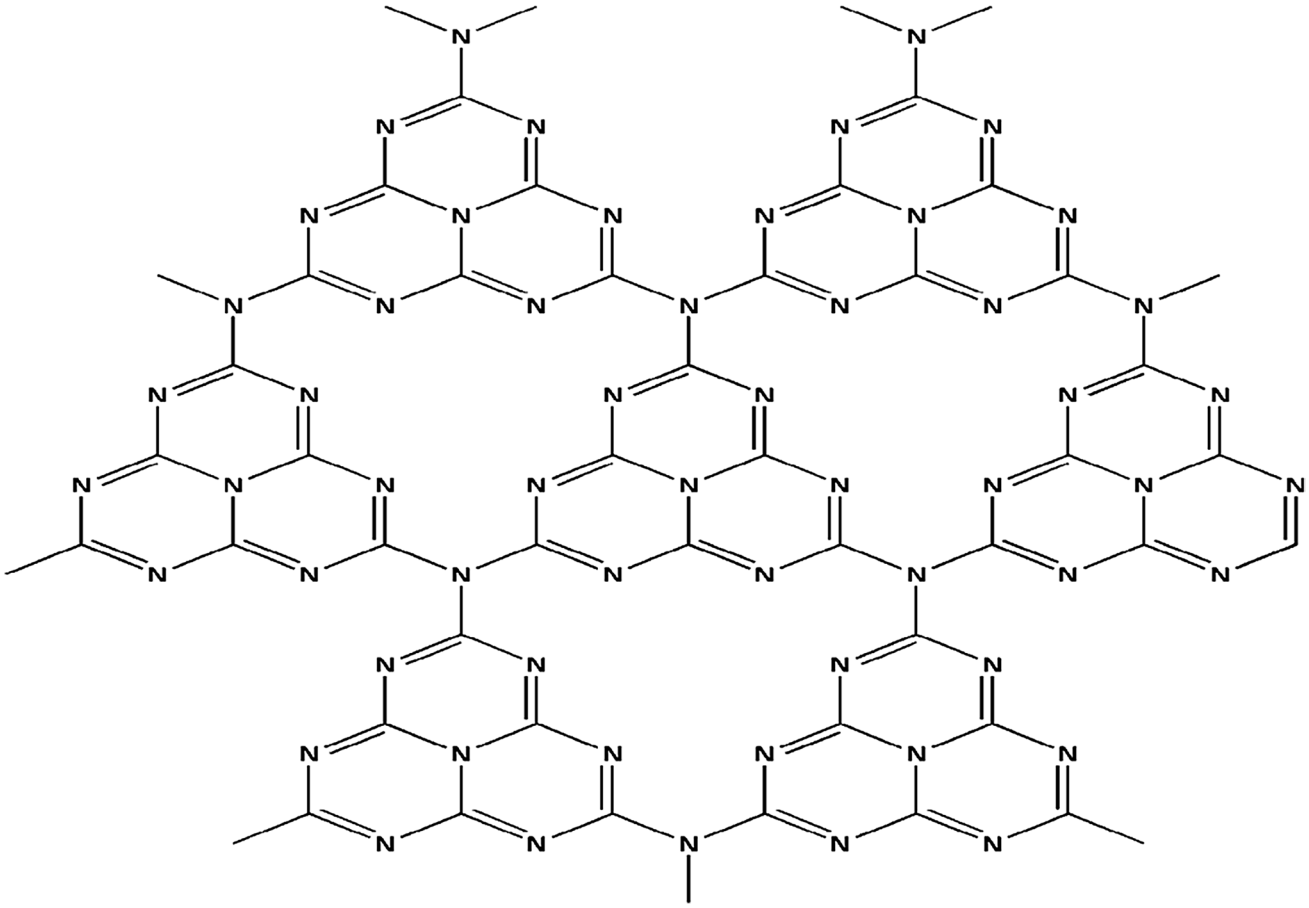

Fig. 4 The structure of graphitic carbon nitrate consists of two low-cost earth-abundant elements: carbon and nitrogen

light absorption, low charge separation, and a small surface area. A significant number of studies have been undertaken to modify this polymeric metal-free to overcome such drawbacks.

The upcoming section will highlight the application of discussed carbon-based nanomaterials, i.e., carbon nanotubes, graphene-based, graphitic carbon nitrate, and their derivatives in adsorption of organic and inorganic pollutants as well as in photocatalysis of organic pollutants in wastewater.

Application of carbon-based nanomaterials in water remediation

A variety of methods such as ion-exchange, coagulation, membrane filtration, electrochemistry, physical and chemical precipitation, chemical oxidation, adsorption, and photocatalysis have been commonly used for the removal of both organic and inorganic pollutants in wastewater (Demirbas 2008; Gupta et al. 2013). However, some of those methods suffer from drawbacks such as high operational cost, transforming the pollutants from one phase to another which results in secondary pollution being produced, difficult in operation, incomplete pollutants removal and are economically not viable (Oguz 2017). Amongst the methods listed above, adsorption and photocatalysis have received significant attention in the field of wastewater remediation. Hence, the upcoming section highlights the application of different types of carbon-based nanomaterials used in the adsorption and photocatalysis remediation of various pollutants in wastewater.

Adsorption

Adsorption is defined as a process in which gas or liquid solutes accumulate (adsorbate) on the surface of a solid (adsorbent) and forms a molecular or atomic film. This technique is regarded as a green, clean, and versatile method for the removal of organic and inorganic pollutants in wastewater due to its high efficiency, easy operation, and low cost (Radaei et al. 2017; Crini et al. 2019; Varghese et al. 2019). It usually occurs in two ways depending on the interaction between adsorbent and adsorbate: chemisorption and

physisorption. Physisorption that is also known as physical adsorption is a reversible exothermic reaction, which occurs due to weak van der Waals forces of attraction between adsorbate and adsorbent. This process takes place with the formation of a multilayer of adsorbate on adsorbent (Demirkıran et al. 2017; Access 2018). On the other hand, chemisorption which is also known as chemical adsorption is an irreversible exothermic reaction that occurs due to electrons exchange and strong chemical bonds formed between adsorbate and adsorbent (Yagub et al. 2014; Demirkıran et al. 2017). Chemisorption takes place with the formation of a uni-layer of adsorbate on the adsorbent. Both chemisorption and physisorption are usually affected by various factors such as temperature, pressure, nature of the adsorbate, and surface area of adsorbent (Access 2018). The performance of the adsorption process is measured based on the removal efficiency of the pollutants and is quite related to the adsorption capacity of the adsorbents being used (Thines et al. 2017). Surface properties such as specific surface area, active sites available on the surface, and the affinity toward the contaminants play a crucial role in the adsorption capacity of pollutants. Adsorbent having a large surface area and proper functionalities are the most commonly used.

Various factors such as temperature, nature of adsorbates, and adsorbents, the presence of other pollutants and other atmospheric and experimental conditions such as pH, temperature, the concentration of pollutants, contact time, and particle size are key factors playing an important role in the adsorption process (Ali 2010). The adsorption studies are usually explained based on various models such as Langmuir, Freundlich, Halsey, Henderson, Smith, Elovich liquid film diffusion, intraparticle diffusion, and Lagergren (Ali 2012). These models operate in a similar version but with a little difference in their approach. Furthermore, those models give a clear understanding of the surface interaction of an adsorbent and the adsorbates. Langmuir and Freundlich are the two commonly used models to predict the interaction between the pollutants and the adsorbent in the field of wastewater remediation (Mubarak et al. 2017). Langmuir adsorption isotherm model is usually used for monolayer coverage, while Freundlich is usually used for heterogeneous surfaces. The nature of adsorption can be studied by calculating parameters such as changes in the free energy of adsorption (ΔG_θ), enthalpy (ΔH_θ), and entropy (ΔS_θ) (Anastopoulos et al. 2019; Sahmoune 2019). To study the surface reaction, the kinetics of the adsorption is studied using pseudo-first-order, pseudo-second-order, Elovich, and intraparticle diffusion kinetic models (Mubarak et al. 2017; Jun et al. 2018). Adsorption isotherms, kinetics, and thermodynamics are summarized in Table 1 together with their formulas and description (Kumar et al. 2018).

Adsorption mechanism involves the adsorption of adsorbate molecules on the surface of adsorbent through molecular interactions, the diffusion of adsorbate molecules from the surface into the interior of the adsorbent to the interior; and the steps can be summarized as follows (Kannan and Sundaram 2001):

- Migration of pollutants from the bulk of the solution to the surface of the adsorbent,
- Diffusion of pollutants through the boundary layer to the surface of the adsorbent,
- Adsorption of pollutants within the active site on the surface of adsorbent and
- Intra-particle diffusion of pollutants into the interior pores of the adsorbent particle.

The adsorption capacity is estimated from the difference between the initial concentration (C_0) and the final concentration (C) of polluted water or wastewater as given by Eq. 1.

$$\text{Adsorption} = \frac{C_0 - C}{C_0} \times 100\% \quad (1)$$

The coming section highlights the application of carbon-based nanomaterials for the adsorption of organic and inorganic pollutants in wastewater.

Adsorption of organic pollutants

Recently, contaminations of water sources by a variety of organic pollutants such as dyes, pesticides, pharmaceutical waste, etc., are posing serious environmental issues across the globe. The discharge of organic pollutants into our water system without pre-treatment can cause harmful effects on living organisms and the ecosystem (Jarde et al. 2001). Most of the organic pollutants are reported to possess toxicity, mutagenic, and a carcinogenic property, i.e., dyes exhibit high toxicity levels even at low concentration (Yang 2011; Shanker 2017). In addition, most of the organic pollutants contain a complex structure that makes them highly resistant to biodegradation and recalcitrant to conventional biological and physical oxidation treatments. More recently, carbon-based nanomaterials have received tremendous attention as adsorbents for the removal of organic pollutants due to their incredibly unique properties. This section reviews the use of carbon nanotubes-based and graphene-based nanomaterials in the remediation of organic pollutants.

Carbon nanotubes for adsorption of organic pollutants Amongst carbon-based nanomaterials, carbon nanotubes have been reported to have strong adsorption ability for polar organic compounds due to their characteristic structure which permits strong interaction of carbon nanotubes with organic compounds through non-covalent forces, such as hydrogen bonding, π–π stacking, electrostatic forces,

Table 1 Adsorption isotherm, kinetics models, and thermodynamics constant parameters and correlation coefficients calculated for various adsorptions onto the various adsorbent

Isotherms	Formulas	Description
Sorption studies	$q_t = \frac{V(C_0 - C_t)}{W} q_e$	C_t = adsorbate amount at time t C_0 = initial adsorbate amount V = volume of the solution W = weight of adsorbent
Langmuir isotherm	$\frac{C_e}{q_e} = \frac{c_e}{q_{max}} + \frac{1}{q_{max} K_L}$	C_e is the equilibrium concentration (mg/L) q_e is the amount of the phenol adsorbed at equilibrium (mg/g) q_{max} is the maximum adsorption capacity K_L is the Langmuir constant related to the energy of the adsorption (L/mg)
Freundlich isotherm	$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$	K_F (L/mg) and $1/n$ are Freundlich constants giving an indicator of the adsorption capacity and the adsorption intensity
Kinetics and thermodynamics		
Kinetics		
Pseudo-first-order	$\log (q_e - q_t) = \log q_e - \frac{K_1}{2.303} t$	q_t is the number of phenolic compounds adsorbed at time t (mg/g), k_1 is the first-order rate constant (min^{-1}) and t is a time in min log $(q_e - q_t)$ versus t to give a linear relationship from which k_1 and q_e can be determined from the slope and intercept
Pseudo-second-order	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$	k_2 is the pseudo-second-order rate constant (L/mg min) (t/q_t) versus t to give a linear relationship from which k_1 and q_e can be determined from the slope and intercept
Intra-particle diffusion model	$q_t = k_{id} t^{\frac{1}{2}} + C_i$	k_{id} is the intra-particle diffusion rate constant (mg/g/$min^{1/2}$), C gives an idea about the thickness of the boundary layer, values of K_{dif} and C were calculated from the slopes of q_t versus $t^{1/2}$
Thermodynamics	$K_0 = \frac{C_0}{C_e}$ $\Delta G^\circ = -RT \ln K_0$	K_0 is equilibrium constant, ΔG° is change in Gibb's free energy, R is gas constant, T is the absolute temperature

van der Waals forces, and hydrophobic interactions (Gupta et al. 2013; Rong et al. 2017). Its mechanisms depend on the properties of the compound of interest (e.g., polar vs. non-polar). The prediction of adsorption of organic pollutants on carbon nanotubes is not straightforward since it depends upon the nature of the interaction between pollutants and carbon nanotubes (Yu et al. 2014; Apul and Karanfil 2015). Properties such as adsorption site, surface area, purity, and surface functional groups presence onto the surface play an important role in the adsorption of organic pollutants by carbon nanotubes. Carbon nanotubes consist of controlled pore size distribution and high surface active sites, results in exceptional sorption efficiency (Madhura et al. 2019).

In addition, carbon nanotubes turn to aggregate in an aqueous solution resulting in the creation of a lot of interstitial space and grooves, which result in high adsorption sites and contribute to an increase in adsorption capacity of organic pollutants. Multi-walled carbon nanotubes have been reported to be more effective in the removal of organic pollutants such as methyl orange, arsenazo(III), and methyl red from wastewater. Meanwhile, single-walled carbon nanotubes have also been reported to have high adsorption properties of organic pollutants due to their high surface area, and large micro-pore volume (Yu et al. 2014). The key factor in determining the cost-effectiveness of carbon nanotubes is regeneration. It suggested that carbon nanotubes can be regenerated by reducing the solution pH value using an acid such as nitric acid (Rong et al. 2017). Hence, this carbon-based nanomaterial has been used as adsorbents for a wide range of organic pollutants.

Most studies have demonstrated that the adsorption capacities of carbon nanotubes can also be increased through the functionalization of this carbon-based nanomaterial, which results in increasing the number of adsorption sites. Zhang et al. (2011) studied the adsorption of sulfamethoxazole on functionalized carbon nanotubes and found that the adsorption was due to hydrophobic, electrostatic, π–π interactions, and hydrogen bonds. They also predict that the adsorption capacity can be improved by surface functionalization of multi-walled carbon nanotubes, which offers adsorption sites and functional groups. Li et al. (2015) also synthesize recyclable carbon-nanotubes/Fe_3O_4 magnetic nanocomposites using the facile hydrothermal method. The adsorption behaviors of synthesized nanocomposites were evaluated for the removal of bisphenol A (BPA) in aqueous solution. It was found that the dominant mechanisms were due to the π–π interactions between the carbon nanotubes and the benzene rings in bisphenol A molecules. Researchers have investigated the capability of various carbon nanotubes to remove a wide range of organic pollutants from wastewaters, and some examples are given in Table 2. In addition, Thines et al. (2017) review quite a number of adsorption studies of organic pollutants using carbon nanotubes-based nanomaterials. Much details and some examples of adsorption of organic pollutants using carbon nanotubes-based nanomaterials can be found on Thines et al. (2017) and Madhura et al. (2019).

Table 2 Removal of organic pollutants using various types of carbon nanotubes-based absorbents. Reproduced with permission from Madhura et al. (2019). Copyright 2019, Springer

Carbon nanotubes-based absorbents	Organic pollutants	Adsorption capacity (mg/g)
Untreated carbon nanotubes		
Single-walled carbon nanotubes	Oxytetracycline	554
	Ciprofloxacin	933.8
	4-Chloro-2-nitrophenol	1.44
	Dissolved organic matter (DOM)	26.1–20.8
Multi-walled carbon nanotubes	Tetracycline	192.7
	Olaquindox	99.7%
	Ciprofloxacin	391
	Oxytetracycline	651.4
	4-Chloro-2-nitrophenol	4.42
	Methylene blue	59.7
Treated carbon nanotubes		
Alkali-activated MWCNTs	Methylene blue	399
Oxidized SWCNTs	Basic red 46 (BR 46)	49.45
MWCNTs activated with KOH	Toluene, ethylbenzene, m-xylene	87.12, 322.05, 247.83
Carbon nanotubes-based nanocomposite		
Chitosan/Fe_2O_3/MWCNTs	Methyl orange	66.90
Calcium alginate/MWCNTs	Methyl orange	12.5
CNTs-C@Fe-chitosan composite	Tetracycline	104
MWCNTs/$CoFe_2O_4$	Sulfamethoxazole	6.98

Graphene-based in adsorption of organic pollutants Also, graphene and graphene-based nanomaterials have been used for the adsorption of organic pollutants. Graphene is considered an ideal material and substitutes for carbon nanotubes in the field of water and wastewater remediation due to its production cost-effectiveness (Madhura et al. 2019). It is reported that the adsorption capacity of graphene-based nanomaterials depends on the nature of adsorbate (ionic or hydrophobic). Graphene as a carbon-based material has a high specific surface area and good chemical stability, which makes it a good material for the adsorption of organic pollutants in wastewater. However, due to van der Waals interaction between neighboring sheets of graphene in water, graphene turns to aggregate which results in reduction in surface area which is not beneficial for the adsorption of pollutants; therefore, proper modification of graphene is required to overcome such drawback (Zhao et al. 2012; Perreault et al. 2015). Graphene that poses a high specific surface area has a large enough area for pollutant removal and functionalization.

The modification of graphene surface area with specific functional groups can be of significant importance since it increases the area of interaction between graphene and the pollutants, resulting in high adsorption capacity. Pristine graphene is reported to be hydrophobic which makes it difficult to disperse in water, which can be improved through chemical modification by adding functional groups onto the surface (Wang et al. 2013), i.e., graphene functionalized into graphene oxide using Hummer methods shows a disrupted conjugation in the graphene plane and abundant functional groups, such as epoxide, hydroxyl, carboxyl, and carbonyl, on its surfaces (Lü et al. 2012). The presence of those oxygen-containing groups allows graphene oxide to act as adsorbents for a wide range of pollutants.

Graphene oxide is reported to be more effective in the removal of cationic organic pollutants than anionic pollutants due to the strong electrostatic repulsion between graphene oxide and anionic organic compounds (Ramesha et al. 2011). Graphene oxide exhibits high adsorption for basic compounds due to its several functional groups and strong acidity, while graphene possesses hydrophobic surface and presents high adsorption to organic pollutants due to strong π–π interaction (Chowdhury 2014). Large surface area and electron-rich environment make graphene-based materials to serve as an efficient adsorbent for organic pollutants.

The adsorption mechanisms of graphene-based nanomaterials can also be explained based on the type of interaction (i.e., π–π interaction, hydrophobic effect, H-bonding, and electrostatic interaction) between graphene and organic pollutants (Wang and Chen 2015). i.e., for graphene oxide, the presence of oxygen-containing functional groups on the edge can weaken the hydrophobic effect with nonpolar organics and suppress the adsorption on it. Table 3 shows examples of some reported results on adsorption studies of organic pollutants using graphene-based nanomaterials. The table only gives examples of few adsorption studies carried out on adsorption of various pollutants using graphene-based nanomaterials at different conditions; hence, it cannot be used for comparison of the efficiency of different graphene-based nanomaterials for adsorption of organic pollutants. Other parameters responsible for the adsorption of organic pollutants listed in Table 3 can be found in the cited references.

Adsorption of inorganic pollutants

The presence of inorganic pollutants in the water system has become one of the most worldwide environmental issues threatening both developing and developed countries. Heavy metals (i.e., Lead, cadmium, nickel, cobalt,

Table 3 Adsorption studies on the removal of organic pollutants from water using graphene-based nanomaterials. Reproduced with permission from Chowdhury (2014). Copyright 2014, Elsevier

Adsorbents	Pollutants	pH	Concentration (mg/L)	Time (h)	Temperature (K)	Adsorption capacity (mg/g)
Graphene	Methyl blue	10.0	20–120	–	333	204.8
	Cationic red	–	20–140	–	333	238.10
	X-GRL	6.3	10–60	6	–	53.19
	Phenol Bisphenol A	–	–	6	–	123.92
Graphene oxide (GO)	Methyl blue	6.0	188–1000	1	298	714
	Methyl violet	6.0	10–50	–	–	2.47
	Rhodamine B	6.0	1–10	–	–	1.24
	Tetracycline	3.6	8.33–333.3	–	–	313.48
	Biphenyl	–	8.33–33.3	–	–	38.9
Reduced graphene oxide (RGO)	Orange G	–	1–60	–	–	5.98

chromium, arsenic, iron, and zinc) as the major part of inorganic pollutants are non-degradable and have a tendency to bio-accumulate, and they pose serious health threats even at very lower concentrations (Baruah et al. 2016; Ahmad et al. 2019; Bashir et al. 2019). Those metals come from different industries such as tannery, electroplating, textile, fertilizer, pesticide, and metal processing industries as well as mining sectors. Most of them are non-biodegradable, highly toxic, and carcinogenic in nature (Malik et al. 2016; Talaiekhozani and Rezania 2017; Abdi et al. 2018). Therefore, the removal of heavy metals from water before releasing them into the environment is of greater importance. The maximum accepted concentration levels of some heavy metals are shown in Table 4 together with their corresponding effects on human health once the limits are exceeded.

Many technologies have been employed for the removal of heavy metals from wastewater; however, adsorption has proven to be an economical and efficient method for removing heavy metals (Karnib et al. 2014). Recently, the uses of carbon-based nanomaterials as adsorbents for the removal of heavy metals have received tremendous attention owing to their large specific surface area and concentrated pore-size distribution (Yu et al. 2018). Graphene-based and carbon nanotubes-based nanomaterials have been widely used in the removal of heavy metals from wastewater owing to their large surface area, scalable production, tunable surface chemistry, non-corrosive property, and the presence of a surface oxygen-containing functional groups (Xu et al. 2018b). In this section, graphene-based and carbon nanotubes-based nanomaterials used in the removal of heavy metals from wastewater are discussed with respect to their properties, and examples of some previously reported studies are given.

Graphene-based nanomaterials in adsorption of inorganic pollutants Graphene-based nanomaterials have been widely used for the removal of toxic metals ions in wastewater owing to their large surface area. Graphene is reported to be insoluble and hard to disperse in all solvents due to strong van der Waals interactions that can hamper adsorption of metal ions; hence, a significant number of studies have been undertaken on functionalizing graphene to overcome such limitations. Moreover, graphene oxide that is the derivatives of graphene is much more hydrophilic than graphene; hence, it is the commonly used graphene-based nanomaterials for the removal of heavy metals in wastewater. In addition to large quantities of oxygen-containing atoms on the surface of graphene oxide in the forms of epoxy, hydroxyl, and carboxyl groups, the large surface area of graphene oxide enables it to have a large adsorption capacity toward heavy metals (Sitko et al. 2013).

The adsorption capacities of various heavy metals against graphene-based nanomaterials are shown in Table 5. Sitko et al. (2013) conducted studies on adsorption of Zn(II), Cu(II), Cd(II), Pb(II), Cr(VI), and U(VI) using graphene oxide, and their adsorption efficiency are shown in Table 5. The adsorption models were best fitted by Langmuir, suggesting that the adsorption of those heavy metals on graphene oxide is monolayer coverage. The type of adsorption was investigated by conducting kinetics studies, and it was found to be chemisorption involving the strong surface complexation of metal ions with the oxygen-containing groups on the surface of graphene oxide. The review conducted by Chowdhury also reported the results of batch studies on the use of graphene, cetyltrimethylammonium bromide (CTAB)-modified graphene, graphene/multi-walled carbon nanotubes amongst others for the removal of metals ions in wastewater and some parameters can be found on the cited reference (Chowdhury 2014).

Carbon nanotubes in adsorption of inorganic pollutants Carbon nanotubes have also been reported to possess excellent adsorption capacity for removal of heavy metal ions from large volumes of aqueous solutions since its discovery in 1991 by Iijima. However, although a significant number of studies have been undertaken on adsorption of heavy metals using carbon nanotubes, its real work is hindered by the lack of surface functional groups such as carboxylate, hydroxyl, sulfate, phosphate, amide, and amino groups (Shao et al. 2010). Recently, it has been reported that the oxidizing of carbon nanotubes using HNO_3, NaClO,

Table 4 Maximum concentration levels of heavy metals in drinking water with their corresponding health effects. Reproduced with permission from Ihsanullah et al. (2016) and Yu et al. (2018). Copyright 2016, 2018, Elsevier, Springer

Heavy metals	Maximum contaminant level (mg/L)	Health effects
Arsenic (As)	10	Skin damage or circulatory system problems, carcinogenic
Cadmium (Cd)	5	Kidney damage
Chromium (Cr)	100	Allergic dermatitis
Copper (Cu)	1300	Gastrointestinal distress, liver or kidney damage
Lead (Pb)	15	Deficits in attention span and learning abilities, kidney problems, blood pressure increases
Mercury (Hg)	2	Kidney damage
Uranium (U)	30	Cancer risk increases, kidney toxicity

Table 5 Adsorption of various inorganic pollutants using graphene-based nanomaterials

Adsorbents	Inorganic pollutants (heavy metals)	Adsorption capacity (mg/g)	References
Graphene oxide	Zn(II)	246	Sitko et al. (2013)
	Cu(II)	117.5	
	Cd(II)	530	
	Pb(II)	842	
	Cr(VI)	232.55	
	U(VI)	299	
Graphene	Pb(II)	22.42	Chowdhury (2014)
	Fe(II)	299.3	
CTAB modified graphene	Cr(VI)	21.57	Chowdhury (2014)
Graphene/MWCNT	Pb(II)	44.5	Chowdhury (2014)
	Hg(II)	75.6	
	Cu(II)	9.8	

Table 6 Maximum adsorption capacities of selected heavy metals using carbon nanotubes-based nanomaterials. Reproduced with permission from Ihsanullah et al. (2016) and Santhosh et al. (2016). Copyright 2016, Elsevier

Heavy metals	Adsorbents	Adsorption capacity (mg/g)
Chromium	MWCNTs	0.37
	Acid-modified MWCNTs	0.50
Cadmium	Acid-modified CNTs	2.02
	HNO_3-oxidized CNTs	5.1
	CNT-COO	3.325 mmol/g
Arsenic	Fe-MWCNT	9.86 ug/g
Mercury	MWCNTs	0.49
	COOH-MWCNT	81.57
	CNT-$CONH_2$	1.658 mmol/g
Copper	HNO_3-modified CNTs	29
	MWCNTs/Fe_3O_4	19
	CNT-OH	1.342 mmol/g

and $KMnO_4$ solutions can help to overcome such drawbacks (Lata and Samadder 2016). To achieve better adsorption, the modification of carbon nanotubes must be selected based on the contaminant of interest. Carbon nanotubes surface modification can enhance the adsorption capacities of metals ions through the introduction of new functional groups that can increase the number of surface adsorption active sites.

The surface modifications include methods such as oxidization, chemical grafting, and physical modifications such as impregnating or coating (Zhang et al. 2016). Table 6 shows the maximum adsorption capacities of heavy metals using carbon nanotubes and their derivatives. Other parameters on the adsorption of heavy metals using carbon nanotubes-based nanomaterials can be found in cited references and some examples are shown in Table 6. Several researchers have modified carbon nanotubes to evaluate the efficiency of the former with the unmodified carbon nanotubes for the removal of various contaminants. From Table 6, it can be concluded that the modified carbon nanotubes show high adsorption capacity as compared to unmodified carbon nanotubes. This can be attributed to the presence of new functional groups onto the surface of carbon nanotubes, which increase the number of adsorption sites on the surface.

The surface functional group of graphene oxide and oxidized carbon nanotubes can provide major adsorption sites to heavy metals removal, due to the presence of electrostatic attraction and chemical bonding such as ion exchange between adsorbent and adsorbate. In addition, the presence of a highly accessible adsorption site and short intra-particle diffusion distance can result in fast adsorption kinetics. Nevertheless, the adsorption of organic and inorganic pollutants using carbon-based nanomaterials is not only limited to the discussed nanomaterials and other nanomaterials such as activated carbon, fullerenes, etc., have also been used. Most of the carbon-based nanomaterials display similar properties toward the removal of both organic and inorganic pollutants through the adsorption process. The choice on which carbon-based nanomaterial to use is usually governed by the cost of production in terms of synthesis of nanomaterials, and the environmental implication in terms of toxicity.

3.1.3 Summary of adsorption mechanisms of organic and inorganic pollutants

The adsorption process is a very useful strategy for the remediation of organic and inorganic pollutants in water. Adsorbents having large adsorption capacity and adsorption rates are the most preferable. To achieve high adsorption efficiency of pollutants removal, a better understanding of adsorption mechanisms between the adsorbent and adsorbate is the key factor. Different physical forces usually govern

their adsorption mechanisms. The main forces controlling adsorption removal are hydrophobic interactions, π–π bonds, electrostatic interactions, and hydrogen bonds (Crini et al. 2019; Tong et al. 2019). Different adsorbent interacts with adsorbate in different manners, depending on their properties such as structure and nature of pollutants and the associated functional groups available onto the surface of the adsorbent. When dealing with the element in adsorption that contains functional groups such as amine, hydroxyl, and carboxyl groups, hydrogen-bonding interaction plays an important role. Meanwhile, for adsorbent with charged functional groups, electrostatic interaction is predominant and hydrophobic interaction is usually dominant for adsorbent with non-polar hydrocarbons.

Carbon-based nanomaterials have shown a significant efficiency for the removal of both organic and inorganic pollutants in water. Carbon nanotubes show high adsorption capacity for the removal of organic pollutants due to their large surface area and high interactions between organic pollutants. The adsorption mechanisms between carbon nanotubes and organic pollutants usually occur through forces such as hydrophobic interactions, π–π stacking interactions, van der Waals forces, electrostatic interactions, and hydrogen bonding interactions, which might act individually or simultaneously (Gupta et al. 2013; Yu et al. 2014; Mashkoor et al. 2020). In addition, surface oxidation of carbon nanotubes can significantly enhance the adsorption efficiency of inorganic pollutants due to the introduction of carboxyl, hydroxyl, and phenol functional groups at the surface of carbon nanotubes.

The adsorption mechanisms of untreated carbon nanotubes and surface oxidation carbon nanotubes are shown in Fig. 5, where for untreated carbon nanotubes, adsorption occurs at the surface of the material, while for oxidative carbon nanotubes adsorption occur at the surface and also through the functional groups available at the surface. Those surface functional groups are the major adsorption site of inorganic pollutants through electrostatic attraction and chemical bonding (Ihsanullah et al. 2016; Madhura et al. 2019). In the case of adsorption of organic pollutants by graphene-based nanomaterials, the adsorption is determined by physisorption between the pollutants and the graphene surface, as such the larger the surface area the greater the adsorption capacity.

Figure 6 represents the general mechanisms of adsorption–desorption removal of organic and inorganic pollutants using graphene-based nanomaterials in water. Desorption mechanisms usually occur in the presence of either acid or base, depending on the nature and compatibility of the materials. The most dominant interaction between organic pollutants and graphene-based nanomaterials is π–π interaction (Chowdhury 2014; Khan et al. 2018). For the removal

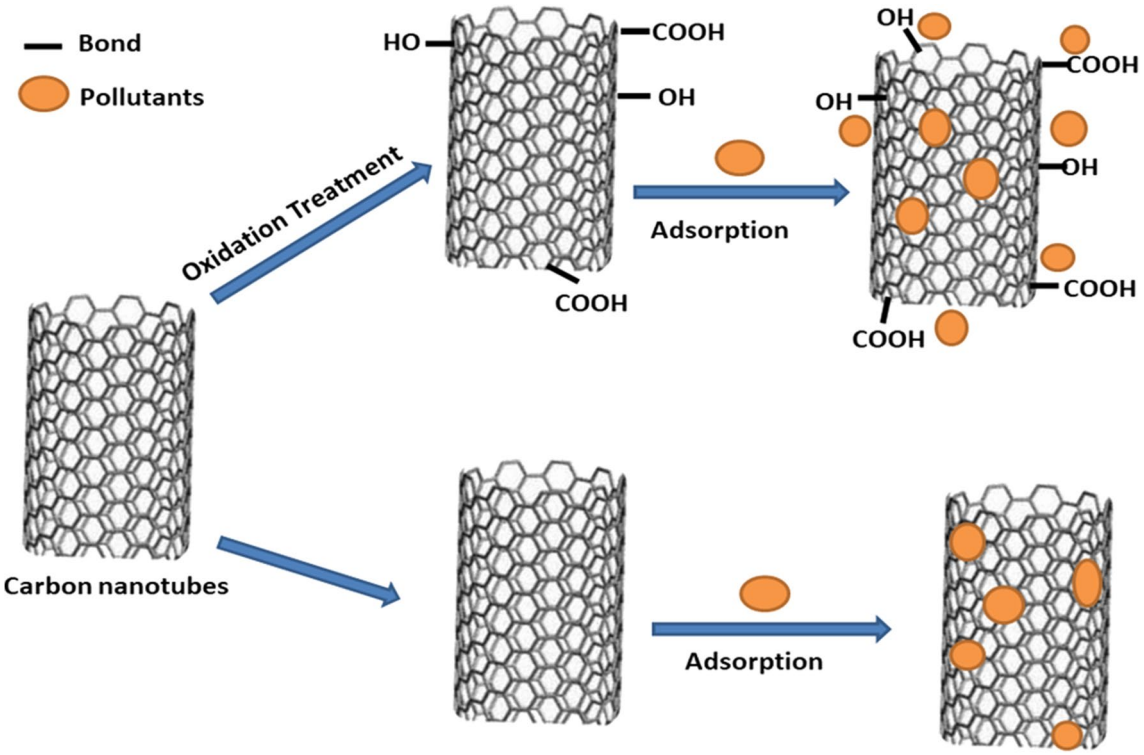

Fig. 5 Adsorption mechanisms of water pollutants by carbon nanotubes and oxidized carbon nanotubes. Oxidation treatment results in introduction of functional groups on the surface of carbon nanotubes

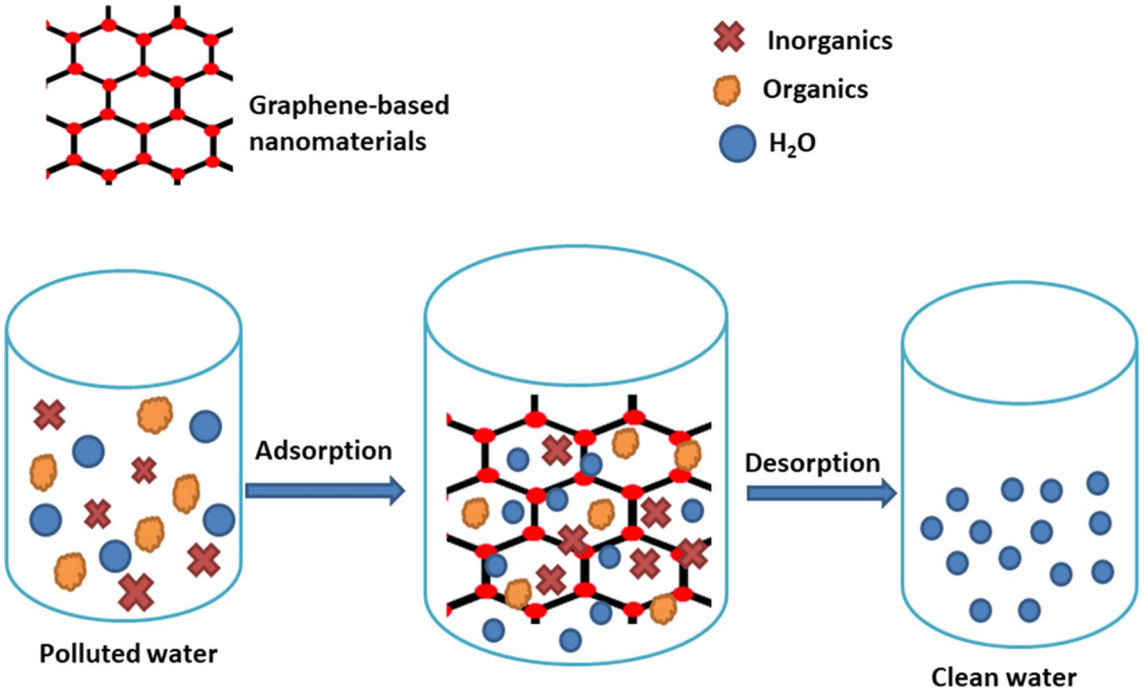

Fig. 6 Mechanism of adsorption–desorption removal of organic and inorganic water pollutants using a graphene-based nanomaterials. Desorption mechanisms usually occur in the presence of either acid or base

of inorganic pollutants, the availability of surface functional groups onto adsorbent is key factors determining the adsorption efficiency. Therefore, graphene derivatives such as graphene oxide and modified graphene show high adsorption capacities toward inorganic pollutants than pristine graphene (Lü et al. 2012). The most common dominant interaction in the adsorption mechanisms of inorganic pollutants by graphene derivatives is electrostatic attractions that are usually between positively charged ions and negatively charged functional groups on graphene derivatives surfaces are the predominant adsorption mechanism (Kemp et al. 2013).

Photocatalysis removal of organic pollutants

Recently, the removal of pollutants by advanced oxidation processes such as Fenton-like oxidation, photocatalysis, sulfate radical-based oxidation, ozonation have emerged as a promising techniques for mineralization of organic pollutants and toxic metal ions (Awfa et al. 2018; Ganiyu et al. 2018; Miklos et al. 2018; Pang et al. 2019). Amongst various advanced oxidation processes methods, photocatalysis has received tremendous attention in wastewater due to its stable, low set-up cost, simplicity of design, and complete mineralization of pollutants into unharmful by-products (Ahmed and Haider 2018; Bishoge et al. 2018). This principle was first applied by to reduce cyanide (CN^-) in water (Acharya et al. 2018). This method has been reported to be an environmentally friendly approach and promising method to remove a wide number of pollutants in water due to its potential to completely mineralize harmful pollutants into un-harmful by-products using solar light irradiation. It has been widely applied for the degradation of organic pollutants; since most of the organic pollutants are highly resistant to biodegradation and recalcitrant to conventional biological and physical oxidation treatments due to their complex structure. In addition, it has also been applied for the reduction in metals iron such as highly toxic chromium(VI) to less toxic chromium(III). The general mechanisms behind photocatalytic degradation and photocatalytic reduction in organic pollutants and chromium(VI), respectively, are shown in Fig. 7. Photocatalytic reduction in chromium(VI) occurs when chromium(VI) interacts with the electrons in the conduction band and undergoes reduction process to give chromium(III) as shown by equation in Fig. 7, while photocatalytic degradation occurs when organic pollutants interact with holes in the valence band and undergo oxidation process.

Generally, based on the electronic structure and energy bandgap (E_g) of the materials, photocatalysts use ultraviolet (UV) or visible light to activate catalysis. This technique does not require any secondary disposal, and also no trace of secondary pollutants are generated (Gunti et al. 2018). Its mechanism is based on the oxidative and reductive reactions which take place at the surface of the semiconductor materials (SMs) as shown by Eq. 2–10 (Ajmal et al. 2014). The graphical representation of mechanisms

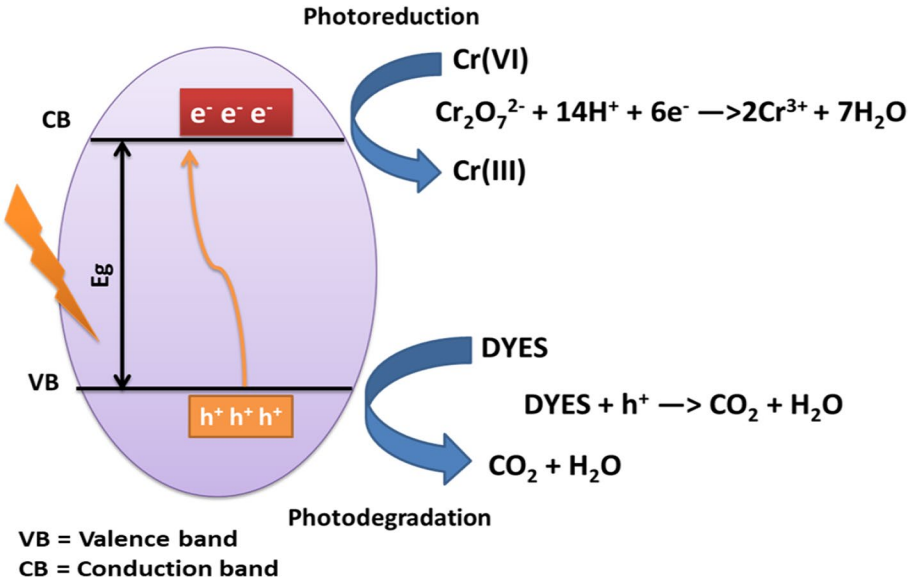

Fig. 7 Photocatalytic reduction of chromium(VI) to chromium(III) and photocatalytic degradation of organic dyes. Both degradation (oxidation) and reduction processes commonly take place on the surface of the photo-excited semiconductor photocatalyst

behind the photocatalytic degradation of organic pollutants is also shown in Fig. 8. This process is initialized when the light energy-carrying photon energy greater or equal to the energy bandgap of the semiconductor material is illuminated onto the surface of the photocatalysts, then the electrons (e^-) from the valence band (VB) get excited and promoted to the conduction band (CB), leaving the holes (h^+) in valence band. The exciting of an electron from valence band to conduction band results in the generation of electron–hole pairs.

$$\text{Semiconductor material} + h\nu(\text{UV/Visible}) \rightarrow \text{Semiconductor material}\left(e^-(\text{CB}) + h^+(\text{VB})\right) \quad (2)$$

The photo-generated holes at the valence band then react with water to produce $OH^{\cdot}$ radical:

$$H_2O(\text{ads}) + h^+(\text{VB}) \rightarrow OH^{\cdot}(\text{ads}) + H^+(\text{ads}) \quad (3)$$

Formed $OH^{\cdot}$ radical on irradiated semiconductor surface is strong oxidizing agents and can attack adsorbed organic

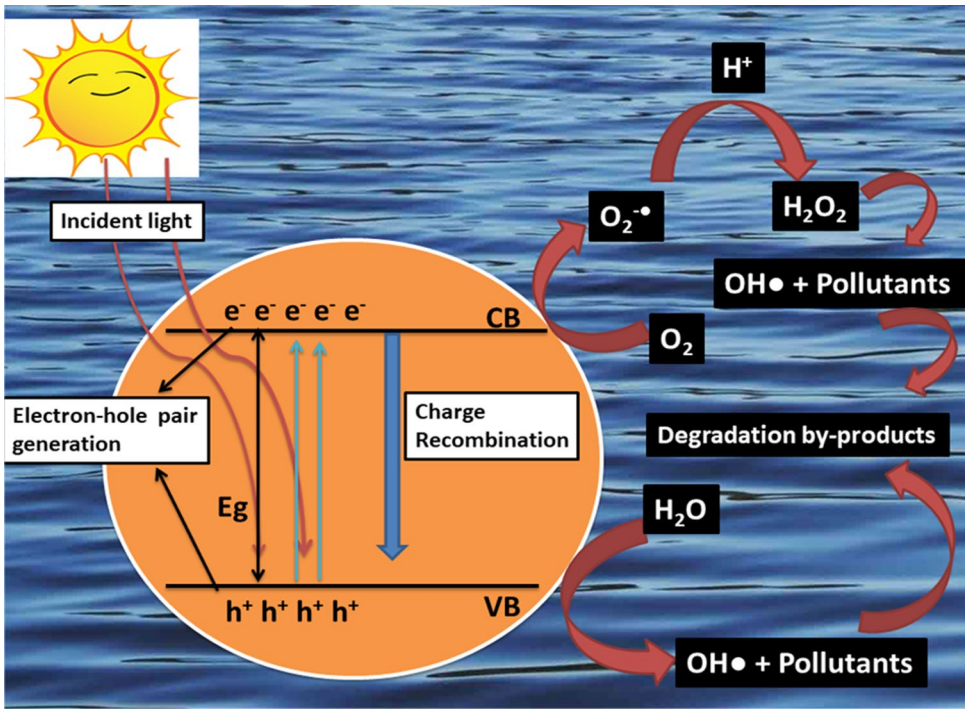

Fig. 8 Photocatalytic mechanism of photocatalytic degradation of organic pollutants presents in water. The most common degradation by-products is water and carbon dioxide

molecules or those that are near to the catalyst surface, causing them to mineralize to an extent depending upon their structure and stability level. Meanwhile, electrons in the conduction band react with oxygen to generate anionic superoxide radical (O_2^{-}):

$$O_2 + e^-(CB) \rightarrow O_2^{-\cdot}(ads) \quad (4)$$

The produced superoxide ions then take part in the oxidization process, and they also help in suppressing electron–hole recombination. Then, superoxide ($O_2^{-\cdot}$) gets protonated forming hydroperoxyl radical ($HO_2^{\cdot}$) and then subsequently H_2O_2 which further dissociates into highly reactive hydroxyl radicals ($OH^{\cdot}$). Then, the hydroxyl-radical species attack vital organic components and decompose them through oxidation reactions:

$$O_2^-(ads) + H^+ \leftrightarrow HOO^{\cdot}(ads) \quad (5)$$

$$2HOO^{\cdot}(ads) \rightarrow H_2O_2(ads) + O_2 \quad (6)$$

$$H_2O_2(ads) \rightarrow 2OH^{\cdot}(ads) \quad (7)$$

$$\text{Pollutants} + OH^{\cdot} \rightarrow \text{pollutants intermediates} \quad (8)$$

$$\text{Pollutants} + h^+(VB) \rightarrow \text{oxidation products} \quad (9)$$

$$\text{Pollutants} + e^-(CB) \rightarrow \text{reduction products} \quad (10)$$

Both oxidation and reduction processes commonly take place on the surface of the photo-excited semiconductor photocatalyst. Since the principle of photocatalytic removal of pollutants from water is a heterogeneous reaction at the liquid–solid interface, the numbers of active sites, as well as the surface area, are the key factors for the catalytic reaction.

As far as photocatalysis is a concern, carbon-based nanomaterials have received tremendous attention as photocatalysis for environmental pollution remediation. Amongst various carbon-based nanomaterials, graphene, carbon nanotubes, and graphitic carbon nitrate are commonly used nanomaterials for this field due to their unique properties (Kumar et al. 2017). In addition, the utilization of carbon-based nanomaterials in synergy with catalyst nanoparticles has been widely explored. Many studies have been carried out on the incorporation of catalytic nanoparticles within the metric of carbon-based nanomaterials. The incorporation results in improved photocatalysis performance of both catalytic and carbon-based nanomaterials. Carbon-based nanomaterials enhanced the photocatalytic degradation of catalyst nanoparticles through (1) increasing the adsorption site, (2) energy bandgap reduction and (3) suppressing the recombination rate of electron and hole generated which are major drawbacks of current used catalytic nanoparticles (Shan et al. 2017; Kumar et al. 2019).

Those carbon-based nanomaterials can also act as supporting material for other semiconductor nanomaterials that can ease the separation process of catalyst from the solution after degradation (increase the reusability of the catalyst). More recently, significant numbers of studies have been conducted on the use of carbon-based nanomaterials and their derivatives together in synergy with catalytic nanoparticles for the photodegradation of organic pollutants in water using solar light irradiation (Melchionna et al. 2016; Piovesana et al. 2016). This section will discuss the use of carbon-based nanomaterials together with their derivatives in the photocatalytic degradation of organic pollutants in water.

Graphene-based nanomaterials in photocatalysis

Graphene-based nanomaterials possess some unique properties such as ultrafast electron transfer, high adsorption capacity, high thermal conductivity (~ 5000 W m^{-1} K^{-1}), extended light absorption range, and enhanced charge separation and charge transport properties which are of great importance in field of photocatalytic degradation of organic pollutants (Kemp et al. 2013). Those superior properties make graphene-based nanomaterials and their derivatives to be promising candidates for photocatalytic degradation of organic pollutants in wastewater. Since graphene is a zero bandgap material, it is usually coupled with other semiconductors catalytic materials. When coupled with other materials, it can enhance the photocatalytic performance by acting as an electron acceptor and transfer which lowers the recombination rate of electron and hole generated and can also increase the light absorption range owing to its exceptional electronic, optical, and mechanical properties (Kumar et al. 2017; Qiu et al. 2018). As represented in Fig. 9, the electrons generated from semiconductor nanomaterials upon light irradiation are transferred to the graphene matrix, which lower the recombination rate of electron–hole generated. Then, those electrons interact with oxygen molecules to form superoxide ($O_2^{-\cdot}$) which then gets protonated to form hydroperoxyl radical ($HO_2^{\cdot}$) and then subsequently H_2O_2 which further dissociates into highly reactive hydroxyl radicals ($OH^{\cdot}$) which are responsible for photodegradation of pollutants. The availability of hydroxyl radicals from both graphene and semiconductor nanomaterials results in enhanced photocatalytic activities.

Since the overall photocatalytic efficiency is significantly hindered by the fast electron–hole recombination and low light absorption, the coupling of graphene or its derivatives with other semiconductor materials can expand the light absorption range from ultraviolet region to visible region, changing bandgap of other material, and suppressing the electron–hole recombination (Li et al. 2018).

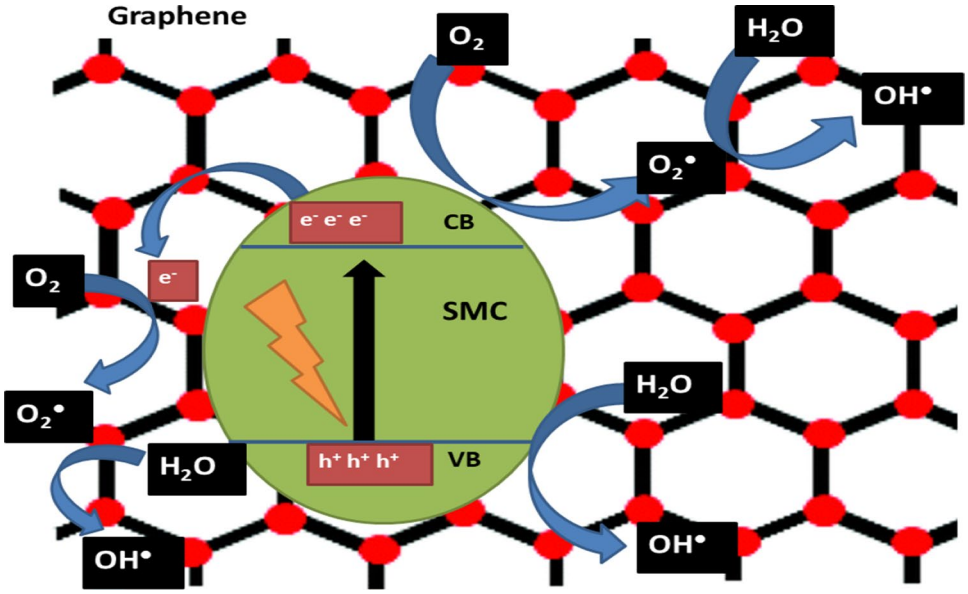

Fig. 9 Photocatalytic mechanisms representing the electron transfer between graphene and other semiconductors (SMC) nanomaterials and the generation of hydroxyl radicals responsible for degradation of various pollutants. Electrons transfer helps in reducing recombination of the photo-induced electrons and holes

Graphene modification and the coupling with other materials contribute to the formation of efficient visible active photocatalysts. In this regard, a significant number of studies have been undertaken on the synthesis of graphene-based nanomaterials and graphene-based-semiconductor-based nanomaterials for environmental remediation.

Du and Deng synthesize N-doped TiO_2 nanoparticles deposited on reduced graphene oxide (rGO) for the visible-light degradation of tetracycline hydrochloride (TC). The synthesized N-TiO_2/rGO shows an enhanced photocatalytic activity as compared to pure TiO_2 and N-TiO_2. The enhanced visible-light photodegradation activity of TC over N-TiO_2/rGO was ascribed to the synergistic effects of enhanced adsorption of tetracycline hydrochloride on reduced graphene oxide, expanded visible light absorption, and efficient charge transport and separation (Du and Deng 2015). CdS/rGO composite was prepared by Gao et al. using a simple hydrothermal process. The synthesized composite exhibits high adsorption and degradation efficiency of Rhodamine B (RhB) dye under visible light irradiation. The enhancement in photocatalytic activity was caused by a decrease in charge recombination, as well as the effective adsorption of Rhodamine B on reduced graphene oxide (Gao et al. 2018). Zhao et al. synthesize $BaTiO_3$/GO nanocomposites via the freeze-drying method for the photocatalytic degradation of methylene blue. It was founded that $BaTiO_3$/GO nanocomposites exhibit higher photocatalytic activities toward the degradation of methylene blue (MB), which was mainly ascribed to the appropriate energy band structure and effective adsorption function due to the presence of graphene oxide (Zhao et al. 2018). Other graphene-based nanomaterials which have been studied for the photocatalytic degradation of various pollutants under the visible light are GO/TiO_2, GR/TiO_2, N, S/TiO_2/RGO, Ag/TiO_2/GO, Ag/TiO_2/RGO, TiO_2/NiO/RGO, RGO/Fe_3O_4/Ag_3PO_4, and Cu_2O/RGO (Nikokavoura and Trapalis 2018).

Carbon nanotubes-based nanomaterials in photocatalysis

Carbon nanotubes have been used as a promising co-catalyst in photocatalysis due to their ability to accept, transport, and store electrons and thus suppress the recombination of electrons with the holes (Ye et al. 2012); which arise as results of high electrical conductivity, excellent electrocatalytic activity, and large specific surface area (Liu et al. 2018). These interesting properties make carbon nanotubes to be the superior catalyst for supporting materials. Meanwhile, the application of carbon nanotubes as a catalyst in large-scale operation is hindered by its high production cost. Carbon nanotubes have been widely coupled with the well-known photocatalyst semiconductors such as ZnO and TiO_2 for better photocatalytic activities as shown in Fig. 10 (Liu et al. 2014; Ahmadi et al. 2017). The photocatalytic activities of those metal-oxide nanomaterials are hindered by some drawbacks such as high energy bandgap and low charge carrier separation, which can be overcome by coupling metal-oxides with carbon-based nanomaterials such as carbon nanotubes (Mallakpour and Khadem 2016). When carbon nanotubes are coupled with other metals oxide, it can help to lower the recombination rate of electron–hole generated as displayed in Fig. 10 and also increase the number of hydroxyl radicals available for degradation of pollutants. Hence, coupling carbon nanotubes with semiconductor materials shows the synergistic influence that causes better photocatalytic efficiency.

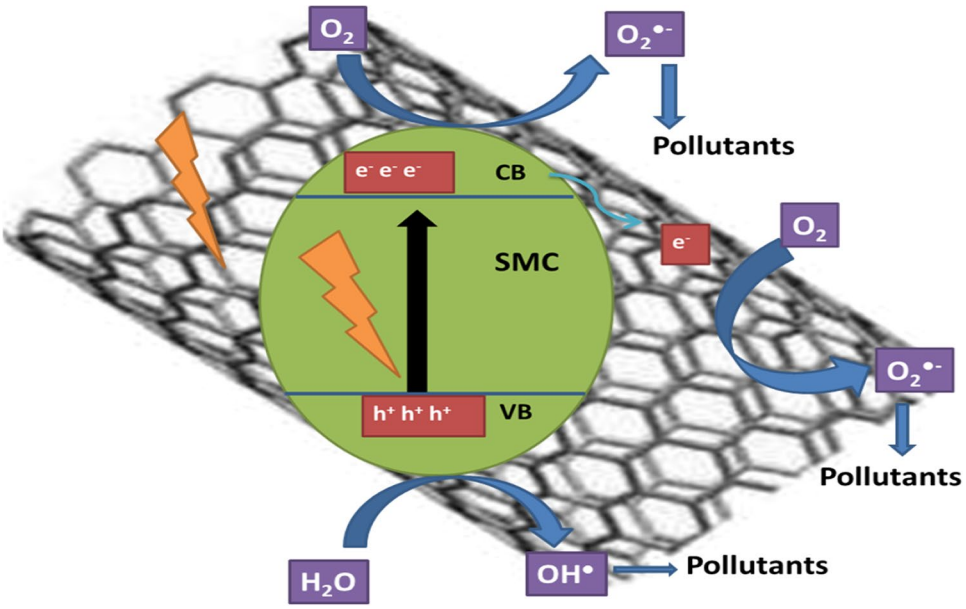

Fig. 10 Photocatalytic mechanisms of carbon nanotubes-based nanomaterials representing the transfer of electron between semiconductor nanomaterial (SMC) and carbon nanotubes matrix for degradation of pollutants

Table 7 Results on various carbon nanotubes-based nanomaterials photocatalysts used for the photocatalytic degradation of organic pollutants together with their synthesis methods, removal efficiency, and irradiation time

Photocatalyst	Method	Pollutant	Removal (%)	Time (min)	References
Cu–TiO_2–CNT	Sol–gel	Methylene blue	81.5	60	Shafei and Sheibani (2019)
Ag_3PO_4@MWCNT@Cr:$SrTiO_3$	–	Malachite green	100	10	Lin et al. (2018)
Ag–ZnS–MWCNTs	Ultrasonic probe	Rhodamine B	87.53	116	Yazdani and Mehrizad (2018)
ZnO–Au/MWCNT	Wet-chemical	Methylene blue	98	40	Chidambaram et al. (2018)
MWCNT/BiOBr	Solvothermal	Rhodamine B	97	75	Chen et al. (2014)
ZnO-Ag/MWCNT	Wet-synthesis	Phenol	81	240	Hosseini et al. (2018)

Various carbon nanotubes-based photocatalysts for the removal of organic pollutants are shown in Table 7 together with their synthetic methods, targeted organic pollutants, removal efficiency, and degradation time. Shafei and Sheibani synthesized Cu–TiO_2–CNT using a sol–gel method for removal of the methylene blue in water. 81.5% removal of methylene blue was achieved in 60 min under visible light irradiation (Shafei and Sheibani 2019). TiO_2 absorbs in the ultraviolet region of the electromagnetic spectrum, but to the introduction of carbon-based matrix-like carbon nanotubes, the photocatalyst was able to degrade methylene blue under visible region, showing that the presence of carbon nanotubes helps in reduction in the energy bandgap of TiO_2. Lin et al. manage to photo degrade malachite green (MG) using Ag_3PO_4@MWCNT@Cr:$SrTiO_3$ in 10 min (Lin et al. 2018). The high efficiency was attributed to the change in surface properties and morphology of Ag_3PO_4 due to the addition of multi-walled carbon nanotubes that introduce more surface-active site for degradation.

Yazdani and Mehrizad also synthesized Ag–ZnS–MWCNT using ultrasonic probe methods for the degradation of Rhodamine B under visible light irradiation and achieve 87.53% removal in 116 min (Yazdani and Mehrizad 2018). The high degradation efficiency was attributed to being due to the excellent electronic property of multi-walled carbon nanotubes that help in suppressing the recombination of electron and hole generated. Chidambaram et al. used ZnO–Au/MWCNT, which was synthesized using the wet-chemical method for the degradation of methylene blue and achieved 98% removal in 40 min under visible light irradiation. The efficiency was attributed to the incorporation of multi-walled carbon nanotubes in ZnO–Au, which enhanced the visible light absorbance and effective separation of electron–hole pairs, leading to higher catalytic efficiency (Zhang and Jaroniec 2018).

Chen et al. (2014) used the solvothermal process to synthesized novel flower-like MWCNT/BiOBr photocatalyst that exhibited a conspicuous improved photocatalytic performance for the degradation of Rhodamine B under visible light irradiation. The improved photocatalytic performance was due to the reduction in electron–hole pair recombination as a result of the presence of multi-walled carbon nanotubes.

Hosseini et al. (2018), aiming to shift the band edge toward longer wavelength, developed a novel Ag-doped ZnO nanoparticle incorporated onto multi-walled carbon nanotubes. The nanomaterial was used for the photocatalytic degradation of phenol, and 81% removal was achieved in 240 min. The results were explained based on shifting of band edge toward longer wavelength due to the presence of Ag dopant and enhancement of visible light absorbance and effective separation of electron–hole pairs due to the presence of multi-walled carbon nanotubes.

Graphitic carbon nitrate in photocatalysis

Recently, a fascinating π-conjugated polymeric graphitic carbon nitrate semiconductor with a suitable electronic structure has been discovered and widely applied in the field of catalysis (Liu et al. 2017). This metal-free polymeric photocatalyst has been a promising candidate in photocatalytic application due to its interesting properties such as medium energy bandgap with the good visible light response (2.7 eV), low production cost, easy availability, high stability, non-toxic as well as easily tailorable structure (Jiang et al. 2017; Liu et al. 2017). It exhibits good photocatalytic activity for the water splitting and the degradation of environmental pollutants under visible light irradiation. Nevertheless, its practical application is restricted by small specific surface area which leads to a fast recombination rate of the photo-induced electrons–holes pair and insufficient solar-light absorption which results in low photocatalytic activities (Cai et al. 2017). In this regards, a significant number of studies such as doping with nonmetal and metals species, morphology control, combination with conductive materials, nanocomposite structure construction with other semiconductors and dye sensitization have been done to enhance the photocatalytic activities of pristine graphitic carbon nitrate (Jiang et al. 2017; Asadzadeh-khaneghah et al. 2018; Mousavi and Habibi-yangjeh 2018).

A variety of organic pollutants such as dyes, phenol, atrazine, and humic acid have been degraded using graphitic carbon nitrate and its derivatives, indicating that graphitic carbon nitrate has the photocatalytic ability to degrade different kinds of organic contaminants from water and wastewater (Xu et al. 2018a). Due to the drawbacks of pristine graphitic carbon nitrate, it usually used in synergistic with other semiconductor nanomaterials to achieve enhanced photocatalytic activities. Figure 11 represents the photocatalytic mechanisms of graphitic carbon nitrate coupled with titanium oxide, where the electrons and holes are transferred between the two semiconductors nanomaterials, which is of significance to overcome the fast recombination rate of electron–hole pairs and also critical for high photocatalytic efficiency.

Meanwhile, some examples of graphitic carbon nitrate-semiconductor-based nanomaterials used for photodegradation of organic pollutants are given in this section. Hao et al. (2017) synthesize g-C_3N_4/TiO_2 using the hydrothermal method for the removal of Rhodamine B. The synthesized g-C_3N_4/TiO_2 shows high photocatalytic degradation of Rhodamine B which was due to the increase in surface area and synergistic heterojunction structure between g-C_3N_4 and TiO_2. Cobalt-doped g-C_3N_4 synthesized by Wang et al. (2019) shows the complete mineralization of Rhodamine B in 25 min. The complete mineralization was explained to be due to the effective charge separation of photo-generated electrons and holes and also due to the sufficient availability of accessible active sites. Shi et al. (2018) synthesize g-C_3N_4/MoS_2 composite using ultrasonic-assisted exfoliation for the removal of Methyl orange. The synthesized

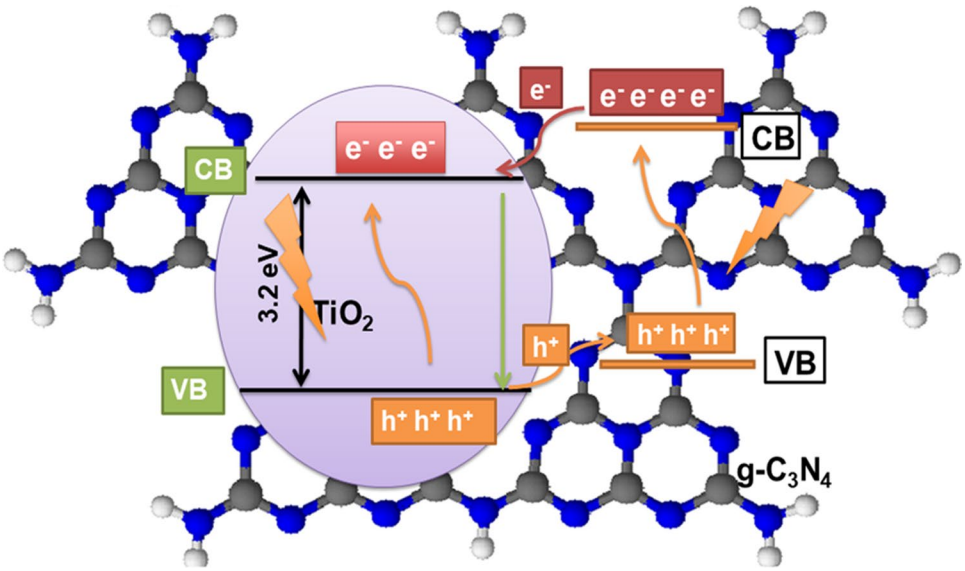

Fig. 11 Photocatalytic mechanisms of graphitic carbon nitrate (g-C_3N_4) coupled with titanium oxide (TiO_2) for enhanced photocatalytic activities through lowering recombination of electron–hole generated

g-C_3N_4/MoS_2 photodegradation 96.5% of methyl orange, which was ascribed to the availability of active sites, aligned energy levels of g-C_3N_4 and MoS_2 and also the efficient charge transfer. Ismael et al. (2018) also manage to remove 80% of methyl orange in 5 h using yFeO_3/g-C_3N_4. The enhanced photodegradation was due to the improved charge separation of photo-generated electrons and holes.

Xiao et al. (2018) synthesized WO_3/g-C_3N_4 using hydrolysis and polymerization process. The synthesized WO_3/g-C_3N_4 hollow microsphere was tested for the photodegradation of tetracycline hydrochloride (TC-HCl) and ceftiofur sodium (CFS). The removal efficiencies were reported to be 82% and 70% for tetracycline hydrochloride and ceftiofur sodium in 2 h, respectively. The mechanisms suggest that enhanced photodegradation was due to the trapping of incident light within the hollow structure and also the higher specific surface area. 80.2% removal of tetracycline was achieved by Jiang et al. (2018) using WO_3/g-C_3N_4/Bi_2O_3 in 60 min. The photocatalytic mechanisms predict that the enhanced degradation can be due to improved visible light irradiation, increased surface area and enhanced charge separation of photo-generated electrons and holes pair. Liu et al. (2019) synthesized g-C_3N_4/Ti_3C_3 using the evaporation-induced self-assembly method. The synthesized g-C_3N_4/Ti_3C_3 shows high degradation efficiency of Ciprofloxacin which was reported to be due to the suppressed recombination of electrons and holes pair and better photogenerated charge separation and migration performance. With respect to the above-reviewed article, it can be concluded that graphitic carbon nitrate and its derivatives play a crucial role in photocatalytic degradation of a wide number of organic pollutants; hence, it has received tremendous attention. The use of carbon-based nanomaterials in photocatalytic removal of organic pollutants is not only limited to the above-missioned literature. Awfa et al (2018) have conducted a critical review on the use of carbonaceous-TiO_2 nanomaterials in photocatalytic removal of emerging pollutants such as personal care products and pharmaceuticals (Awfa et al. 2018).

Conclusion

The presence of organic and inorganic pollutants in our water system is an issue of greater concern across the globe. Those pollutants pose a server threat to both living organisms and ecosystems; hence, their removal from the water system is of greater importance. Although a significant number of processes have been employed for the remediation of pollutants from wastewater, the use of nano-based technology such as adsorption and photocatalysis have been gaining popularity in this field. Adsorption and photocatalysis as nano-based technology hold a substantial promise for overcoming the limitations faced by other conventional methods. The uses of carbon-based nanomaterials have received significant attention as catalysts and as adsorbents for the remediation of organic and inorganic pollutants in wastewater owing to their excellent properties and their availability.

This review highlighted the use of carbon-based nanomaterials and their derivatives as adsorbents as well as catalysts for the remediation of organic and inorganic pollutants from wastewater. Only three types of carbon-based nanomaterials are discussed in this review. However, the application of carbon-based nanomaterials for wastewater remediation is not only limited to the discussed carbonaceous nanomaterials, but other carbonaceous nanomaterials have also been used. The uses of these nanomaterials as adsorbent and catalyst have proved astonishing properties in both laboratory scale and real wastewater treatment. The availability of active sites on the surface of material and strong interactions between the active adsorption sites and the pollutants results in the enhanced adsorption capacity of the materials. In the photocatalytic processes, enhanced efficiency is attributed to the improved light harvesting and reduced recombination of the photo-induced electrons and holes. However, for successful commercialization, further modification on these nanomaterials is needed in order to improve their properties, scaling-up production and reduce the cost-effectiveness.

References

Abdi G, Alizadeh A, Zinadini S, Moradi G (2018) Removal of dye and heavy metal ion using a novel synthetic polyethersulfone nano filtration membrane modifed by magnetic graphene oxide/metformin hybrid. J Membr Sci 552:326–335. https://doi.org/10.1016/j.memsci.2018.02.018

Access O (2018) We are IntechOpen, the world ' s leading publisher of Open Access books Built by scientists, for scientists TOP 1%. Long-Haul Travel Motiv by Int Tour to Penang i:13

Acharya R, Naik B, Parida K (2018) Cr(VI) remediation from aqueous environment through modified-TiO_2-mediated photocatalytic reduction. Beilstein J Nanotechnol 9:1448–1470. https://doi.org/10.3762/bjnano.9.137

Adeleye AS, Conway JR, Garner K et al (2016) Engineered nanomaterials for water treatment and remediation: costs, benefits, and applicability. Chem Eng J 286:640–662. https://doi.org/10.1016/j.cej.2015.10.105

Ahmad L, Arshid M, Aaliya B et al (2019) Detection and removal of heavy metal ions: a review. Environ Chem Lett. https://doi.org/10.1007/s10311-019-00891-z

Ahmadi M, Ramezani H, Jaafarzadeh N (2017) Enhanced photocatalytic degradation of tetracycline and real pharmaceutical wastewater using MWCNT/TiO_2 nano-composite. J Environ Manag 186:55–63. https://doi.org/10.1016/j.jenvman.2016.09.088

Ahmed SN, Haider W (2018) Heterogeneous photocatalysis and its potential applications in water and wastewater treatment: a review. Nanotechnology. https://doi.org/10.1088/1361-6528/aac6ea

Ajmal A, Majeed I, Malik RN et al (2014) Principles and mechanisms of photocatalytic dye degradation on TiO_2 based photocatalysts:

a comparative overview. RSC Adv 4:37003–37026. https://doi.org/10.1039/c4ra06658h
Ali I (2010) The quest for active carbon adsorbent substitutes: Inexpensive adsorbents for toxic metal ions removal from wastewater. Sep Purif Rev 39:95–171. https://doi.org/10.1080/15422119.2010.527802
Ali I (2012) New generation adsorbents for water treatment. Chem Rev 112:5073–5091. https://doi.org/10.1021/cr300133d
Ali I, Asim M, Khan TA (2012) Low cost adsorbents for the removal of organic pollutants from wastewater. J Environ Manag 113:170–183. https://doi.org/10.1016/j.jenvman.2012.08.028
Anastopoulos I, Robalds A, Tran HN et al (2019) Removal of heavy metals by leaves-derived biosorbents. Environ Chem Lett 17:755–766. https://doi.org/10.1007/s10311-018-00829-x
Anderson MG, Mcdonnell J, Ximing C et al (2006) The challenge of micropollutants. Sci Technol. https://doi.org/10.1126/science.1127291
Anjum M, Miandad R, Waqas M et al (2016) Remediation of wastewater using various nano-materials. Arab J Chem. https://doi.org/10.1016/j.arabjc.2016.10.004
Apul OG, Karanfil T (2015) Adsorption of synthetic organic contaminants by carbon nanotubes: a critical review. Water Res 68:34–55. https://doi.org/10.1016/j.watres.2014.09.032
Asadzadeh-khaneghah S, Habibi-yangjeh A, Seifzadeh D (2018) Graphitic carbon nitride nanosheets coupled with carbon dots and BiOI nanoparticles: boosting visible-light-driven photocatalytic activity. J Taiwan Inst Chem Eng 87:98–111. https://doi.org/10.1016/j.jtice.2018.03.017
Awfa D, Ateia M, Fujii M, Johnson MS (2018) Photodegradation of pharmaceuticals and personal care products in water treatment using carbonaceous-TiO_2 composites: a critical review of recent literature. Water Res 142:26–45. https://doi.org/10.1016/j.watres.2018.05.036
Baruah S, Najam M, Joydeep K (2016) Perspectives and applications of nanotechnology in water treatment. Environ Chem Lett 14:1–14. https://doi.org/10.1007/s10311-015-0542-2
Bashir A, Ahmad L, Sozia M et al (2019) Removal of heavy metal ions from aqueous system by ion-exchange and biosorption methods. Environ Chem Lett 17:729–754. https://doi.org/10.1007/s10311-018-00828-y
Bishoge OK, Zhang L, Suntu SL et al (2018) Remediation of water and wastewater by using engineered nanomaterials: a review. J Environ Sci Health Part A 4529:1–18. https://doi.org/10.1080/10934529.2018.1424991
Boikanyo D, Masheane ML, Nthunya LN et al (2018) Carbon-supported photocatalysts for organic dye photodegradation. Elsevier, Amsterdam
Cai A, Wang Q, Chang Y, Wang X (2017) Graphitic carbon nitride decorated with S, N co-doped graphene quantum dots for enhanced visible-light-driven photocatalysis. J Alloys Compd 692:183–189. https://doi.org/10.1016/j.jallcom.2016.09.030
Cha C, Shin SR, Annabi N et al (2013) Carbon-based nanomaterials: multifunctional materials for biomedical engineering. ACS Nano 7:2891–2897. https://doi.org/10.1021/nn401196a
Chen Z, Wang L, Xia J et al (2014) Efficient visible light photocatalytic activity of g-C3N4/α-Fe_2O_3composites synthesized via a reactable ionic liquid. Fresenius Environ Bull 23:1107–1115. https://doi.org/10.1016/j.ceramint.2013.09.001
Chidambaram S, Vijay A, Kumar GM et al (2018) Three-dimensional (3D) flower-like nanoarchitectures of ZnO-Au on MWCNTs for visible light photocatalytic applications. Appl Surf Sci 449:631–637. https://doi.org/10.1016/j.apsusc.2017.11.236
Chowdhury SBR (2014) Recent advances in the use of graphene-family nanoadsorbents for removal of toxic pollutants from wastewater. Adv Colloid Interface Sci 204:35–56. https://doi.org/10.1016/j.cis.2013.12.005
Crini G, Lichtfouse E (2020) Advantages and disadvantages of techniques used for wastewater treatment. Environ Chem Lett 17:145–155. https://doi.org/10.1007/s10311-018-0785-9
Crini G, Lichtfouse E, Wilson LD, Morin N (2019) Conventional and non-conventional adsorbents for wastewater treatment. Environ Chem Lett 17:195–213. https://doi.org/10.1007/s10311-018-0786-8
Das R, Leo BF, Murphy F (2018) The toxic truth about carbon nanotubes in water purification: a perspective view. Nanoscale Res Lett. https://doi.org/10.1186/s11671-018-2589-z
Demirbas A (2008) Heavy metal adsorption onto agro-based waste materials: a review. J Hazard Mater 157:220–229. https://doi.org/10.1016/j.jhazmat.2008.01.024
Demirkıran N, Özdemir GDT, Saraç M, Dardağan M (2017) Adsorption of methylene blue from aqueous solutions by pyrolusite ore. Mong J Chem 18:5–11
Du F, Deng F (2015) Heralded entanglement concentration for photon systems with linear-optical elements. Sci China Phys Mech Astron 58:1–8. https://doi.org/10.1016/j.cplett.2017.11.037
Feng M, Zhang P, Zhou HC, Sharma VK (2018) Water-stable metal-organic frameworks for aqueous removal of heavy metals and radionuclides: a review. Chemosphere 209:783–800. https://doi.org/10.1016/j.chemosphere.2018.06.114
Feng M, Dionysiou DD, Sharma VK (2019) Black phosphorous-based nanostructures in environmental remediation: current status and future perspectives. Chem Eng J. https://doi.org/10.1016/j.cej.2019.123460
Ganiyu SO, Zhou M, Martínez-Huitle CA (2018) Heterogeneous electro-Fenton and photoelectro-Fenton processes: a critical review of fundamental principles and application for water/wastewater treatment. Appl Catal B Environ 235:103–129. https://doi.org/10.1016/j.apcatb.2018.04.044
Gao H, Mo Z, Guo R et al (2018) Formation of snowflake-like CdS/reduced graphene oxide composite for efficient photocatalytic organic dye degradation. J Mater Sci Mater Electron 29:5944–5953. https://doi.org/10.1007/s10854-018-8567-5
Gopinath A, Kadirvelu K (2018) Strategies to design modified activated carbon fibers for the decontamination of water and air. Springer, Berlin
Grey D, Garrick D, Blackmore D et al (2013) Water security in one blue planet: twenty-first century policy challenges for science. Philos Trans R Soc A Math Phys Eng Sci. https://doi.org/10.1098/rsta.2012.0406
Gunatilake SK (2015) Methods of removing heavy metals from industrial wastewater. Multidiscip Eng Sci Stud 1:12–18. https://doi.org/10.13140/RG.2.1.3751.1848
Gunti S, Kumar A, Ram MK (2018) Nanostructured photocatalysis in the visible spectrum for the decontamination of air and water. Int Mater Rev 63:257–282. https://doi.org/10.1080/09506608.2017.1379264
Gupta VK, Kumar R, Nayak A et al (2013) Adsorptive removal of dyes from aqueous solution onto carbon nanotubes: a review. Adv Colloid Interface Sci 193–194:24–34. https://doi.org/10.1016/j.cis.2013.03.003
Hao R, Wang G, Jiang C et al (2017) In situ hydrothermal synthesis of g-C_3N_4/TiO_2 heterojunction photocatalysts with high specific surface area for Rhodamine B degradation. Appl Surf Sci 411:400–410. https://doi.org/10.1016/j.apsusc.2017.03.197
Holt MS (2000) Sources of chemical contaminants and routes into the freshwater environment. Food Chem Toxicol 38:S21–S27
Hosseini F, Kasaeian A, Pourfayaz F et al (2018) Novel ZnO-Ag/MWCNT nanocomposite for the photocatalytic degradation of

phenol. Mater Sci Semicond Process 83:175–185. https://doi.org/10.1016/j.mssp.2018.04.042
Ihsanullah AA, Al-Amer AM et al (2016) Heavy metal removal from aqueous solution by advanced carbon nanotubes: critical review of adsorption applications. Sep Purif Technol 157:141–161. https://doi.org/10.1016/j.seppur.2015.11.039
Ismael M, Elhaddad E, Taffa DH, Wark M (2018) Solid state route for synthesis of $YFeO_3$/g-C_3N_4 composites and its visible light activity for degradation of organic pollutants. Catal Today 313:47–54. https://doi.org/10.1016/j.cattod.2018.02.003
Jarde O, Boulu G, Havet E et al (2001) Fractures transversales complètes du talus: Intérêt de l'irm pour la détection des nécroses ischémiques. Acta Orthop Belg 67:60–67. https://doi.org/10.1016/j.jiec.2018.06.028
Jayaraman T, Murthy AP, Elakkiya V et al (2018) Recent development on carbon based heterostructures for their applications in energy and environment: a review. J Ind Eng Chem 64:16–59. https://doi.org/10.1016/j.jiec.2018.02.029
Jiang L, Yuan X, Pan Y et al (2017) Environmental doping of graphitic carbon nitride for photocatalysis: a review. Appl Catal B Environ 217:388–406. https://doi.org/10.1016/j.apcatb.2017.06.003
Jiang L, Yuan X, Zeng G et al (2018) In-situ synthesis of direct solid-state dual Z-scheme WO_3/g-C_3N_4/Bi_2O_3 photocatalyst for the degradation of refractory pollutant. Appl Catal B Environ 227:376–385. https://doi.org/10.1016/j.apcatb.2018.01.042
Jilani A, Hafiz M, Othman D et al (2018) Graphene and its derivatives: synthesis, modifications, and applications in wastewater treatment. Environ Chem Lett 16:1301–1323. https://doi.org/10.1007/s10311-018-0755-2
Jun LY, Mubarak NM, Yee MJ et al (2018) An overview of functionalised carbon nanomaterial for organic pollutant removal. J Ind Eng Chem 67:175–186. https://doi.org/10.1016/j.jiec.2018.06.028
Kannan N, Sundaram MM (2001) Kinetics and mechanism of removal of methylene blue by adsorption on various carbons—a comparative study. Dye Pigment 51:25–40. https://doi.org/10.1016/S0143-7208(01)00056-0
Karnib M, Kabbani A, Holail H, Olama Z (2014) Heavy metals removal using activated carbon, silica and silica activated carbon composite. Energy Procedia 50:113–120. https://doi.org/10.1016/j.egypro.2014.06.014
Kemp KC, Seema H, Saleh M et al (2013) Environmental applications using graphene composites: water remediation and gas adsorption. Nanoscale 5:3149–3171. https://doi.org/10.1039/c3nr33708a
Khan A, Khuda F, Elseman AM et al (2018) Innovations in graphene-based nanomaterials in the preconcentration of pharmaceuticals waste. Environ Technol Rev 7:73–94. https://doi.org/10.1080/21622515.2018.1457726
Kumar S, Kumar A, Bahuguna A et al (2017) Two-dimensional carbon-based nanocomposites for photocatalytic energy generation and environmental remediation applications. Beilstein J Nanotechnol 8:1571–1600. https://doi.org/10.3762/bjnano.8.159
Kumar TKMP, Mandlimath TR, Revathi PSSK, Kumar SKA (2018) Nanoscale materials as sorbents for nitrate and phosphate removal from water. Environ Chem Lett 16:389–400. https://doi.org/10.1007/s10311-017-0682-7
Kumar A, Rittika P, Gaurav T et al (2019) Carbon nitride, metal nitrides, phosphides, chalcogenides, perovskites and carbides nanophotocatalysts for environmental applications. Environ Chem Lett 17:655–682. https://doi.org/10.1007/s10311-018-0814-8
Lata S, Samadder SR (2016) Removal of arsenic from water using nano adsorbents and challenges: a review. J Environ Manag 166:387–406. https://doi.org/10.1016/j.jenvman.2015.10.039
Li S, Gong Y, Yang Y et al (2015) Recyclable CNTs/Fe_3O_4 magnetic nanocomposites as adsorbents to remove bisphenol A from water and their regeneration. Chem Eng J 260:231–239. https://doi.org/10.1016/j.cej.2014.09.032
Li X, Shen R, Ma S et al (2018) Graphene-based heterojunction photocatalysts. Appl Surf Sci 430:53–107. https://doi.org/10.1016/j.apsusc.2017.08.194
Lin Y, Wu S, Li X et al (2018) Microstructure and performance of Z-scheme photocatalyst of silver phosphate modified by MWCNTs and Cr-doped $SrTiO_3$ for malachite green degradation. Appl Catal B Environ 227:557–570. https://doi.org/10.1016/j.apcatb.2018.01.054
Liu P, Guo Y, Xu Q et al (2014) Enhanced photocatalytic performance of ZnO/multi-walled carbon nanotube nanocomposites for dye degradation. Ceram Int 40:5629–5633. https://doi.org/10.1016/j.ceramint.2013.10.157
Liu J, Xu H, Xu Y et al (2017) Applied catalysis B: environmental graphene quantum dots modified mesoporous graphite carbon nitride with significant enhancement of photocatalytic activity. Applied Catal B Environ 207:429–437. https://doi.org/10.1016/j.apcatb.2017.01.071
Liu H, Ren M, Zhang Z et al (2018) A novel electrocatalytic approach for effective degradation of Rh-B in water using carbon nanotubes and agarose. Environ Sci Pollut Res 25:12361–12372. https://doi.org/10.1007/s11356-018-1516-2
Liu N, Lu N, Su Y et al (2019) Fabrication of g-C_3N_4/Ti_3C_2 composite and its visible-light photocatalytic capability for ciprofloxacin degradation. Sep Purif Technol 211:782–789. https://doi.org/10.1016/j.seppur.2018.10.027
Lu F, Astruc D (2018) Nanomaterials for removal of toxic elements from water. Coord Chem Rev 356:147–164. https://doi.org/10.1016/j.ccr.2017.11.003
Lü K, Zhao GX, Wang XK (2012) A brief review of graphene-based material synthesis and its application in environmental pollution management. Chin Sci Bull 57:1223–1234. https://doi.org/10.1007/s11434-012-4986-5
Madhura L, Singh S, Kanchi S et al (2019) Nanotechnology-based water quality management for wastewater treatment. Springer, Berlin
Malik DS, Jain CK, Yadav AK (2016) Removal of heavy metals from emerging cellulosic low-cost adsorbents: a review. Appl Water Sci 7:2113–2136. https://doi.org/10.1007/s13201-016-0401-8
Mallakpour S, Khadem E (2016) Carbon nanotube-metal oxide nanocomposites: fabrication, properties and applications. Chem Eng J 302:344–367. https://doi.org/10.1016/j.cej.2016.05.038
Mashkoor F, Nasar A (2020) Carbon nanotube-based adsorbents for the removal of dyes from waters: a review. Environ Chem Lett. https://doi.org/10.1007/s10311-020-00970-6
Melchionna M, Beltram A, Montini T et al (2016) Highly efficient hydrogen production through ethanol photoreforming by a carbon nanocone/Pd@TiO_2 hybrid catalyst. Chem Commun 52:764–767. https://doi.org/10.1039/c5cc08015k
Miklos DB, Remy C, Jekel M et al (2018) Evaluation of advanced oxidation processes for water and wastewater treatment—a critical review. Water Res 139:118–131. https://doi.org/10.1016/j.watres.2018.03.042
Mousavi M, Habibi-yangjeh A (2018) Magnetically recoverable highly efficient visible-light-active g-C_3N_4/Fe_3O_4/Ag_2WO_4/AgBr nanocomposites for photocatalytic degradations of environmental pollutants. Adv Powder Technol 29:94–105. https://doi.org/10.1016/j.apt.2017.10.016
Mubarak NM, Sazila N, Nizamuddin S et al (2017) Adsorptive removal of phenol from aqueous solution by using carbon nanotubes and magnetic biochar. NanoWorld J. https://doi.org/10.17756/nwj.2017-043

Nikokavoura A, Trapalis C (2018) Graphene and g-C_3N_4 based photocatalysts for NO_x removal: a review. Appl Surf Sci 430:18–52. https://doi.org/10.1016/j.apsusc.2017.08.192

Oguz E (2017) Fixed-bed column studies on the removal of Fe^{3+} and neural network modelling. Arab J Chem 10:313–320. https://doi.org/10.1016/j.arabjc.2014.10.008

Organization World Health (WHO) (2001) Global water supply and sanitation

Pang Y, Luo K, Tang L, Li X, Yu J, Guo J, Liu Y, Zhang Z, Yue R, Li L (2019) Carbon-based magnetic nanocomposite as catalyst for persulfate activation: a critical review. Environ Sci Pollut Res 26:32764–32776

Perreault F, Fonseca De Faria A, Elimelech M (2015) Environmental applications of graphene-based nanomaterials. Chem Soc Rev 44:5861–5896. https://doi.org/10.1039/c5cs00021a

Piovesana S, Capriotti AL, Cavaliere C et al (2016) New magnetic graphitized carbon black TiO_2 composite for phosphopeptide selective enrichment in shotgun phosphoproteomics. Anal Chem 88:12043–12050. https://doi.org/10.1021/acs.analchem.6b02345

Pumera M (2010) Graphene-based nanomaterials and their electrochemistry. Chem Soc Rev 39:4146–4157. https://doi.org/10.1039/c002690p

Qiu B, Xing M, Zhang J (2018) Recent advances in three-dimensional graphene based materials for catalysis applications. Chem Soc Rev 47:2165–2216. https://doi.org/10.1039/c7cs00904f

Radaei E, Alavi Moghaddam MR, Arami M (2017) Application of artificial neural network on modeling of reactive blue 19 removal by modified pomegranate residual. Environ Eng Manag J 16:2113–2122

Ramesha GK, Vijaya Kumara A, Muralidhara HB, Sampath S (2011) Graphene and graphene oxide as effective adsorbents toward anionic and cationic dyes. J Colloid Interface Sci 361:270–277. https://doi.org/10.1016/j.jcis.2011.05.050

Rong XX, Lei C, Zhong S, Xiang M (2017) Nanomaterials for water pollution monitoring and remediation. Environ Chem Lett 15:23–27. https://doi.org/10.1007/s10311-016-0595-x

Sadegh H, Ali GAM, Gupta VK et al (2017) The role of nanomaterials as effective adsorbents and their applications in wastewater treatment. J Nanostructure Chem 7:1–14. https://doi.org/10.1007/s40097-017-0219-4

Sahmoune MN (2019) Evaluation of thermodynamic parameters for adsorption of heavy metals by green adsorbents. Environ Chem Lett 17:697–704. https://doi.org/10.1007/s10311-018-00819-z

Santhosh C, Velmurugan V, Jacob G et al (2016) Role of nanomaterials in water treatment applications: a review. Chem Eng J 306:1116–1137. https://doi.org/10.1016/j.cej.2016.08.053

Sarkar B, Mandal S, Tsang YF et al (2018) Designer carbon nanotubes for contaminant removal in water and wastewater: a critical review. Sci Total Environ 612:561–581. https://doi.org/10.1016/j.scitotenv.2017.08.132

Shafei A, Sheibani S (2019) Visible light photocatalytic activity of Cu doped TiO_2-CNT nanocomposite powder prepared by sol–gel method. Mater Res Bull 110:198–206. https://doi.org/10.1016/j.materresbull.2018.10.035

Shan SJ, Zhao Y, Tang H, Cui FY (2017) A mini-review of carbonaceous nanomaterials for removal of contaminants from wastewater. IOP Conf Ser Earth Environ Sci. https://doi.org/10.1088/1755-1315/68/1/012003

Shanker U (2017) Degradation of hazardous organic dyes in water by nanomaterials. Environ Chem Lett 15:623–642. https://doi.org/10.1007/s10311-017-0650-2

Shao D, Hu J, Wang X (2010) Plasma induced grafting multiwalled carbon nanotube with chitosan and its application for removal of UO, Cu^{2+}, and Pb^{2+} from aqueous solutions. Plasma Process Polym 7:977–985. https://doi.org/10.1002/ppap.201000062

Shi L, Ding W, Yang S et al (2018) Rationally designed MoS_2/protonated g-C_3N_4 nanosheet composites as photocatalysts with an excellent synergistic effect toward photocatalytic degradation of organic pollutants. J Hazard Mater 347:431–441. https://doi.org/10.1016/j.jhazmat.2018.01.010

Shi E, Xu Z, Wang W et al (2019) Ag_2S-doped core-shell nanostructures of Fe_3O_4@Ag_3PO_4 ultrathin film: major role of hole in rapid degradation of pollutants under visible light irradiation. Chem Eng J 366:123–132. https://doi.org/10.1016/j.cej.2019.02.018

Sitko R, Turek E, Zawisza B et al (2013) Adsorption of divalent metal ions from aqueous solutions using graphene oxide. Dalton Trans 42:5682–5689. https://doi.org/10.1039/c3dt33097d

Smith SC, Rodrigues DF (2015) Carbon-based nanomaterials for removal of chemical and biological contaminants from water: a review of mechanisms and applications. Carbon 91:122–143. https://doi.org/10.1016/j.carbon.2015.04.043

Sun YP, Ha W, Chen J et al (2016) Advances and applications of graphitic carbon nitride as sorbent in analytical chemistry for sample pretreatment: a review. TrAC Trends Anal Chem 84:12–21. https://doi.org/10.1016/j.trac.2016.03.002

Talaiekhozani A, Rezania S (2017) Application of photosynthetic bacteria for removal of heavy metals, macro- pollutants and dye from wastewater: a review. J Water Process Eng 19:312–321. https://doi.org/10.1016/j.jwpe.2017.09.004

Thines RK, Mubarak NM, Nizamuddin S et al (2017) Application potential of carbon nanomaterials in water and wastewater treatment: a review. J Taiwan Inst Chem Eng 72:116–133. https://doi.org/10.1016/j.jtice.2017.01.018

Tong Y, McNamara PJ, Mayer BK (2019) Adsorption of organic micropollutants onto biochar: a review of relevant kinetics, mechanisms and equilibrium. Environ Sci Water Res Technol 5:821–838. https://doi.org/10.1039/c8ew00938d

Varghese AG, Annie S, Latha PMS (2019) Remediation of heavy metals and dyes from wastewater using cellulose-based adsorbents. Environ Chem Lett 17:867–877. https://doi.org/10.1007/s10311-018-00843-z

Wang J, Chen B (2015) Adsorption and coadsorption of organic pollutants and a heavy metal by graphene oxide and reduced graphene materials. Chem Eng J 281:379–388. https://doi.org/10.1016/j.cej.2015.06.102

Wang S, Sun H, Ang HM, Tadé MO (2013) Adsorptive remediation of environmental pollutants using novel graphene-based nanomaterials. Chem Eng J 226:336–347. https://doi.org/10.1016/j.cej.2013.04.070

Wang W, Xu Z, Zhang X et al (2018) Rapid and efficient removal of organic micropollutants from environmental water using a magnetic nanoparticles-attached fluorographene-based sorbent. Chem Eng J 343:61–68. https://doi.org/10.1016/j.cej.2018.02.101

Wang L, Guo X, Chen Y et al (2019) Cobalt-doped g-C_3N_4 as a heterogeneous catalyst for photo-assisted activation of peroxymonosulfate for the degradation of organic contaminants. Appl Surf Sci 467–468:954–962. https://doi.org/10.1016/j.apsusc.2018.10.262

Wen J, Xie J, Chen X, Li X (2017) A review on g-C_3N_4-based photocatalysts. Appl Surf Sci 391:72–123. https://doi.org/10.1016/j.apsusc.2016.07.030

WHO (2017) WHO (World Health Organization), progress on drinking water, sanitation and hygiene

Xiao T, Tang Z, Yang Y et al (2018) In situ construction of hierarchical WO_3/g-C_3N_4 composite hollow microspheres as a Z-scheme photocatalyst for the degradation of antibiotics. Appl Catal B Environ 220:417–428. https://doi.org/10.1016/j.apcatb.2017.08.070

Xu L, Wang J (2017) The application of graphene-based materials for the removal of heavy metals and radionuclides from water and

wastewater. Crit Rev Environ Sci Technol 47:1042–1105. https://doi.org/10.1080/10643389.2017.1342514

Xu B, Boshir M, Zhou JL et al (2018a) Graphitic carbon nitride based nanocomposites for the photocatalysis of organic contaminants under visible irradiation: progress, limitations and future directions. Sci Total Environ 633:546–559. https://doi.org/10.1016/j.scitotenv.2018.03.206

Xu J, Cao Z, Zhang Y et al (2018b) A review of functionalized carbon nanotubes and graphene for heavy metal adsorption from water: preparation, application, and mechanism. Chemosphere 195:351–364. https://doi.org/10.1016/j.chemosphere.2017.12.061

Yagub MT, Sen TK, Afroze S, Ang HM (2014) Dye and its removal from aqueous solution by adsorption: a review. Adv Colloid Interface Sci 209:172–184. https://doi.org/10.1016/j.cis.2014.04.002

Yang M (2011) A current global view of environmental and occupational cancers. J Environ Sci Health Part C Environ Carcinog Ecotoxicol Rev 29:223–249. https://doi.org/10.1080/10590501.2011.601848

Yang S, Gong Y, Zhang J et al (2013) Exfoliated graphitic carbon nitride nanosheets as efficient catalysts for hydrogen evolution under visible light. Adv Mater 25:2452–2456. https://doi.org/10.1002/adma.201204453

Yazdani EB, Mehrizad A (2018) Sonochemical preparation and photocatalytic application of Ag-ZnS-MWCNTs composite for the degradation of Rhodamine B under visible light: Experimental design and kinetics modeling. J Mol Liq 255:102–112. https://doi.org/10.1016/j.molliq.2018.01.154

Ye A, Fan W, Zhang Q et al (2012) CdS-graphene and CdS-CNT nanocomposites as visible-light photocatalysts for hydrogen evolution and organic dye degradation. Catal Sci Technol 2:969–978. https://doi.org/10.1039/c2cy20027a

Yu JG, Zhao XH, Yang H et al (2014) Aqueous adsorption and removal of organic contaminants by carbon nanotubes. Sci Total Environ 482–483:241–251. https://doi.org/10.1016/j.scitotenv.2014.02.129

Yu G, Lu Y, Guo J et al (2018) Carbon nanotubes, graphene, and their derivatives for heavy metal removal. Adv Compos Hybrid Mater 1:56–78. https://doi.org/10.1007/s42114-017-0004-3

Zhang L, Jaroniec M (2018) Toward designing semiconductor-semiconductor heterojunctions for photocatalytic applications. Appl Surf Sci 430:2–17. https://doi.org/10.1016/j.apsusc.2017.07.192

Zhang D, Pan B, Wu M et al (2011) Adsorption of sulfamethoxazole on functionalized carbon nanotubes as affected by cations and anions. Environ Pollut 159:2616–2621. https://doi.org/10.1016/j.envpol.2011.05.036

Zhang Y, Wu B, Xu H et al (2016) Nanomaterials-enabled water and wastewater treatment. NanoImpact 3–4:22–39. https://doi.org/10.1016/j.impact.2016.09.004

Zhang C, Li Y, Shuai D et al (2019) Chemosphere Graphitic carbon nitride ($g\text{-}C_3N_4$)-based photocatalysts for water disinfection and microbial control: a review. Chemosphere 214:462–479. https://doi.org/10.1016/j.chemosphere.2018.09.137

Zhang Y, Zhao Y, Xu Z et al (2020) Carbon quantum dots implanted CdS nanosheets: efficient visible-light-driven photocatalytic reduction of Cr(VI) under saline conditions. Appl Catal B Environ 262:118306. https://doi.org/10.1016/j.apcatb.2019.118306

Zhao J, Ren W, Cheng HM (2012) Graphene sponge for efficient and repeatable adsorption and desorption of water contaminations. J Mater Chem 22:20197–20202. https://doi.org/10.1039/c2jm34128j

Zhao Z, Sun Y, Dong F (2015) Graphitic carbon nitride based nanocomposites: a review. Nanoscale 7:15–37. https://doi.org/10.1039/c4nr03008g

Zhao Y, Zhang X, Liu J et al (2018) Graphene oxide modified nanosized $BaTiO_3$ as photocatalyst. Ceram Int 44:15929–15934. https://doi.org/10.1016/j.ceramint.2018.06.013