



Review

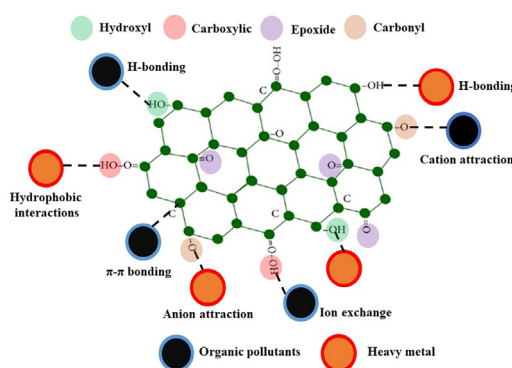
Graphene-based materials for effective adsorption of organic and inorganic pollutants: A critical and comprehensive review

Dibya Ranjan Rout^a, Hara Mohan Jena^{a,*}, Omirserik Baigzenhenov^b, Ahmad Hosseini-Bandegharai^c^a Department of Chemical Engineering, National Institute of Technology, Rourkela 769008, Orissa, India^b Department of Metallurgical Sciences, Satbayev University, Almaty, Kazakhstan^c Faculty of Chemistry, Semnan University, Semnan, Iran

HIGHLIGHTS

- Graphene, GO, and rGO based polymers, and composites are reviewed for organic and inorganic pollutants removal.
- Equilibrium isotherm, kinetics, thermodynamics, mechanisms, and regeneration studies are reviewed.
- Function of material composite for pollutants removal was summarized.
- Gaps and challenges in the literature studies are presented.
- Perspectives of future research directions for graphene-based adsorbent were presented.

GRAPHICAL ABSTRACT



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ABSTRACT

Water scarcity has been felt in many countries and will become a critical issue in the coming years. The release of toxic organic and inorganic contaminants from different anthropogenic activities, like mining, agriculture, industries, and domestic households, enters the natural waterbody and pollutes them. Keeping this in view in combating the environmental crises, removing pollutants from wastewater is one of the ongoing environmental challenges. Adsorption technology is an economical, fast, and efficient physicochemical method for removing both organic and inorganic pollutants, even at low concentrations. In the last decade, graphene and its composite materials have become the center of attraction for numerous applications, including wastewater treatment, due to the large surface area, highly active surface, and exclusive physicochemical properties, which make them potential adsorbents with unique physicochemical properties, like low density, chemical strength, structural variability, and the possibility of large-scale fabrications. This review article provides a thorough summary/critical appraisal of the published literature on graphene-, GO-, and rGO-based adsorbents for the removal of organic and inorganic pollutants from wastewater. The synthesis methods, experimental parameters, adsorption behaviors, isotherms, kinetics, thermodynamics, mechanisms, and the performance of the regeneration-desorption processes of these substances are scrutinized. Finally, the research challenges, limitations, and future research studies are also discussed. Certainly, this review article will benefit the research community by getting substantial information on suitable techniques for synthesizing such adsorbents and utilizing them in water treatment and designing water treatment systems.

* Corresponding author at: Department of Chemical Engineering, National Institute of Technology Rourkela, Odisha 769008, India.

E-mail addresses: 518ch1008@nitrrkl.ac.in (D.R. Rout), hmjena@nitrrkl.ac.in (H.M. Jena), o.baigzenhenov@satbayev.university (O. Baigzenhenov).

Contents

1.	Introduction	2
2.	Synthesis and properties of graphene-based materials	4
2.1.	Graphene, rGO, and GO.	4
2.2.	Graphene-based composites	5
2.2.1.	Graphene-modified carbon nanotubes (CNTs) composites	5
2.2.2.	Graphene-based nanocomposites.	6
2.2.3.	Graphene-based polymer composites	6
3.	Pollutant removal applications using graphene-based adsorbents	6
3.1.	Adsorption of organic pollutants	6
3.1.1.	Adsorption of phenolic pollutants using graphene-based adsorbents	6
3.1.2.	Adsorption of synthetic dyes using graphene-based adsorbents.	8
3.1.3.	Graphene-based adsorbents for the sorption of organic pollutants	12
3.2.	Use of graphene-based adsorbents for adsorption of heavy metals.	12
4.	Critical consideration of kinetic, equilibrium and thermodynamic studies.	16
4.1.	Kinetic consideration of pollutants adsorption by graphene-based materials	16
4.2.	Equilibrium consideration of pollutants adsorption by graphene-based materials	17
4.3.	Thermodynamic consideration of pollutants adsorption by graphene-based materials	18
5.	Desorption and regeneration studies.	18
6.	Challenges and future studies and recommendations.	19
7.	Conclusions	19
	CRedit authorship contribution statement	19
	Data availability	19
	Declaration of competing interest	19
	References	20

1. Introduction

The availability of fresh drinking water is important to maintain a healthier life. Intensive industrialization, uncontrolled urbanization, excessive use of natural water resources, and growing population have substantially affected water quality (Baig et al., 2019). Continuous discharge of pollutants from industrial, domestic, agricultural, and municipal activities into natural water resources worsens the quantity and quality of usable water resources (Chowdhury et al., 2016; Liu et al., 2021). Numerous organics, like personal care products, endocrine disrupting compounds (EDCs), polycyclic aromatic hydrocarbons, herbicides, pesticides, synthetic dyes, etc., and inorganic heavy metals pollutants have been found in natural water resources worldwide (Chakraborty et al., 2022). Short- and long-term exposures to these pollutants can prompt serious health-related complications. Heavy metals are among the most toxic contaminants encountered in the aquatic environment because of their persistence, magnification potential/bioaccumulation, and high toxicity. The presence of heavy metals in water resources and prolonged exposure to them can cause skin anemia, diarrhea, vomiting, heart disease, nephropathy, respiratory disease, renal failure, tumor, diabetes, hypertension, and lung cancer (Rout and Jena, 2022a, 2022b). The presence of synthetic dyes in water and exposure to them causes heart failures, damages the liver and kidneys, decreases fertility rate, and causes carcinogenic, teratogenic, and mutagenic influences on human cells). The presence of organics such as EDCs, phenolic pollutants, insecticides, domestic products, and pesticides in water causes various health effects on humans and aquatic organisms (Al-Musawi et al., 2022).

To improve water quality, reduce health complications and illnesses, and produce a suitable environment for aquatic organisms, action must be taken to treat continuously discharged wastewater from various sources. At present, various methods are used for the treatment of these highly contaminated effluents, including sedimentation/flocculation/coagulation (Cheng et al., 2021), chemical precipitation (Pohl, 2020), electrochemical separation (Thamaraiselvan et al., 2021), ion exchange (Charles et al., 2016), adsorption (Rout and Jena, 2022c, 2022d, 2021), membrane filtration (Thamaraiselvan et al., 2021), photocatalytic degradation (Rout et al., 2022), and biological treatments (Cherniak et al., 2022). Nevertheless, several of these treatment methods have some limitations, including

high operating costs, large volume of generated sludges, subsequent disposal issues, time-consuming process, and technical limitations for industrial applications (Rout and Jena, 2022e).

Fig. 1 demonstrate several conventional technologies used for water treatment and their drawbacks. Nevertheless, among the mentioned techniques, the adsorption method is a versatile advantageous one, because of flexibility, economical, operational simplicity, and insensitivity to toxic pollutants and, when is used to treat the contaminated wastewater, brings about a high removal efficiency, reduces the capital and operating costs, and eliminates the need for secondary treatment (Rout and Jena, 2022f). So far, various types of adsorbents such as biological, organic, mineral materials, biomass, agricultural waste, polymeric materials, zeolites, activated carbon, industrial by-products, graphene-based composites, clay minerals, etc. have been conventionally synthesized and exploited over the years for removal of organic and inorganic contaminants (Abuzalat et al., 2022). Among these various adsorbents, carbonaceous materials and their composites, including activated carbon, graphene, carbon nanotubes, fullerenes, etc., have been widely utilized as adsorbents because of their extraordinary properties, such as abundant pore structure, chemical stability, large specific surface area, ability to be altered for specific applications, ease of physical and chemical modifications, and capability to remove various pollutants (Xiong and Jivkov, 2018). Graphene and its derivatives are considered as the most advanced adsorbent materials among all the carbonaceous materials because of their unique characteristics (Table 1). Graphene and its derivatives have excellent properties such as large delocalized π -electron system, enhanced active sites, high chemical stability, and very high surface area, making them efficient materials for wastewater treatment application (Ranjan Rout and Mohan Jena, 2022).

Geim and Novoselov in 2004 developed a single-layer sheet of carbon, called graphene. In graphene sheets, the carbon atoms are filled in a honeycomb-like lattice structure and arranged in a flat two-dimensional (2D) layer (Geim and Novoselov, 2007). In terms of its dimensions, it can be rolled to 1D-carbon nanotubes, stacked to 3D graphite, and wrapped to 0D fullerene, thus completing the carbon family (Fig. 2) (Saleh, 2016). The delocalized π -electrons present on the graphene provide stability as compared to other nanosystems. Graphene has an exceptional thermal conductivity of 3000 W/m.K, an electron mobility of 200,000 cm²/V.s, and the optical transparency of nearly 97.3 % (Rout et al., 2019). The thickness of

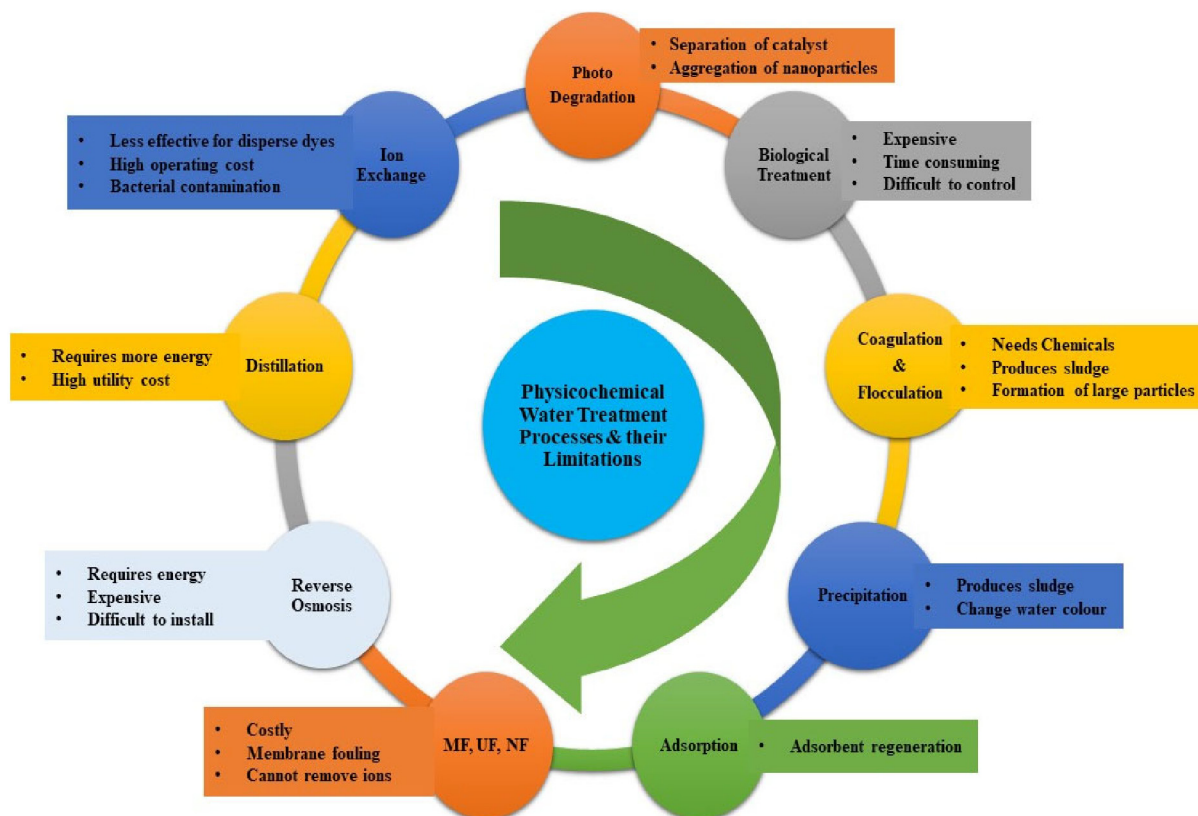


Fig. 1. Conventional wastewater treatment and their disadvantages.

graphene is just 0.335 nm and is the thinnest material ever produced (Ni et al., 2007). The most important characteristic of graphene is its high surface area, and the value is $\sim 2630 \text{ m}^2/\text{g}$, which is much higher than those of carbon nanotubes ($1315 \text{ m}^2/\text{g}$) and graphite ($\sim 10 \text{ m}^2/\text{g}$) (Sahu et al., 2021). Due to the unique properties of graphene, researchers and scientists all over the world have given full attention to this advantageous substance. At present, in various engineering fields and disciplines, graphene has been used in different technologies such as energy storage devices, electromagnetic shielding, organic light-emitting diodes, biosensors, coating protections, dye batteries, aerospace, biomedical devices, sound sensors, integrated circuits, and wastewater treatment as well (Zhou et al., 2015). The applications of graphene have encouraged the research community all over the world to not only focus just on graphene but also explore the applications of other connected materials like reduced graphene oxide (rGO) and graphene oxide (GO).

Researchers worldwide have shown tremendous research interest for the environmental applications of graphene-based compounds, like adsorption of pollutants in aqueous solutions. This interest has been motivated day by day because of the various properties of graphene and its derivatives,

which are suitable for the adsorption of various organic and inorganic pollutants. GO and rGO, respectively the oxidized and reduced forms of graphene, have been widely used as adsorbents for various organic and inorganic pollutants from aqueous solution. However, GO and rGO have slightly different properties compared to pristine graphene. The pristine graphene has Young's modulus of 1000 GPa, whereas for GO, it is 200 GPa, and for rGO, it is 250 GPa. There is no functional groups in pristine graphene, whereas the GO and rGO contain various functional groups on their edges and surface like hydroxyl ($-\text{OH}$), carboxyl ($-\text{COOH}$), and carbonyl ($-\text{C}=\text{O}$) moieties (Rout and Jena, 2022d). The existence of these functional groups on rGO and GO makes them suitable for the adsorption of various inorganic and organic contaminants. The dissociation of $-\text{COOH}$ group existent on the surface of GO and rGO to $-\text{COO}^- + \text{H}^+$ causes adsorption of positive ions like heavy metal ions and other cationic pollutants, and the carbonyl groups form chelation with positive species by oxygen lone pair. The ionization of epoxy groups ($-\text{O}-$) and ($-\text{C}-\text{OH}$) forms ($-\text{C}^+$), which creates a positive environment that is suitable for adsorption of anions and negatively charged species (Freire et al., 2018). Also, the presence of cyclic aromaticity in GO and rGO can interact with other aromatic pollutants through electrostatic and $\pi-\pi$ interaction. All these above interactions are available at the surface of GO and rGO, which are suitable for adsorption applications.

Till date, several graphene-, GO-, and rGO-based composite adsorbents has been investigated for the effective removal of organic and inorganic pollutants from wastewater including endocrine-disrupting compounds (Al-Musawi et al., 2022), oil spills (Diraki et al., 2019), heavy metal ions (Joya-Cárdenas et al., 2022; Ranjan Rout and Mohan Jena, 2022), phenols (Rout and Jena, 2022a, 2022c), chlorophenols (Rout and Jena, 2022b), pesticides (Ghanbarlou et al., 2020) dyes (Rout and Jena, 2022c, 2021), emerging pollutants (Khalil et al., 2020), and micro plastics (Sharma et al., 2021). Fig. 3(a) illustrates the last seven years of published research related to heavy metals, dyes, organic pollutants, and phenolic pollutants removal by graphene-, rGO-, and GO-based adsorbents. It is obvious from

Table 1

Single-layer graphene properties at room temperature (Chowdhury and Balasubramanian, 2014).

Characteristics	Value
BET specific surface area	$2630 \text{ m}^2/\text{g}$
C—C bond length	0.142 nm
Electron mobility	$200,000 \text{ cm}^2/\text{V.s}$
Young's modulus	1100 GPa
Optical transparency	97 %
Thermal conductivity	3000 W/m.K
Carrier density	10^{12} cm^{-2}
Resistivity	$10-6 \Omega \text{ cm}$
Fractural strength	125 GPa

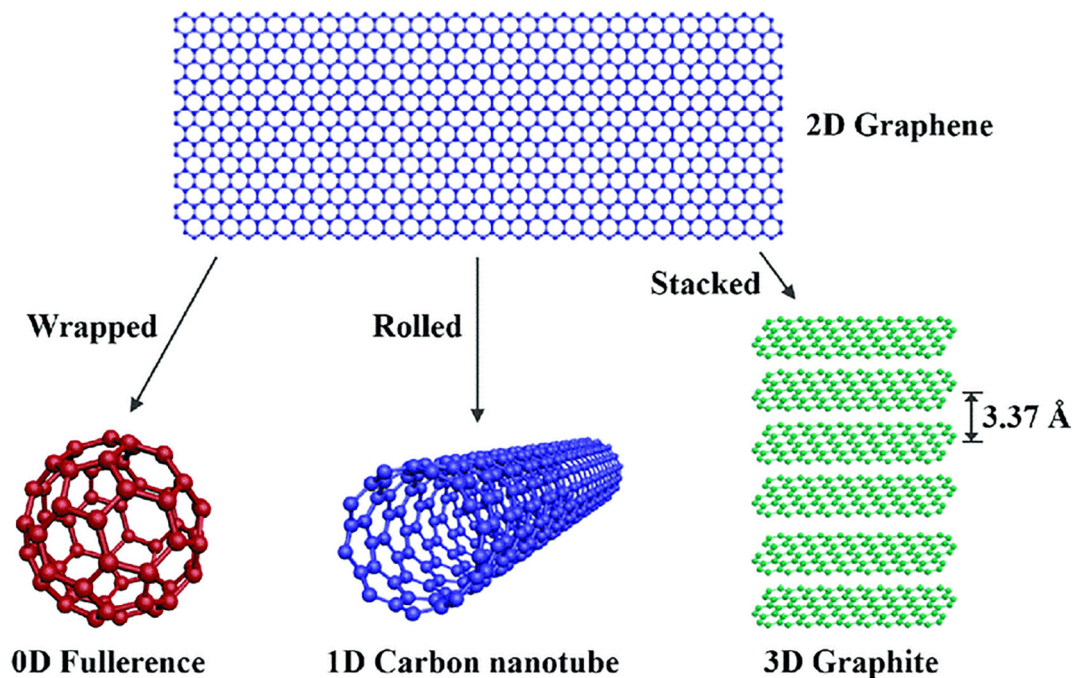


Fig. 2. Graphene, the mother of all graphitic forms from 2D graphene to 0D fullerene, 1D carbon nanotube, and 3D graphite (Zhao et al., 2020).

Fig. 3(a) that the application of graphene-based adsorbents for adsorption of different pollutants is rapidly growing year by year. As a result, the review articles also increase on this subject year to year. Fig. 3(b) shows the trend. There are review articles accessible in the literature on organic pollutants removal (Baig et al., 2019), dye removal (Khurana and Saxena, 2017), and heavy metals removal (Kong et al., 2021) by adsorption using GO/rGO-based adsorbents. However, very few review articles are available that collectively deal with removal of heavy metals, organic contaminants, phenolic pollutants, and dyes from wastewaters using graphene-based adsorbents.

Considering the above facts, this review paper presents the significant studies that have already published and used graphene and its derivatives as adsorbent for the removal of heavy metals, phenolic compounds, organic pollutants, and dyes. Meanwhile, the synthesis, adsorption performance, experimental adsorption conditions, parameter studies,

isotherm evaluations, kinetic studies, and maximum adsorption capacities are discussed. The thermodynamic calculations, desorption analyses, and adsorption mechanisms are also addressed. The current review paper also addresses the limitations, challenges, and prospects of graphene-, rGO- and GO-based adsorbents in wastewater treatment industry.

2. Synthesis and properties of graphene-based materials

2.1. Graphene, rGO, and GO

Fig. 4a shows the crystal structure of graphene. It can be seen that the carbon atoms are closely packed in a honeycomb-like structure through π and σ -bonds. Graphene is a 2-D material and the thickness of one layer of carbon is 0.335 nm (Ni et al., 2007). There are various synthesis routes available for the synthesis of graphene, such as bottom-up synthesis from

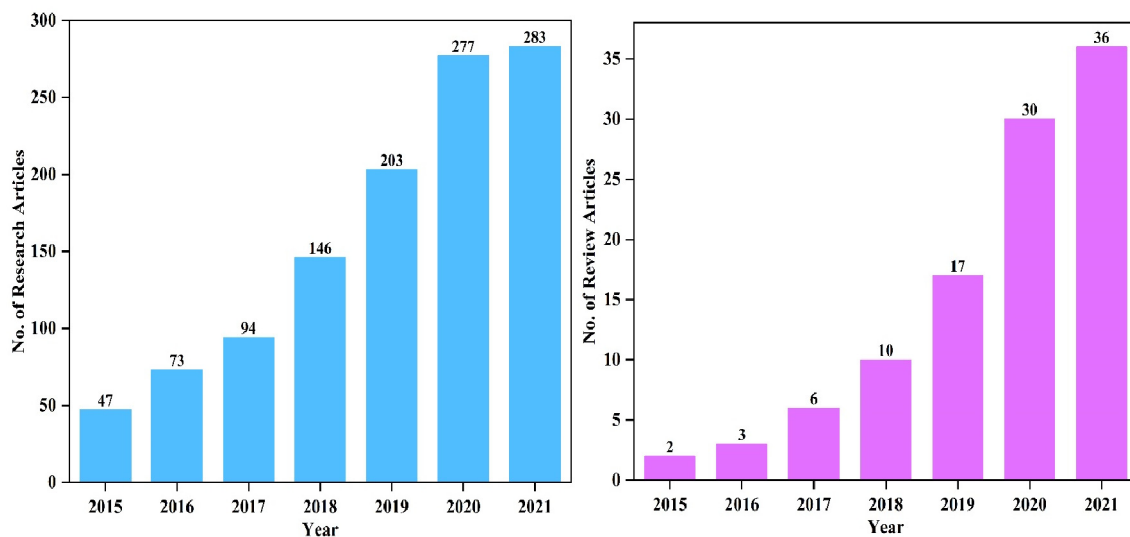


Fig. 3. (a) Number of research articles and (b) Number of review articles published in last seven-year period for adsorption of organic and inorganic pollutants by exploiting graphene-, GO-, and rGO-based adsorbents, obtained from Web of Science using the keywords “graphene-based adsorbents”, “adsorption”, “organic pollutants”, and “inorganic pollutants”.

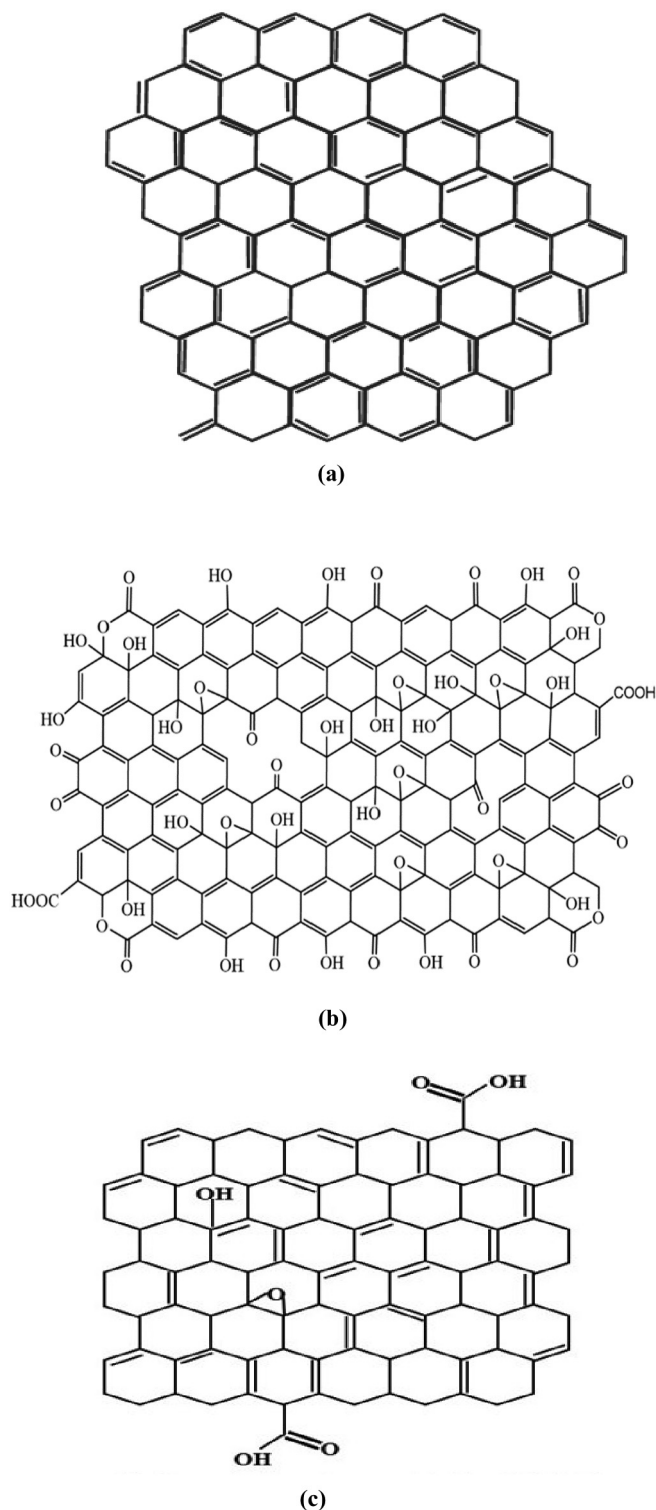


Fig. 4. Crystal structure of (a) Graphene, (b) GO, and (c) rGO.

organic molecules (Neppolian et al., 2012), chemical vapor decomposition (CVD) (Zhang et al., 2013), chemical reduction of exfoliated graphene oxide (Wei and Liu, 2010), carbon nanotube unzipping (Jiao et al., 2009), liquid phase utilization (Becerril et al., 2008), and epitaxial growth of SiC (Ouerghi et al., 2012). Table 2 describes the advantages and limitations of various graphene synthesis methods. Among all these methods, the chemical reduction of GO is a standout method for the preparation of bulk amount of graphene, despite its limitations. Nevertheless, the mass production of single-layer graphene is very costly and the compounds and

dispersions produced during the synthesis of graphene are almost never monodisperse.

GO is the oxidized form of graphene and, in the surface of GO, various oxygenated functional groups are present, which makes it a reactive species (Fig. 4b) (Jiříčková et al., 2022). Also, GO is a mono-layer graphite oxide, which can be fabricated by the exfoliation of multilayer graphite oxide by microwave, or arc discharge, rapid heating, mechanical stirring, and sonication (Zhao et al., 2015). There are various synthesis procedures available for GO synthesis, from which the improved Hummer's method is the best for GO synthesis. Improved Hummer's method is an economically valuable process compared to the synthesis of single-layer graphene. In this method, the chemical oxidation of graphite powder occurs in an acid medium, which results in the decoration of —COOH groups at the edges, whereas —OH and —C=O groups are generated in the basal planes (Rout and Jena, 2022e; Verma et al., 2022). Because of these functional groups, GO has hydrophilicity in nature, which is suitable for water treatment. Owing to the presence of various functional moieties on the surface of GO, the thickness of single-layer GO is 0.7–1.2 nm, higher than that of pristine graphene (0.335 nm) (Peng et al., 2017). GO may be characterized as an exceptionally generous solid like an indulgent membrane, liquid crystal, colloid, two-dimensional polymer, anisotropic and even amphiphile (Krishnan et al., 2012). Due to the presence of functional groups on GO, it can be functionalized with other materials for wide uses. Reduced graphene oxide (rGO) is synthesized by the chemical reduction of GO, hydrothermal, and thermal annealing methods (Fig. 4c). In rGO, some of the oxygenated functional groups are reduced and enable its recurring modification by non-covalent physical adsorption of both minor molecules and polymers by van der Waals interactions or $\pi\text{--}\pi$ stacking (Dreyer et al., 2010). Consequently, rGO and its composites have become a promising material for various applications, and water treatment is among them.

2.2. Graphene-based composites

Because of the strong inter-planar interactions, graphene layers are inclined to collective and restack to form graphite (Naushad, 2019). On the other hand, GO comprises weak binding affinity for negatively charged ions and molecules because of robust electrostatic repulsion between them, as on the surface of GO, various kinds of oxygenated functional moieties are present. In addition, after adsorption, graphene and its derivatives are difficult to be desorbed and separated from treated water, initiating secondary pollution. To overcome these drawbacks, functionalization of graphene, GO, and rGO with other nanomaterials and dissimilar molecules by covalent or non-covalent bonding has been done to form nanocomposites with the characteristic features of all the substrate molecules (Chowdhury and Balasubramanian, 2014).

2.2.1. Graphene-modified carbon nanotubes (CNTs) composites

For synthesizing graphene-based CNTs composites as adsorbents, difficulties may arise at the initial stages of the synthesis, as the dispersion of graphene and CNTs in a solvent, particularly in water, to form a stable, and highly concentrated solution is very difficult. For example, ultrasonic exfoliation of graphene and its derivative materials in water or organic solvents results in graphene nanoplatelet solutions. However, in the solutions, the concentration of graphene is less, thereby limiting its application for mass production. Reactive surfactants have been proposed for synthesizing graphene-based composite with CNTs, such as low molecular weight formaldehyde-phenol oligomers. The presence of methylol groups in the surfactants possesses high reactivity, which modifies the surface of graphene or CNTs and, as a result, it imparts water solubility (Papageorgiou et al., 2017). This modification is apparently helpful in synthesizing of various nanocomposites based on GO, rGO, graphene, and CNTs (Bera and Das, 2022; Nikonova et al., 2021). The presence of reactive functional groups on their surface enhances their distribution and compatibility as a result, they can be exploited as adsorbents for wastewater treatment.

Table 2

Advantages and limitations of various methods used for graphene synthesis.

Synthesis procedure	Advantages	Limitations
CVD	- High quality graphene. - Mass production. - Large area. - Limited number of defects.	- Poor scalability. - Expensive.
Micromechanical exfoliation	- Excellent quality of graphene. - Simple process. - Better suited for fundamental research. - Few defects.	- Not suitable for mass production. - Poor reproducibility.
Colloidal suspension	- Suitable for chemical functionalization. - High volume of production. - Scalable.	Significant number of defects.
Epitaxial growth	- Few defects. - High quality of graphene.	- High temperature required. - High cost.
Reduction of GO	- Economical and facile technique. - Mass production.	Significant number of defects
Unzipping of CNTs	- Better control over functionalization and the edge quality. - Scalable with controlled width and edge structures.	- More expensive compared to chemical exfoliation of graphite oxide or graphite. - Low yield.

2.2.2. Graphene-based nanocomposites

Because of its amazing features and characteristics, there is a never-ending consideration for using graphene as a prominent substrate for synthesizing graphene-based nanocomposites. The aggregation problem of graphene can be overcome by intercalating organic and inorganic particles within graphene layers (MacHado and Serp, 2012). Nowadays, there is a great number of composites available which contain metal/metal oxide molecules with graphene, GO, and rGO, such as Mg (Safari et al., 2020) Au (Leong et al., 2021), Ag (Wei et al., 2021), Pt (Altuncı and Körbahti, 2022), Pd (Salagare et al., 2022), Ni (Li et al., 2012), Fe (Shan et al., 2021), Co (Fachina et al., 2022), metal oxides like TiO₂ (Shen et al., 2021), ZnO (Z. Chen et al., 2021), Fe₃O₄ (Wang et al., 2022), MnO₂ (Aquatar et al., 2022), Co₃O₄ (Gabris et al., 2022), Al₂O₃ (Ramutshatsha-Makhwedzha et al., 2022), SiO₂ (Hassanin et al., 2022), etc. Numerous routs have been employed to synthesize graphene-based composites such as UV/microwave assisted reduction, solvothermal and/or hydrothermal, in situ growth strategies, ex situ hybridizations, etc.

2.2.3. Graphene-based polymer composites

Three types of polymer composites are available such as polymer-functionalized graphene nanolayers, graphene-modified polymer composites, and layered graphene-polymer films. Based on interaction between graphene layers and 3D arrangement, the classification of graphene-based polymer composites can be implemented (Yuan et al., 2013). Polymers like polypyrrole (Gao et al., 2021), polystyrene (de Farias et al., 2022), polyaniline (Ullah et al., 2022), polyurethane (Alisani et al., 2022), polyvinyl alcohol (Rattanakunsong et al., 2022), polycarbonate (Sabet and Mohammadian, 2022), etc. were used to fabricate graphene-based polymer composites. These polymer composites have numerous properties like high thermal stability, high thermal conductivity, elastic modulus, reduced gas permeability, fracture toughness, and high impact strength.

3. Pollutant removal applications using graphene-based adsorbents

Currently, the adsorption treatment method is an effective and efficient procedure for removal of inorganic and organic pollutants. Various influential parameters, like initial concentration, solution pH, adsorbent dosage, temperature, agitation rate, and contact time are optimized (Chowdhury and Balasubramanian, 2014). The adsorption equilibrium data is commonly fitted with well-known isotherm models such as Freundlich and Langmuir, sometimes along with other less-used two- or three-parameter models. The Langmuir isotherm considers monolayer adsorption, whereas Freundlich isotherm model is commonly used for the heterogeneous surface where multilayer adsorption occurs. The kinetic data of the adsorption processes are fitted by pseudo-first-order, pseudo-second-order, intraparticle diffusion, Elovich, and Boyd kinetic model. The use of GO, rGO,

graphene, and their modified polymers and composites as an adsorbent for wastewater treatment is increasing day by day. Because of their exclusive properties (e.g., tremendous mobility of charge carriers, presence of various functional groups, and great specific surface area), graphene-based composite materials have become the most effective and efficient adsorbents in wastewater treatment. Adsorption of organic contaminants (phenolic compounds, dyes, pesticides, and other organic contaminants) and heavy metals by these materials are given in the next sub-sections.

3.1. Adsorption of organic pollutants

This section describes the already published works on the adsorption of numerous organic pollutants such as phenolic pollutants, dyes, and other organic contaminants onto graphene-based adsorbents.

3.1.1. Adsorption of phenolic pollutants using graphene-based adsorbents

Phenolic pollutants are organic compounds with hydroxyl groups and benzene rings attached to other aromatic compounds. Phenol is the starting material for the synthesis of various polymers. According to the United States Environmental Protection Agency (USEPA), phenolic pollutants are considered priority pollutants and have severe negative effects on human health (Li et al., 2013). The effluents generated from various industrial activities such as pharmaceutical, refinery, petroleum, plastic, coking, fertilizer industries, etc., and domestic waste contain high amounts of phenols (Husain and Ulber, 2011). Phenols and chlorophenols poisoning include damage to human skin, lungs, kidney, liver, and digestive tracts (Rout and Jena, 2022g). The US Food and Administration (USFDA) has set 0.001 mg/L as the concentration of phenol in bottled drinking waters and 0.01 mg/L for groundwater. Consequently, concentration of phenolic pollutants in water should be reduced before it is released into environment. Various graphene-based composites have been exploited for the adsorption of phenolic compounds from wastewater, summarized in Table 3.

Wang et al. (2015) produced a novel 3D graphene aerogel mesoporous silica adsorbent for adsorption of four phenolic pollutants such as hydroquinone, resorcinol, catechol, and phenol. The equilibrium time for all four pollutants was observed at 120 min and the optimal temperature was 25 °C. The maximum sorption capacities were 67, 22, 66, and 90 mg/g for hydroquinone, resorcinol, catechol, and phenol, respectively. From the isothermal studies, it was grasped that for phenol Freundlich model was the best-fitted model, whereas for the other three pollutants, the Langmuir model was perfectly fitted. Liu et al. (2016) utilized GO supported by bimetallic oxide composite (Fe₂O₄@mSiO₂/GO) to remove p-nitrophenol effectively. The data obeyed Langmuir model with maximum uptake of 1548.78 mg/g, higher than other graphene-based adsorbents. The process was spontaneous in nature and physisorption occurred in the process. Fan et al. (2017) used pristine graphene for the adsorption of chlorophenols and the uptake capacities for 2-chlorophenol (2-CP), 4-chlorophenol

Table 3

Adsorption of phenolic pollutants in aqueous solution using graphene-based adsorbents.

Adsorbent	Adsorbate	Maximum capacity (mg/g)	Conc. (mg/L)	pH	Time (min)	Temp. (°C)	Isotherm model	Ref.
rGO-MNPs	BPA	125	20	6	90	25	Langmuir	(Zhang et al., 2014)
MMIP	BPA	106.38	100	6	5	25	Langmuir	(Wang et al., 2016)
M-DF-RGO	2,4-DCP	130	300	6	30	25	Freundlich	(Shen et al., 2018)
rGO-CD	BPA	346	15	7	300	25	Langmuir	(Sun et al., 2019)
Cu-BDC@GO	BPA	182.2	200	4	30		Freundlich	(Ahsan et al., 2019)
3D GO	4-CP	237.7	20	5	60	25	Freundlich	(Wang et al., 2019)
GO-PANI/Fe ₃ O ₄	BPA	31.80	100	3	60		Langmuir	(Rekos et al., 2019)
GO-PVPP	2,4,6-TCP	466.77	200	4	100	30.15	Freundlich	(Lv and Li, 2020)
GO-Fe ₃ O ₄ /PRd	β -naphthol	226.2	45	7	25	40	Freundlich	(Parvin et al., 2020)
GO-Fe ₃ O ₄ /PRd	Phenol	191	45	7	25	40	Freundlich	(Parvin et al., 2020)
NRGO	2-MAQ	9.29	1	7		25	Freundlich	(Song et al., 2021)
nZVI-GO-Cu	BPA	21.59	10	7	10	35	Langmuir	(Yousefinia et al., 2021)
RGO- β CD-ECH	2-CP	674.155	300	7	60	25	Langmuir	(Rout and Jena, 2022d)
RGO	Phenol	602.41	300	8	75	30	Langmuir	(Rout and Jena, 2022e)
CS-PANI@GO	Phenol	198.254	300	7	45	30	Langmuir	(Rout and Jena, 2022h)

(4-CP), 2,4-dichlorophenol (2,4-DCP), and 2,4,6-trichlorophenol (2,4,6-TCP) were 88.1, 114.2, 155.3, and 175.8, mg/g, respectively. The authors found that Langmuir and PSO models were the best-fitted models. The sorption process was endothermic and spontaneous.

Shen et al. (2018) used magnetite/diazonium functionalized-rGO composite for the removal of chlorophenols. The maximum uptake of M-DF-RGO for 2,4-DCP and 4-CP were 127.33 and 55.09 mg/g, respectively, at pH 6. The intermolecular attractions between adsorbate and adsorbent such as H-bonding and π - π interactions were operative in this sorption process and the surface of adsorbent was heterogeneous. The spent adsorbent was easily isolated from the solution by an external magnetic field and, after five regeneration cycles, the removal was still 80 %. Sun et al. (2019) assembled β -cyclodextrin with reduced graphene oxide to

synthesize a novel 3D adsorbent to remove BPA from an aqueous solution efficiently. The maximum adsorption capacity was 346 mg/g at pH 7. The Langmuir isotherm model was the best-fitted model, suggesting monolayer adsorption. The authors claimed that the π - π interaction, host-guest complexes, hydrogen bonding, and pore preservation were the main mechanisms for adsorption (Fig. 5).

Ahsan et al. (2019) synthesized a hybrid nanocomposite consist of metal-organic and graphene oxide for the adsorption of BPA from water. The maximum uptake for this composite was 182.2 mg/g at pH 7. The main mechanism of this adsorption process was the π - π interaction between the π -electrons of benzene ring of BPA and the π -electrons of composite. Wang et al. (2019) prepared a 3D graphene for the adsorptive removal of 4-CP and the data obeyed by Freundlich isotherm model,

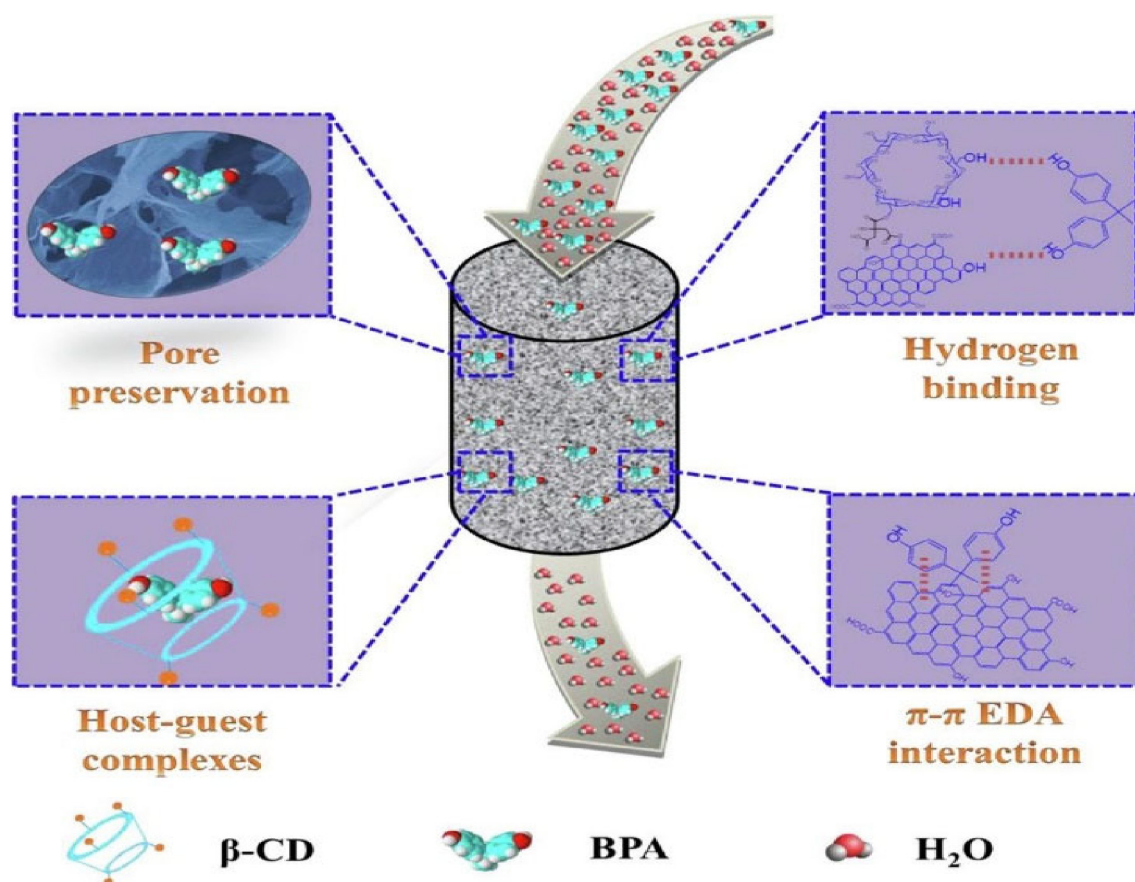


Fig. 5. Adsorption mechanism of BPA onto r-GO-CD (Sun et al., 2019).

suggesting a heterogeneous surface structure. The maximum uptake was 237.7 mg/g, and the regeneration study showed that, after five cycles, the removal was still 90.3 %. The adsorption mechanism was demonstrated by electrostatic attraction, H-bonding, hydrophobic effect, the synergy of heteroatom, and π - π interactions between 3D GO and 4-CP (Fig. 6). Rekos et al. (2019) utilized GO-PANI/Fe₃O₄, a graphene-based magnetic composite for adsorption of BPA with capacity of 31.80 at pH 3.0. The main mechanism for adsorption were (i) H-bonding between benzene rings of BPA and oxygenated functional groups of the composite and (ii) the π - π interactions between π electrons of benzene rings present in BPA and the π electrons of graphene oxide.

Graphene Oxide–crosspolyvinylpyrrolidone (GO–PVPP) hybrid microspheres was synthesized to remove 2,4,6-TCP efficiently (Lv and Li, 2020). The sorption equilibrium data were well followed Freundlich isotherm model, which suggests multilayer adsorption. The kinetic data followed PSO model, by which the authors claimed that chemisorption occurs in the process. The maximum capacity of the adsorbent was 466.77, which showed the high adsorption capacity of this adsorbent. The process was spontaneous and endothermic in nature. The formation of π - π interaction and H-bonds between 2,4,6-TCP and GO–PVPP were critical to the adsorption process. Karamipour et al. (2021) utilized MOF/GO composite for phenol adsorption from an aqueous solution with maximum uptake of 212.76 mg/g. The equilibrium data obeyed PSO kinetic model and Langmuir isotherm models. The adsorbent was also used for real water samples and the results showed that 98 % phenol removal occurs. Nitrogen-doped reduced graphene oxide, as a new adsorbent, was synthesized for adsorption of phenol and p-nitrophenol (Zhao et al., 2021). Langmuir isotherm and PSO kinetic model perfectly fits the experimental data with maximum uptake of 155.82 and 80.60 mg/g for phenol and p-nitrophenol, respectively, at pH 6. The regeneration study showed excellent results, with above 80 % removal after five cycles.

The reduced form of graphene oxide was recruited as a sorbent for phenol removal and the sorption capacity was 602.41 mg/g at neutral pH and room temperature (25 °C) (Rout and Jena, 2022e). It was observed that the adsorption performance was enhanced by the reduction of GO. The π - π interactions and electrostatic attraction were the main driving force for adsorption. The regeneration study shows that the phenol removal remained at 78.3 % after five cycles. Ranjan Rout and Mohan Jena (2022) have synthesized a new adsorbent which consists of reduced graphene oxide modified epichlorohydrin cross-linked beta-cyclodextrin (RGO- β CD-ECH) composite for the sorption of phenolic compounds, such as 2-CP, phenol, and 2,4-DCP (Rout and Jena, 2022d). The authors reported that the maximum uptake of this composite for these phenolic pollutants was 674.155, 659.475, and 702.853 mg/g, respectively. The modification of β CD could

enhance the adsorption capacity as it forms host-guest inclusion complex with the phenolic pollutants. The π - π interaction, electrostatic attraction, hydrogen bonding, and host-guest inclusion complexes were the main driving force for adsorption (Fig. 7). The equilibrium adsorption time was 60 min and, at pH 7, maximum adsorption and performance occur. After five cycles of regeneration, 73.98, 79.85, and 77.45 % removal was achieved for phenol, 2,4-DCP, and 2-CP, respectively. For a quick look, the adsorption data of various graphene-based sorbents for the adsorption of phenolic pollutants are summarized in Table 4.

3.1.2. Adsorption of synthetic dyes using graphene-based adsorbents

Water pollution due to contamination with dyes is the most serious concern in today's world. Many processing units in leather treatment, plastic, pulp and paper, textile, food, pharmaceutical, and paint industries exploit a considerable amount of dye and discharge the effluents containing dyes into environmental ecosystems (Rout and Jena, 2022c). In the dye processing industry, the dye is introduced at various manufacturing stages and unwanted environmental and human contact is possible. The presence of dyes in water bodies prevents the light from passing, reducing the photosynthesis process of aquatic plants and the dissolved oxygen levels in the waters. Therefore, quick treatments, efficient, and cost-effective methods are required to eliminate the dyes before releasing them into the water. The key impact of dyes in the environment are death of microorganisms in soil and staining of water bodies, thus removing dyes from the industrial effluent is of paramount importance. Several treatment technologies have been employed to process these environmental toxic effluents, including solvent extraction, reverse osmosis, membrane separation, and coagulation-flocculation (Mezohegyi et al., 2012). Some authors used graphene-based adsorbents for adsorption of dyes from waters. This section describes the works of various authors already published for sorption of dyes utilizing graphene-based substances.

Table 4 summarizes the experimental conditions, adsorption capacity, and isotherm models of various graphene-, GO-, and rGO-based composites modified by metal oxides, polymers, and organic-inorganic compounds for the adsorption of dyes. Most of the dyes follow the Langmuir isotherm model, PSO model, intra-particle diffusion mechanism, and endothermic process. Sarkar et al. (2014) prepared amine-functionalized rGO–carbon nanotube hybrid as an efficient adsorbent and exploited it for MV and MO uptake, which showed sorption capacity of 298 and 294 mg/g for these dyes, respectively. The authors reported that Langmuir and PSO models were the best-fitted models. The authors recycled the spent adsorbent and again used for adsorption and claimed that after five cycles the removal of MV remains the same whereas the removal of MO drops from 99.76 to 99.6 %. Lai et al. (2020) developed an eco-friendly three-

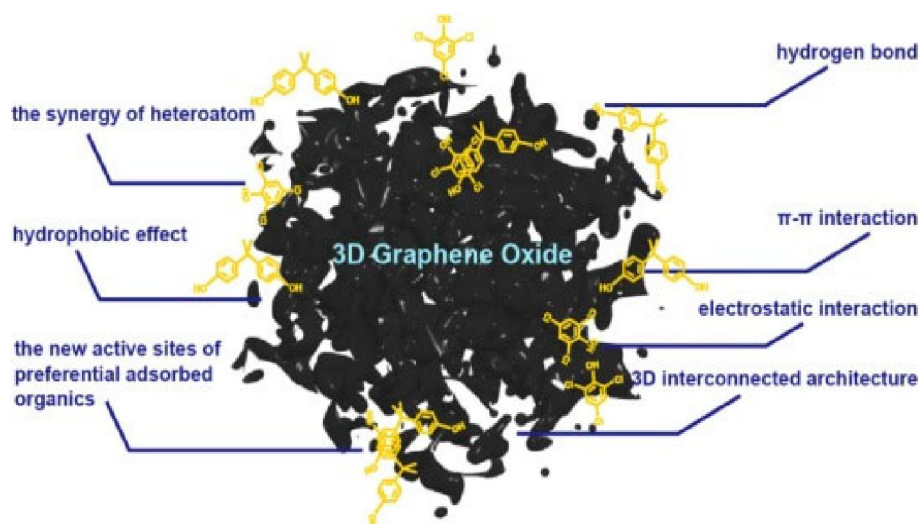


Fig. 6. Multiple factors for phenolic compounds immobilization on 3D GO (Wang et al., 2019).

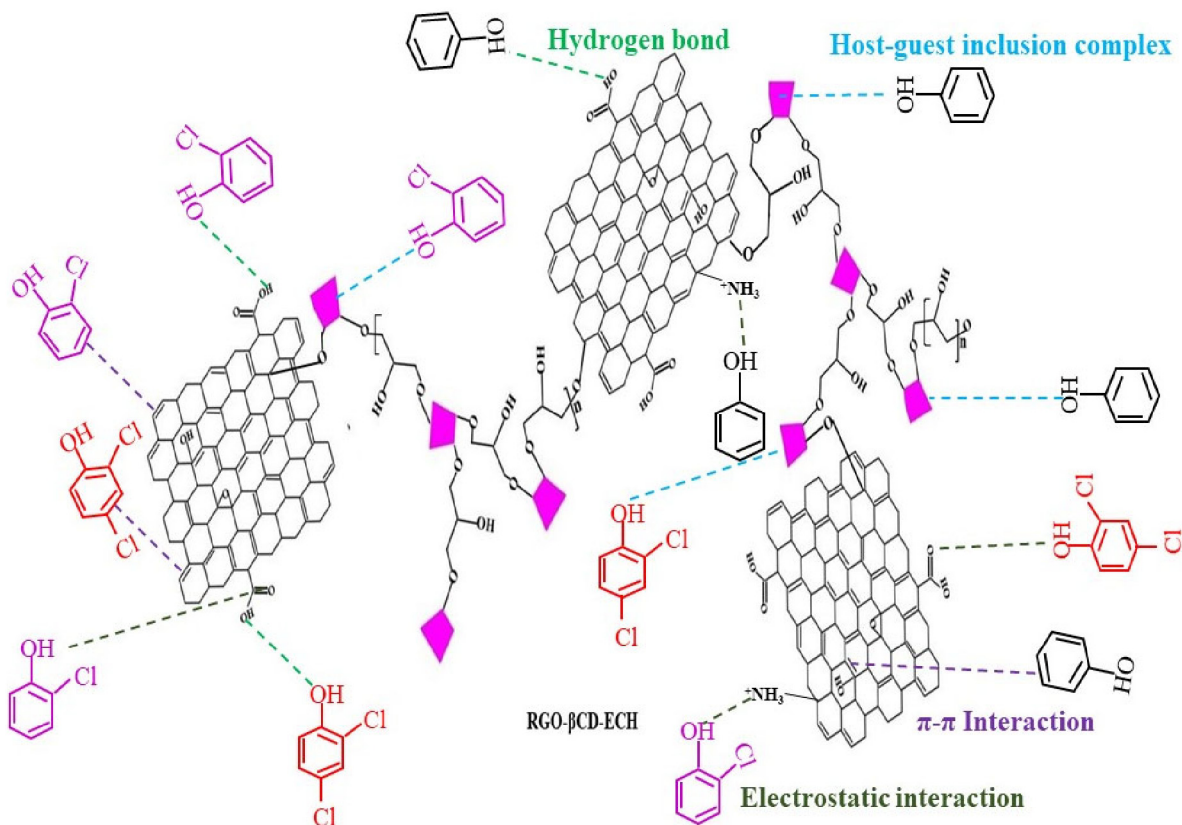


Fig. 7. Schematic diagram proposed mechanism for removal of phenolic compounds (Rout and Jena, 2022d).

dimensional graphene-oxide chitosan adsorbent for uptake of RB5 from waters, with maximum uptake of 638.93 mg/g, within 10 min only. The authors claimed that the main mechanisms were π - π and electrostatic interactions. Rong et al. (2020) have synthesized 3D magnetic sulfur/nitrogen co-doped RGO nanohybrid as an effective adsorbent for removing of neutral, cationic, and anionic dyes such as NR, CR, and MB dyes. The uptakes of these dyes were 877.19, 909.09, and 171.53 mg/g, respectively, and the equilibrium time was only 15 min. The sorption data obeyed Langmuir isotherm. The adsorption-desorption experiments were performed

using ethanol as an ideal eluting agent and the authors claimed that after 6th cycle, the adsorption capacity is 86 % of the initial amount.

Adel et al. (2021) have assembled GO and MgFe_2O_4 via electrostatic interactions to form a magnetically separable and recycled novel adsorbent for MB uptake in water, with 24.81 mg/g uptake, in just 10 min of adsorption. The adsorption process was endothermic and positive entropy value suggested random arrangements of MB dye on the adsorbent surface. The authors reported that, by using an external magnet, the adsorbent could be easily separated. After five consecutive sorption cycles, the sorbent

Table 4

Sorption of dyes from aqueous solution utilizing graphene-based adsorbents.

Adsorbent	Adsorbate	Maximum capacity (mg/g)	Conc. (mg/L)	pH	Time (min)	Temp. (°C)	Isotherm model	Ref.
EG	MB	511.7	500	10	10	30	Langmuir	(Xue et al., 2016)
PAN/ β -CD/GO	CV	16.47	100		10	25	Langmuir	(Abd-Elhamid et al., 2019a)
GO-AC	MB	147	60	12	40	50	Langmuir	(Abd-Elhamid et al., 2019b)
rGO- Co_3O_4	IB	794	60		480	25	Langmuir	(Assis et al., 2020)
mCS/GO-QAS	BB4	650	600	6	30	25	Temkin	(de Figueiredo Neves et al., 2020)
SA/GO@ Fe_3O_4 /CS	MB	21.325	30	7	180		Langmuir	(Ma et al., 2021)
MCS/GO-PEI	Amarnath	93.81	100	5	8		Langmuir	(Li et al., 2021)
MCS/GO-PEI	CR	162.07	100	5	10		Langmuir	(Li et al., 2021)
SA/GO@ Fe_3O_4 /CS	MB	21.325	30	7	60	25		(Ma et al., 2021)
CN/GO	RhB	917.78	400	6	360	25	Freundlich	(Martins et al., 2021)
NiFe_2O_4 @GO	MB	76.34	100	7	60	30	Langmuir	(Bayantong et al., 2021)
COPYGO	MB	663.018	400	7.2	120	50	Langmuir	(Anuma et al., 2021)
COPYGO	CR	659.056	400	5	120	50	Langmuir	(Anuma et al., 2021)
P(AAm-IA)/GO-PEI	CV	774.46	150	7	30	25	Freundlich	(Tamer et al., 2021)
CD-GAM	RhB	388	400		10		Langmuir	(Nie et al., 2021)
GO- $\text{S-LazO}_2(\text{CO}_3)$	MG	555.5		4	30	30	Freundlich	(Eftekhari et al., 2022)
SA-GO	Tatrazine	420.363	50		60	23	Langmuir	(Lentz et al., 2022)
RGO- β CD-ECH	MG	902.125	500	8	90	30	Langmuir	(Rout and Jena, 2022c)
APG	MB	821.05	250	7	65	40	Langmuir	(Deb et al., 2022)
PVA/PHPAm/GO	MB	714.8	200	7	180	30	Langmuir	(Rahmatpour et al., 2022)
GO-MF	RhB	233.22	150	6	180	25	Langmuir	(Vo and Vo, 2022)
α - MnO_2 NRs/GO-Chitosan	MB	328.9	200	7	24	25	Langmuir	(Rajendiran et al., 2022)

retains 75 % of its reactivity on dye molecules. Nie et al. (2021) reported cyclodextrin self-assembled graphene oxide aerogel microsphere and used for uptake of RhB, MB, and MO dye from waters, with respectively 388, 439, and 167 mg/g uptake capacities within 10 min only. The data followed Langmuir and PSO models. The authors recycled the used adsorbent using 1 w% NaOH for anionic dyes and 1 w% HCl for cationic dyes and reported that >80 % removal was achieved after five cycles. The authors claimed the sorption mechanism was due to π - π interactions, supramolecular interaction, and host-guest mechanism between dye and adsorbent (Fig. 8).

Martins et al. (2021) prepared carbon nitride/graphene oxide nanocomposite as an effective adsorbent for removal of basic RhB dye, with 917.78 mg/g uptake. The data follows Freundlich isotherm and PSO kinetic, which suggests that multilayered adsorption and chemisorption occurred in the process, as the authors claimed. After recycling three times with ethanol, the adsorbent had the possibility to confer 90 % removal. The authors reported that the main mechanisms were an electrostatic attraction and π - π interactions between the negatively charged adsorbent and the positively charged RhB dye. Anuma et al. (2021) utilized polypyrrole functionalized cobalt oxide graphene composite for MB and CR removal. The data obeyed Langmuir model and the uptake was 663.018 and 659.056 mg/g for MB and CR, respectively. Spontaneous and endothermic adsorption occurred for both pollutants. After five cycles of regeneration with ethanol and 0.5 M NaOH, the adsorbent still removed 89 and 90.1 % for MB and CR, respectively. The researchers claimed that the adsorption process was chemisorption. The authors also used this adsorbent for real wastewater

and reported that the removal was lower than the single-component system because of the existent of various organic, inorganic, and impurities present in the real wastewaters, which competes for adsorption.

Rajendiran et al. (2022) fabricated a novel composite consisting of graphene-oxide grafted chitosan with MnO₂ nanorods decorated on it to effectively remove toxic MB dye. The maximum uptake was 328.9 at pH 7, and the equilibrium time was 24 min. Electrostatic interactions between negatively charged MnO₂NRs and the positively charged MB dye and π - π electron acceptor-donor interactions enhances the adsorption. The maximum sorption capacity of methylene blue (MB) dye onto PVA/PHPAm/GO nanocomposite hydrogel was 714.8 mg/g, at neutral pH 7, 30 °C temperature, and 200 mg/L initial concentration. The adsorption was endothermic and spontaneous. The authors suggests that dipole-dipole hydrogen bonding, π - π interaction, and electrostatic attraction were the main driving force for adsorption (Fig. 9). After five cycles of regeneration using HCl solution as an eluting agent, the removal was still 70 % (Rahmatpour et al., 2022). Mensah et al. (2022) utilized a novel nano-ferromagnetic activated graphene adsorbent for MB dye adsorption and the results revealed that the uptake capacity was 348.30 mg/g in only 40-min adsorption period. The process was endothermic and the physical adsorption occurred as the value of enthalpy was <40 kJ/mol. Also, after five adsorption cycles, 79.75 % removal was still achieved.

Vo and Vo (2022) synthesized a novel graphene oxide-covered melamine foam adsorbent to efficiently remove CR, MB, MO, and RhB from wastewater with the uptake of 184.93, 258.56, 206.92, and 233.22 mg/g,

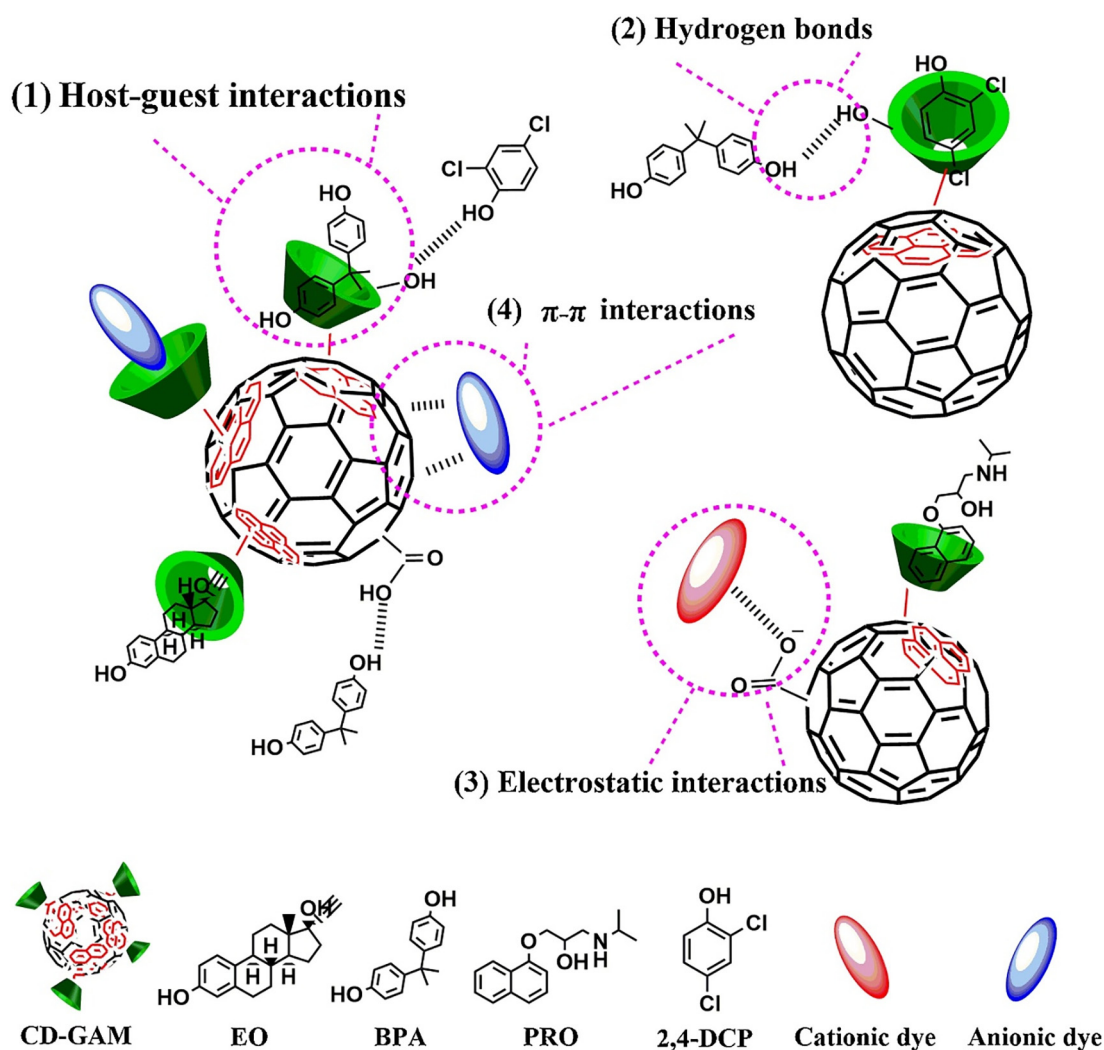


Fig. 8. Schematic illustrating of the adsorption mechanisms of CD-GAM for dyes and organic micro pollutants (Nie et al., 2021).

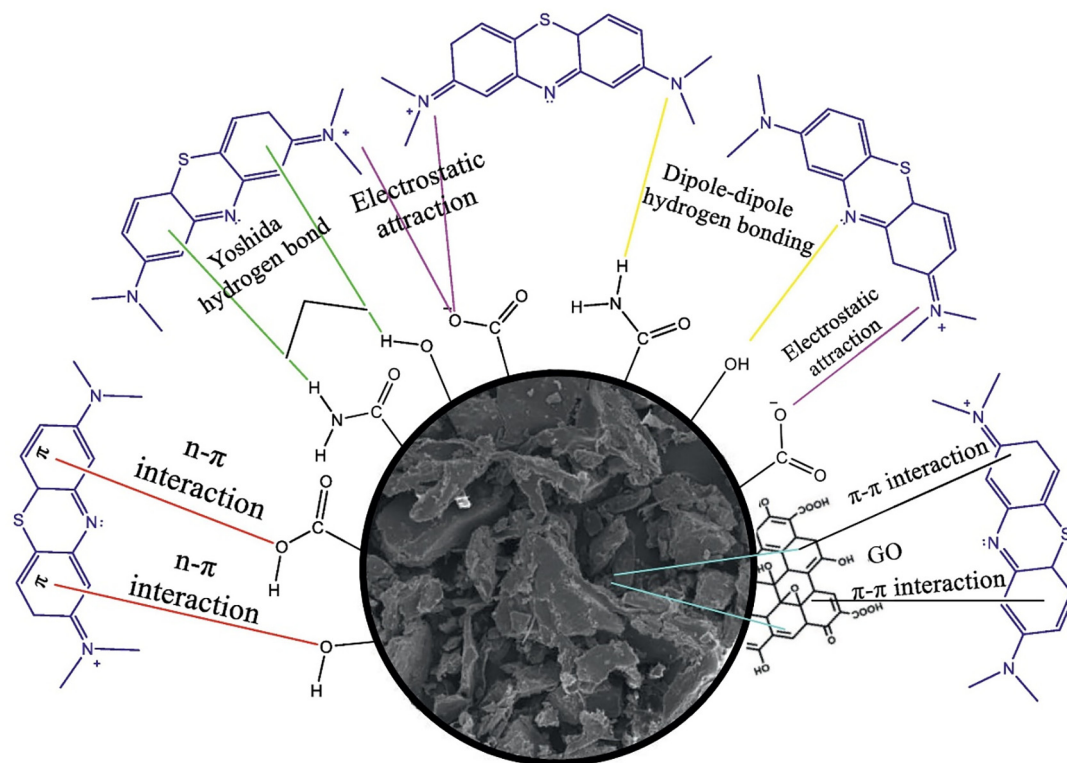


Fig. 9. Schematic illustration of MB adsorption mechanism by the PVA/PHPAm/GO semi-IPN nanocomposite hydrogel (Rahmatpour et al., 2022).

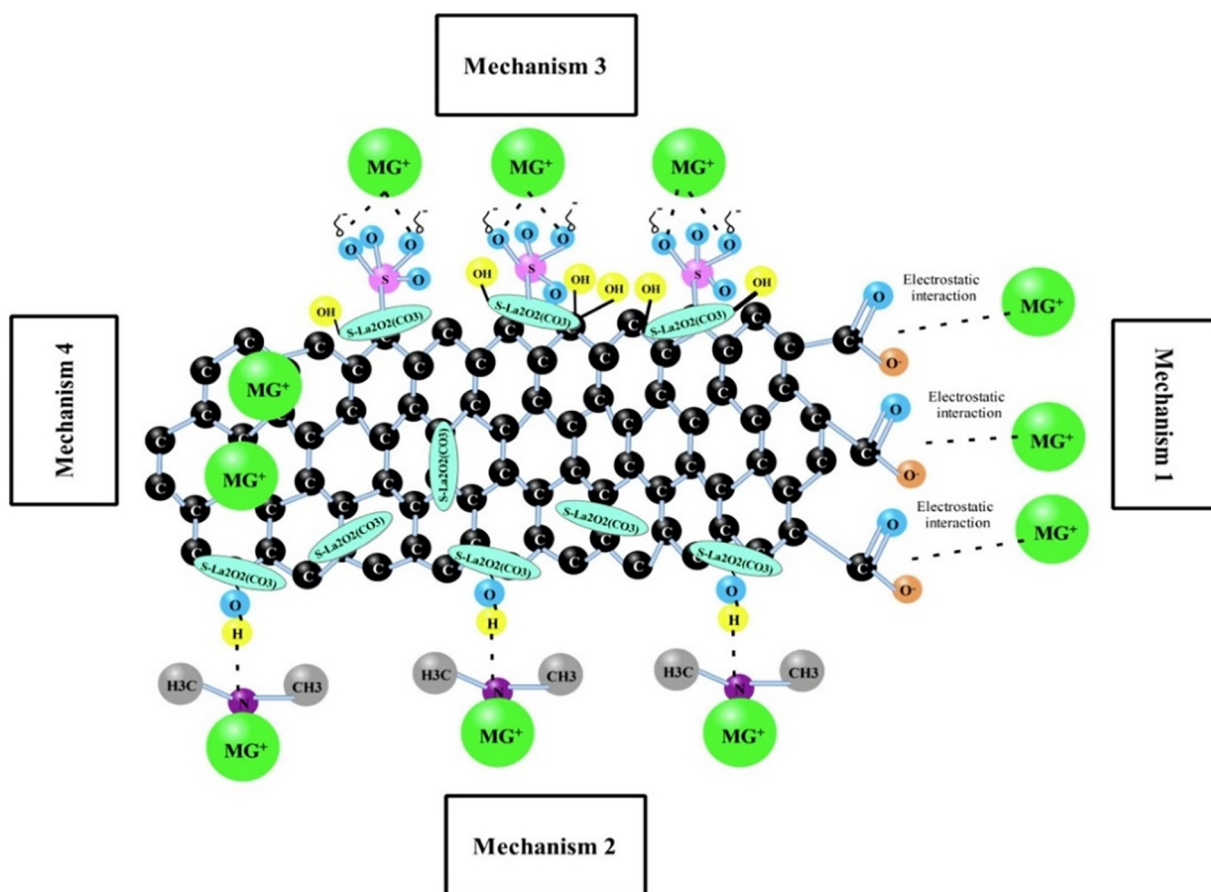


Fig. 10. Mechanism of interaction between MG with GO-S-La₂O₂(CO₃) nanocomposite (Eftekhari et al., 2022).

respectively. After seven adsorption-desorption cycles using ethanol as the eluting agent, the removal for MB, CR, MO, and RhB were 94, 88, 76, and 71.3 %, respectively, suggesting adsorbent stability. Eftekhari et al. (2022) have synthesized a novel graphene oxide-sulfated lanthanum oxy-carbonate sorbent for MG dye removal from water. The adsorption followed the Freundlich model, vouchsafing heterostructure of the adsorbent, maximum uptake was 555.5 mg/g, and film diffusion was the rate-controlling stage. The mechanism of interaction between MG and GO-S-La₂O₂(CO₃) were illustrated in Fig. 10. Rout and Jena (2022a) synthesized a new composite consisting of RGO-supported beta-cyclodextrin cross-linked with epichlorohydrin for the uptake of MG dye (902.125 mg/g). The sorption was an endothermic, spontaneous, and chemisorption process, as the authors claimed. The data obeyed Langmuir isotherm, which vouchsafes monolayer sorption on the adsorbent surface. The authors also used a fixed-bed column study to uptake MG dye. The adsorbent was recycled by using low boiling solvent methanol or ethanol as an eluting agent and after five cycles, 90.3 % removal was still achievable. The authors claimed that the synthesized adsorbent could be a new proposing candidate for real wastewater treatment. The authors reported that the main mechanisms for MG dye uptake were host-guest inclusion complex, H-bonding, electrostatic attraction, and π - π interaction.

3.1.3. Graphene-based adsorbents for the sorption of organic pollutants

Beside the above-mentioned phenols and dyes, numerous other organic pollutants like pharmaceuticals, aromatic compounds, pesticides, herbicides, and antibiotics have also been removed from water using graphene-based adsorbents. These pollutants are the outcomes of the pharmaceutical industry, coking industry, agrochemical manufacturing units, agricultural land, and other industrial activities. These pollutants are carcinogenic and very toxic in nature and affect the endocrine system and physicochemical properties of water (Lawal et al., 2020). This section describes the works of various authors already published, which exploit the graphene-based composites as sorbents for removal of other organic pollutants.

A water-stable graphene oxide-based composite consisting of graphene oxide, activated carbon, and chitosan was synthesized for the adsorption of acetaminophen (ACP), carbamazepine (CBZ), BPA, caffeine (CAFF), and triclosan (TCS) from water (Delhiraja et al., 2019). The maximum uptake of these pollutants was 137.7, 11.2, 13.25, 14.8, and 14.5 mg/g, respectively, and the Langmuir model best fitted the isotherms. The authors reported that, by using a polar solvent (methanol), desorption of CAFF, BPA, and ACP was achieved 70–80 %, whereas by using nonpolar solvent (hexane), 60 % desorption was achieved for CBZ and TCS. Lawal et al. (2020) synthesized a noncovalent graphene oxide composite functionalized with ionic liquid 1-hexyl 3-decahexyl imidazolium for the uptake of sulfamethoxazole (SMZ), carbamazepine (CBZ), and ketoprofen (KET). The uptake capacities were 89.847, 58.54, and 84.172 mg/g within just 10 min of adsorption. The sorption data followed the Langmuir model, suggesting monolayer type of adsorption took place in the process. The authors claimed that after seven cycles of desorption using ethanol as eluting agent, the removal percentage reduced to 75, 63, and 58 % for SMZ, KET, and CBZ, respectively.

Moradi et al. (2022) utilized a ternary composite consisting of maltodextrin/reduced graphene oxide/copper oxide to remove pharmaceuticals such as diclofenac and amoxicillin with uptake capacity of 12.836 and 12.903 mg/g, respectively. A new magnetically separable adsorbent with Fe₃O₄ and AE co-modified graphene (MAEGO) was synthesized to remove tetracycline, levofloxacin, MB, and MO, having an uptake capacity of 315.25, 229.53, 500, and 257.14 mg/g, respectively (Lin et al., 2021). The data obeyed the PSO and Langmuir model, which suggests that chemisorption and monolayer adsorption occur in the process, as the authors claimed. The authors also recycled the adsorbent by using 1 M NaOH as an eluting agent, and reported reduction of adsorption capacity for TC from 305.9 to 226.7 mg/g. A novel magnetic nano adsorbent (GO- α -Fe₂O₃Co₃O₄) was synthesized by the utilization of iron and cobalt nanoparticles combined with GO for adsorption of a pharmaceutical pollutant, caffeine, from water (Andrade et al., 2022). The maximum uptake of caffeine

was 28.94 mg/g for 10 mg/L initial concentration. The process was spontaneous, exothermic, and thermodynamically favorable. The author claimed that the main mechanism for adsorption was hydrogen bonds between nitrogen atoms of amino groups of the caffeine molecule with the hydrogen atoms of -OH groups of GO, and the π - π interaction between cobalt, iron, and GO molecules with the π electrons of caffeine molecules (Fig. 11). Xiong et al. (2022) fabricated a recyclable, robust, and versatile biochar graphene oxide composite as a sorbent for the efficient removal of doxycycline from waters. The maximum uptake of the composite was 796.8 mg/g and the sorption data obeyed the Langmuir isotherm model. The authors reported that electrostatic attraction, hydrogen bondings, and π - π stacking were the main mechanism for adsorption of doxycycline onto BC-GO composite.

Januário et al. (2022) synthesized a novel activated carbon functionalized with graphene oxide (BC-GO) adsorbent for adsorptive removal of COVID-19 treatment drugs, such as dipyrone and chloroquine, from water. The maximum uptake of these drugs using BC-GO adsorbent was 62.43 and 37.65 mg/g. The adsorption data obeyed the Langmuir isotherm model and the adsorption process was endothermic. The authors also used this adsorbent for real wastewater and reported that 81.9 % removal was achieved. The authors suggest that, because of the ionic and pH effects, π - π interactions and H-bonding govern the adsorption process (Fig. 12). Neves et al. (2022) prepared a new membrane consisting of hydrolyzed polyacrylonitrile containing GO modified with safranin for uptake of propanol drug with uptake capacity 200.6 mg/g. The adsorption data followed the Freundlich model, which suggested multilayer adsorption and heterogeneous surface. The authors reported that π - π interactions, cation exchange, and electrostatic interactions govern the adsorption process.

M. Liu et al. (2022) utilized magnetic chitosan GO composite adsorbent for sulfosalicylic acid removal from an aqueous solution. The adsorption was exothermic, spontaneous, and entropy-driven process. The adsorbent was recycled using 0.01 mol/L NaOH solution and 96.9 % removal was achieved after three cycles. The proposed mechanisms were complexation, H-bonding, π - π interactions, and electrostatic interactions. Feng et al. (2022) fabricated a novel adsorbent consisting of beta-cyclodextrin immobilized rGO and multiwall carbon nanotubes for efficient removal of naproxen from aquatic environments. The data followed the Freundlich isotherm model, suggesting multilayer adsorption; the maximum uptake was 132.09 mg/g. The authors suggested that the mechanism for adsorption of naproxen was host-guest inclusion complex between cavities of beta-cyclodextrin and naproxen, hydrophobic interaction between adsorbent and naproxen, electrostatic interaction, H-bonding and π - π interactions. Tian et al. (2021) utilized graphene oxide aerogels for the uptake of perfluorooctanoic acid (PFOA) in water, with a 1575 mg/g uptake capacity. The Freundlich model perfectly followed the process, suggesting a heterogeneous adsorbent surface. For a quick look, the adsorption of various organic pollutants is summarized in Table 5.

3.2. Use of graphene-based adsorbents for adsorption of heavy metals

Many surface water and groundwater resources are polluted by various heavy metal ions such as Fe, Cr, Pb, Hg, Ni, Cd, Cu, and As due to the continuous discharges of these pollutants from various industries like metal plating, painting, mining, tanneries, smelting, automobile manufacturing, petroleum refineries, etc. When these metal ions surpass the acceptable level, they elicit various health-related effects on humans, and they are not suitable for aquatic organisms. Graphene, the new-generation material, has been used regularly to remove heavy metals from wastewaters. This section describes the works of various authors already published for heavy metals removals using graphene-based adsorbents.

Madadrang et al. (2012) introduced N-(trimethoxysilylpropyl) ethylene diamine triacetic acid (EDTA-silane) chelating groups to GO for uptake of Pb(II) from waters. The maximum capacity was 525 mg/g and the experimental data followed PSO kinetics and Langmuir isotherm model. Kumar et al. (2014) synthesized a magnetic graphene oxide nanohybrid (GO-MnFe₂O₄) by coprecipitation technique for enhanced uptake of Pb(II), As

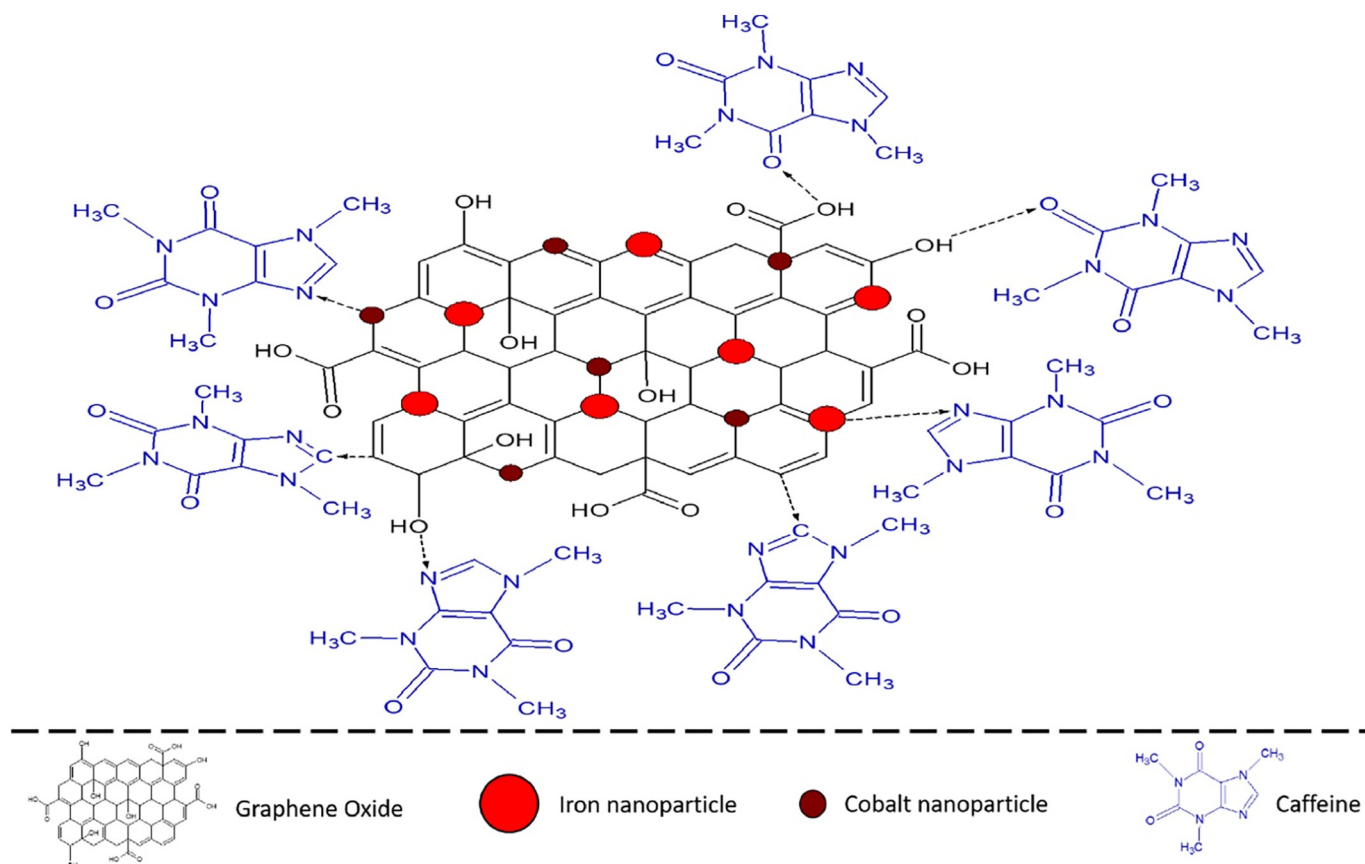


Fig. 11. Proposed caffeine adsorption mechanism by GO# α -Fe₂O₃Co₃O₄ (Andrade et al., 2022).

(V), and As(III) in water. The uptake process was pH-, temperature-, and concentration-dependent, with maximum uptake obtained at pH 5 for Pb (II), pH 4 for As(V), and pH 5 for As(III). The experimental uptake data perfectly fitted with PSO and Langmuir model with maximum uptake of 673, 207, and 146 mg/g for Pb(II), As(V), and As(III), respectively. The sorption process was endothermic and spontaneous. The authors claimed that the

main mechanisms for adsorption were cation exchange reaction between Pb(II) ions and the surface functional moieties of GO such as —OH and —COOH at optimum pH and the reactions are given below:

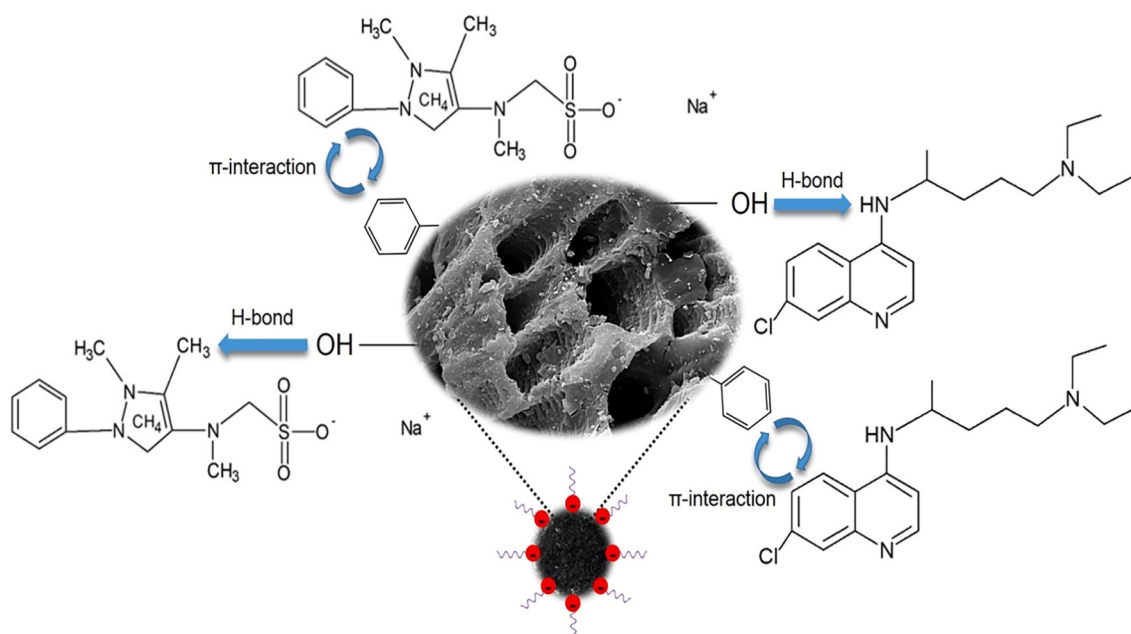


Fig. 12. Possible interaction mechanisms between the B-rGO and the oxytetracycline (Januário et al., 2022).

Table 5

Sorption of various organic pollutants by graphene-based substances.

Adsorbent	Adsorbate	Maximum capacity (mg/g)	Conc. (mg/L)	pH	Time (min)	Temp. (°C)	Isotherm model	Ref.
GO-IL	SMZ	89.847	200	6	10	25	Langmuir	(Lawal et al., 2020)
GO-IL	KET	84.172	200	8	10	25	Langmuir	(Lawal et al., 2020)
GO-IL	CBZ	58.54	200	7	10	25	Langmuir	(Lawal et al., 2020)
GO/g-C ₃ N ₄ -Fe ₃ O ₄	TC	120	300	3	300	50	Langmuir	(Sahoo et al., 2020)
CNTs/L-cys@GO/SA	Ciprofloxacin	200	400	6		15	Langmuir	(Ma et al., 2020)
rGO/CNC	Toluene	454.54	150	7	30	25	Langmuir	(Shadkam et al., 2021)
B-rGO	Oxytetracycline	130.4	50	5	60	20	Freundlich	(El Hadki et al., 2021)
AGO	PFOA	1575	1000	1.6	120	25	Freundlich	(Tian et al., 2021)
GAC-GO	Chloroquine	37.65	100	6	1080	35	Langmuir	(Januário et al., 2022)
Fe-MCG	SSA	135	200	2.9	50	20	Langmuir	(M. Liu et al., 2022)
β-CD/rGO-MWCNTs	Naproxen	132.09	80	6	600	40	Freundlich	(Feng et al., 2022)



The M presents Fe or Mn in the composite, and the complexation between metal ions and functional moieties was responsible for sorption of Pb(II) ions onto the composite and the reactions were:



The authors reported that, with an increasing in pH from acidic to basic medium, the discharge of proton starts from —COOH and —OH groups present on the composite surface and, as a result, the sorption of Pb²⁺ ions starts enhancing. However, as the pH exceeds 5, the Pb²⁺ reacts with —OH groups of the solution to form Pb(OH)₂ precipitate, suppressing the adsorption process.

Lingamdinne et al. (2016) synthesized an inverse spinel nickel ferrite with graphene oxide as a base material (GONF) for Pb(II) and Cr(III) adsorption in an aqueous solution. The removal of Pb(II) and Cr(III) were increased with pH up to 5.5 for Pb(II) and 4.0 for Cr(III) and then the adsorbent saturates. It was observed that the isotherm data was obeyed by Langmuir isotherm model for both Pb(II) and Cr(III), with maximum sorption capacity of 25 and 45.5 mg/g, respectively. The results described that the main mechanism for adsorption of these heavy metals were complexation and chemical interactions between metal ions and active functional moieties such as —C—O—, —C—C=C—, and —OH present on the composite along with oxygen present in the Fe—O bond of ferrite. Alizadeh et al. (2017) synthesized a sulfonated magnetic graphene oxide (GO/Fe₃O₄/SO₃H) nanohybrid for uptake of toxic Cr(VI) in waters with sorption capacity of 222.22 mg/g. The optimal conditions were pH 3, contact time 60 min, and temp. 298 K. The Langmuir isotherm model perfectly obeyed the sorption data with endothermic and spontaneous processes. At low pH values, the sulfonate, hydroxyl, and carboxyl moieties existent on the adsorbent surface become positively charged with the help of protons and attract the negatively charged Cr₂O₇²⁻ and HCrO₄⁻ through electrostatic attraction. Also, at low pH, the Cr(VI) starts reducing to form Cr(III) by the electrons present in hydroxyl groups and π-electrons of GO. A new adsorbent was synthesized by grafting 4-sulfophenylazo groups on rGO for the removal of heavy metals in an aqueous solution (Zhang et al., 2018). The isotherm data followed Langmuir model and the maximum uptake for Cd(II), Cr(VI), Pb(II), Cu(II), and Ni(II) was calculated from this model, which were 267, 191, 689, 59, and 66 mg/g, respectively. The authors claimed that the main sorption mechanisms were the ion exchange betwixt heavy metal ions and Na⁺ ions of sorbent and the coordination reaction between N-atoms of sorbent with heavy metal ions.

Park et al. (2019) utilized reduced graphene oxide/magnetite/silver monohybrids for the uptake of toxic heavy metals such as Cu(II), Pb(II), Co(II), Zn(II), Ni(II), and Cd(II) in water. The sorption performance was in the order of Cu(II) > Zn(II) > Ni(II) > Co(II) > Pb(II) > Cd(II). The authors suggest that the main mechanism for adsorptions were surface complexations, ion exchanges, and electrostatic interaction betwixt the metal ions and rGO/magnetite/silver NH composite (Fig. 13). Baruah et al. (2019)

reported a new Ni—Fe layered double hydroxide with N-doped GO sorbent via the coprecipitation method for the adsorption of Pb(II) and Cd(II) ions in water. The maximum sorption capacity for Pb(II) and Cd(II) were 986 and 971 mg/g, respectively. The authors reported that after three cycles of regeneration, using 0.1 mM HCl solution, the adsorbent retained 70 % of the adsorption capacity. Mahmoudi et al. (2020) synthesized GO silica composite for efficient sorption of Cd(II) from aqueous solutions. The equilibrium data followed the Freundlich isotherm model, suggesting heterogeneous surface and multilayer sorption. The maximum uptake estimated from the Langmuir model was 43.35 mg/g, and the sorption was exothermic and spontaneous. The main mechanisms for adsorption of Cd(II) were π-π interaction between the Cd(II) ions and the composite, along with complexation between —OH, —COOH and ketone groups of GO present on the composite with the Cd(II) ions. Chaabane et al. (2020) synthesized functionalized graphene oxide sheets (GO-EDA-CAC-BPED) by using various chemicals for sorption of Cu(II), Ni(II), and Co(II) metals ions from an aqueous solution. The maximum sorption capacities were 220.123, 179.981, and 142.85 mg/g for Cu(II), Ni(II), and Co(II), respectively. Both film and intra-particle diffusion occurs in the adsorption process. The adsorption data followed Freundlich and PSO model. As per the authors' claim, the surface of the adsorbent was heterogeneous in nature, multilayer adsorption occurred in the process, and chemisorption controlled the adsorption. The adsorption process was spontaneous, feasible, and endothermic.

A novel adsorbent was synthesized by incorporating Fe₃O₄ nanoparticles onto graphene oxide modified chitosan composite for efficient removal of Cu(II) and Cr(VI) ions from aqueous solutions (Anush et al., 2020). Maximum uptake capacities were 111.11 and 142.85 mg/g for Cr(VI) and Cu(II), respectively. Langmuir isotherm and PSO were the best-fitted models. The process was spontaneous, endothermic, and randomness occurred at the solid-solution interface. The maximum sorption of Cr(VI) was observed at pH 3, because with an increasing in pH, the concentration of —OH ions in the solution starts to increase, which compete with the Cr(VI) ion for the sorption on the positively charged surface, and as a result, performance decreases. Kong et al. (2020) fabricated a ternary GO-HBP-NH₂-CMC nanocomposite for the adsorption of heavy metals from aqueous solution. Langmuir isotherm model well fitted with experimental adsorption, which suggests a monolayer sorption process. The maximum sorption capacities for Pb²⁺ and Cu²⁺ were 152.86 and 137.48 mg/g, respectively. Both external diffusion and pore diffusion were controlling the sorption process, as the author claimed. The main mechanisms were ion exchange between O-containing groups and metal ions and metallic ion complexation with N-containing groups. A novel composite GO-Si-CS was synthesized by coating silica on GO, then functionalized with chitosan, and used for adsorption of Pb(II) from an aqueous solution (Azizkhani et al., 2020). As the authors claimed, the adsorption followed the Freundlich and PSO models, suggesting a multilayer adsorption and chemisorption process. The maximum uptake capacity calculated from Langmuir model was 256.41 mg/g. The functional moieties existent on the surface of silica, chitosan, GO and π-π interaction were the main parameters for the efficient removal of Pb(II) onto GO-Si-CS.

The capability of polypyrrole functionalized cobalt oxide graphene oxide (COPYGO) composite for the uptake of Pb(II) from aqueous solutions

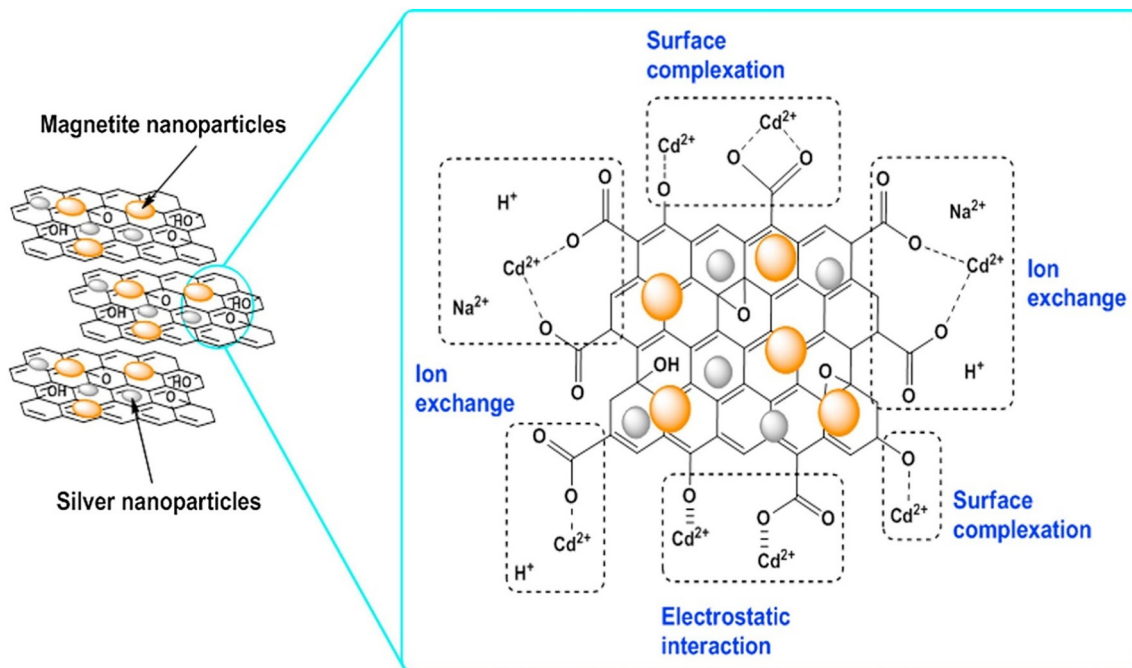


Fig. 13. Proposed adsorption mechanisms for Cd(II) ions on the rGO/magnetite/silver NH sample (Park et al., 2019).

was presented by Anuma et al. (2021). A batchwise sorption experiments were conducted for Pb(II) and Cd(II), which revealed maximum uptake of 780.363 and 794.188 mg/g, respectively. The optimal conditions for batch adsorption were pH 5.5 for Pb(II) and 6.1 for Cd(II), temperature 50 °C, adsorbent dosage 0.33 g/L, and optimum contact times were 250 min for Pb(II) and 150 min for Cd(II). The isotherm data obeyed the Langmuir isotherm and PSO kinetic model, suggesting that monolayer

adsorption and chemisorption occur. From thermodynamic analysis, it was concluded that the above process was spontaneous and endothermic. The authors claimed that electrostatic attraction between negatively charged O and N functional groups existent on the composite surface and positively charged pollutants and the complexation between hydroxyl (—OH) and carboxyl (—COOH) groups and pollutants were responsible for the sorption of Pb(II) onto the sorbent surface (Fig. 14). For acidic pH

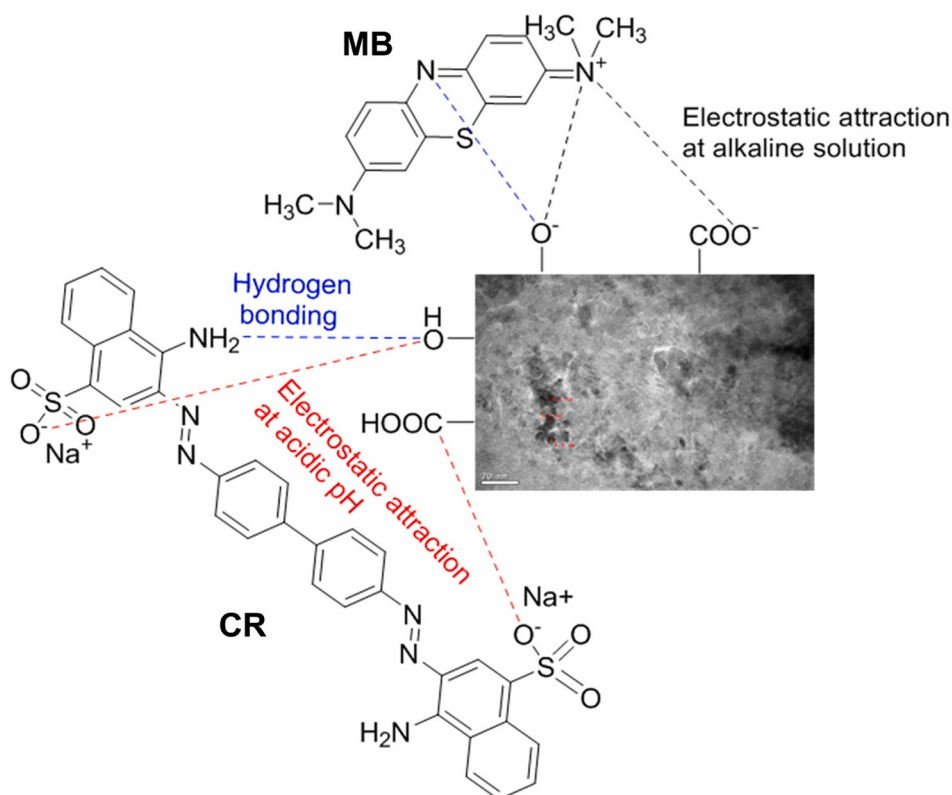


Fig. 14. Proposed mechanism for the pollutants (MB, CR, Pb(II) & Cd(II)) sorption on the COPYGO (Anuma et al., 2021).

values, the adsorption performance was lower as the —OH and —COOH groups of GO on the composite are protonated and become positively charged, and as a result, the adsorbent repels the positive Pb^{2+} ions. As pH increases, the deprotonation starts, which results in the adsorption of more pollutant onto the surface, however for pH above 5.5 and 6.1, the Pb(II) and Cd(II) ions forms Pb(OH)_2 and Cd(OH)_2 precipitates, so the performance of adsorption decreases. Attia et al. (2021) fabricated an antibacterial graphene-polypyrrole composite for uptake of Mn^{2+} in water which was pH-dependent. The Langmuir isotherm model obeyed the adsorption data suggesting monolayer adsorption and the maximum uptake was 56.18 mg/g at a pH of 5.5.

Ranjan Rout and Mohan Jena (2022) synthesized a new graphene-based composite for the uptake of Cr(VI) from aqueous solutions and reported 1321.01 mg/g adsorption capacity at pH 1.0 by using only 5 mg of adsorbent in 50 mL solution having 100 mg/L Cr(VI) concentration. The adsorption data obeyed by Langmuir isotherm and PSO kinetic model. The rate-limiting step of the adsorption was intraparticle diffusion. The sorption was an entropy-driven, spontaneous, and endothermic process. The authors also performed the fixed-bed column study to know the practical applicability of this adsorbent and the results obtained were very satisfactory. The authors reported that after five cycles of regeneration exploiting 1 N NaOH or 1 M HCl solution as an eluting agent, the removal was 89.25 %. The main mechanisms for this adsorption were (i) electrostatic interaction between negatively charged HCrO_4^- , $\text{Cr}_2\text{O}_7^{2-}$, and CrO_4^{2-} ions and positively

charged protonated — COOH^+ and — OH^+ groups, (ii) π - π interaction between graphene network and the pollutants, (iii) host-guest inclusion complex between Cr(VI) ions and βCD molecules, and (iv) reduction of Cr(VI) to Cr(III) (Fig. 15). Z. Liu et al. (2022) prepared and used GO functionalized with polyamide-amine and microcrystalline cellulose to adsorb Cu(II) , Cd(II) , and Pb(II) ions in waters. The maximum uptake of these metal ions were 280.1, 418.4, and 680.3 mg/g for Cu(II) , Cd(II) , and Pb(II) , respectively. The sorption followed Langmuir and PSO models. Good adsorption was due to the chelation or complexation between N and O-containing groups of the sorbent with metal ions. For a quick look, the adsorption data of various graphene-based sorbents for the adsorption of heavy metal ions are summarized in Table 6.

4. Critical consideration of kinetic, equilibrium and thermodynamic studies

4.1. Kinetic consideration of pollutants adsorption by graphene-based materials

Several mathematical relations have been recruited to describe adsorption processes versus contact time. These relations can be categorized into two models: (i) those describing diffusion processes and (ii) those describing reaction models. Both categories of kinetic models have been applied for describing the kinetic processes of adsorption on graphene-based adsorbents. Most of the studies have mentioned that pseudo-second order model

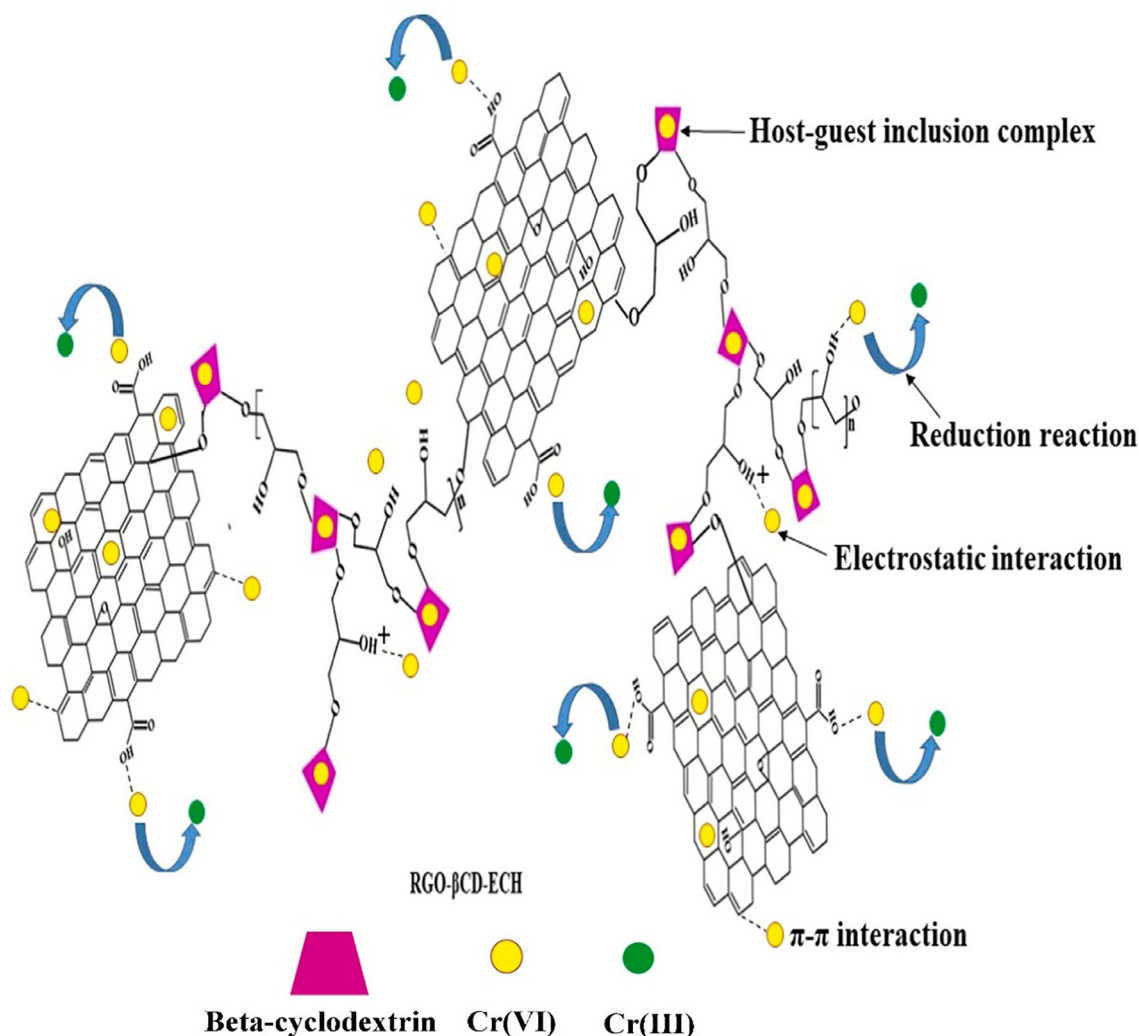


Fig. 15. Schematic mechanism diagram proposed for Cr(VI) removal (Ranjan Rout and Mohan Jena, 2022).

Table 6

Heavy metals adsorption using graphene-based adsorbents.

Adsorbent	Adsorbate	Maximum capacity (mg/g)	Conc. (mg/L)	pH	Time (min)	Temp. (°C)	Isotherm model	Ref.
GONF	Pb(II)	25	25	5.5	120	35	Langmuir	(Lingamdinne et al., 2016)
GO/Fe ₃ O ₄ /SO ₃ H	Cr(VI)	222.22	100	3	240	25	Langmuir	(Alizadeh et al., 2017)
rGO/magnetite/silver NH	Cd(II)	386.806	112	3	30	25	Langmuir	(Park et al., 2019)
NiFe-CO ₃ -LDH-NGO	Pb(II)	986	1000	7	60	25	Langmuir	(Baruah et al., 2019)
NiFe-CO ₃ -LDH-NGO	Cd(II)	971	1000	7	60	25	Langmuir	(Baruah et al., 2019)
SGO	Cd(II)	43.35	120	5	40	40	Freundlich	(Mahmoudi et al., 2020)
SBMGO	Cr(VI)	142.85	100	3	150	30	Langmuir	(Anush et al., 2020)
SBMGO	Cu(II)	111.11	100	6.8	150	30	Langmuir	(Anush et al., 2020)
MnFe ₂ O ₄ /GO	Ni(II)	152.67	350	8	270	25	Langmuir	(Thi Mong Thy et al., 2020)
GO-HBP-NH ₂ -CMC	Pb(II)	137.48	100	5	240	25	Langmuir	(Kong et al., 2020)
GO-HBP-NH ₂ -CMC	Cu(II)	152.86	100	5	240	25	Langmuir	(Kong et al., 2020)
GO-Si-CS	Pb(II)	256.41 ± 4	120	6	60	30	Freundlich	(Azizkhani et al., 2020)
GO/PEI/CMC	Cu(II)	302.04	330	5.5	195	25	Langmuir	(Liu et al., 2020)
MoS ₂ /rGO	Cr(VI)	80.8	200	2	180	25	Sips	(Zhou et al., 2020)
COPYGO	Pb(II)	780.363	500	5.5	250	50	Langmuir	(Anuma et al., 2021)
G-PPy	Mn	56.18	250	5.5	90	25	Langmuir	(Attia et al., 2021)
GOA	Ni(II)	91.74	200	6	120	30	Langmuir	(Huong et al., 2021)
PVA/GO	Sr(II)	20.07	22.16	7	360	25	Freundlich	(Huo et al., 2021)
RGO-βCD-ECH	Cr(VI)	1321.01	300	1	75	30	Langmuir	(Ranjan Rout and Mohan Jena, 2022)
GO/HPAMAM/DAC	Cd(II)	418.4	100	6	150	25	Langmuir	(Z. Liu et al., 2022)
GO/HPAMAM/DAC	Pb(II)	680.3	100	6	150	25	Langmuir	(Z. Liu et al., 2022)

gives the highest goodness-of-fit with the experimental data. The PSO kinetic model is presented as the following mathematical relation:

$$q_t = \frac{q_e^2 \cdot K_2 \cdot t}{[K_2 \cdot (q_e) \cdot t + 1]}$$

where q_t is the adsorption capacity (mg/g) at a of graphene-based adsorbent at any time (t), K_2 (g/mg.min) is the rate constant of PSO model, and q_e (mg/g) is the equilibrium adsorption capacity.

In fact, obeying this model by kinetic data reveals that the graphene-based adsorbents have copious adsorption sites for adsorption of pollutants (Wang and Guo, 2020a). This physical meaning confirms the high potential of graphene-based material for being used as sorbents in waters and wastewater treatment plants.

However, using kinetic studies and goodness-of-fit of data with PSO model, many researchers make erroneous interpretations about the mechanism of adsorption by graphene-based materials. Unfortunately, many authors have claimed that obeying the PSO model by the experimental data shows that a chemisorption process is happening during the adsorption of pollutants onto graphene-based materials. Such interpretation means that the adsorption process is progressed by involving valence forces via sharing electrons between pollutant and adsorbent (Tran et al., 2017), or a chemical bond is elicited between the adsorbent and adsorbate. In fact, drawing such a conclusion from kinetic data is erroneous, and no claim can be made about adsorption mechanism only by simply scrutinizing kinetic behavior. Instead, it should be mentioned that obeying PSO model only shows that interaction between adsorbate and adsorption sites is the rate-controlling step in the adsorption process. On the other hand, many researchers have exploited the linearized equations for kinetic studies of sorption process, using graphene-based adsorbents, which leads to erroneous results and conclusions. Therefore, it should be recommended that, in the future studies, the researchers use the nonlinear fitting of kinetic data, since kinetic equations are typically nonlinear mathematical relations (Lima et al., 2021).

4.2. Equilibrium consideration of pollutants adsorption by graphene-based materials

Isotherm models can provide some information about the adsorption mechanism, and such studies are important for designing adsorption systems for the full-scale industrial treatment plants. Tabulated data of the adsorption systems (Tables 3-6), using graphene-based materials, revealed that most of the studied system obey two isothermal models, i.e. Langmuir

and Freundlich models. The theoretical Langmuir equation assumes that (i) the number of accessible adsorption sites are constant and all of the sites are energetically independent and identical, (ii) when a pollutant molecule or ion is adsorbed on a site, no more molecule or ion can be adsorbed on that site, (iii) adsorption is a reversible process, and (iv) pollutants molecules which have occupied neighbour sites have no interaction with each other (Tran et al., 2017). Langmuir model can be presented by the following mathematical relation:

$$q_e = \frac{Q_{\max}^0 + K_L C_e}{1 + K_L C_e}$$

where $Q_{\max}^0$ (mg/g) is the maximum saturated monolayer sorption capacities of adsorbents, C_e (mg/L) is the concentration of pollutant at equilibrium, q_e (mg/g) is the amount of pollutant uptake at equilibrium, and K_L (L/mg) is a constant related to the affinity betwixt the graphene-based sorbent and the pollutant.

Freundlich model is an empirical isotherm, which is exploited to explain equilibrium data, and adsorption features for heterogeneous surfaces, representing a multilayer sorption process. The nonlinear form of the Freundlich model can be presented as the following equation (Wang and Guo, 2020b).

$$q_e = K_f C_e^{1/n}$$

where K_f ($\text{mg}^{1-(1/n)} \cdot \text{L}^{1/n}/\text{g}$) and n (dimensionless) represent the Freundlich constant.

The tabulated data above (Tables 3-6) reveals that, based on the type of pollutants and the features of the graphene-based adsorbents used, both mono-layer and multi-layer adsorption can occur in the adsorption processes.

A critical consideration of equilibrium studies, using graphene-based materials as adsorbent, shows that these adsorbents have high adsorption capacities for all types of pollutants, again indicating their high potential for being used in full-scale water and wastewater pollutants.

Also, unlike the manner adopted by some authors who have used linearized equations for modeling equilibrium data of adsorption of pollutants onto graphene-based adsorbents, it should be noted that equilibrium isotherms must be solved by nonlinear regression analyses.

As the current work is a comprehensive review article, critical consideration of isothermal study cause mentioning another mistake which is repeated in some literature related to adsorption systems. Using graphene-based adsorbents, to prove the strong affinity and robust interaction

between adsorbent and adsorbate, some authors have recruited the separation factor, R , as the following equation (Bo et al., 2022; F. Chen et al., 2021; Zhang et al., 2021):

$$R = \frac{1}{K_L + C_0}$$

where K_L and C_0 are the Langmuir isotherm constant and initial concentration of adsorbate. This equation was introduced by (Hall et al., 1966), in 1966, and the separation factor (R) was proposed as a factor capable to reflect the essential characteristics of the Langmuir model. Some authors have utilized the value of R to show the feasibility of an adsorption process and prove the strong affinity of adsorbent towards the adsorbate and robustness of adsorbent-adsorbate interaction. An R value equal to zero is used as an indication for irreversibility of equilibrium and, hence, extremely high affinity of the adsorbent for adsorption of the targeted adsorbate; for $0 < R < 1$ value is taken as an indication for the favorability of adsorption, and lower R values vouchsafe the greater favorability of the adsorption process; for $R = 1$ is indicative of linear cases; an $R > 1$ is assumed to be indicative of unfavorability of the adsorption process. In addition, Hall et al. have emphasized that the separation factor is only applied to the cases where the adsorption processes obey the Langmuir isotherm model (Hall et al., 1966). There are some controversies in the literature about the wrong use and mistaken conclusions raised from the usage of R value. It should be noted that, according to mathematical relation, the Langmuir constant K_L is mathematically always greater than zero ($K_L > 0$), no matter whether the adsorbent has a strong affinity towards adsorbate or not. In fact, without any exception, the values of R always fall in the range of 0–1 for all adsorbent-adsorbate systems, regardless of the amount of C_0 value. Such values for R lead to the incorrect conclusions which implies the favorability of the adsorption process, for all adsorption systems. Therefore, the separation factor is not a suitable indication for the examination of the affinity of the sorbent towards the adsorbate, favorability of the sorption processes, and/or the robustness of the adsorbate-adsorbent interaction.

4.3. Thermodynamic consideration of pollutants adsorption by graphene-based materials

Unfortunately, using Van't Hoff equation, many research groups involved with using graphene-based adsorbents for waters and wastewaters treatment have recruited wrong constants, like distribution coefficient (K_d ; L/g) and other inadequate constants (Cui et al., 2015; Dai et al., 2020; He et al., 2022; Paton-Carrero et al., 2022; Rathour et al., 2022; Yang and Cao, 2022), for calculating thermodynamic parameters, using the following equation:

$\Delta G^\circ = -RT \ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$, where K is the constant, R (8.314 J·mol⁻¹·K⁻¹) is the ideal gas constant, ΔG° is the standard Gibbs free energy change, ΔH° is the change in the standard enthalpy, and ΔS° is the change in the entropy.

Table 7

Regeneration results of various graphene-based adsorbents.

Adsorbent	Adsorbate	Eluent	Number of cycles	Efficiency	Ref.
GO/Fe ₃ O ₄ /SO ₃ H	Cr(VI)	HNO ₃	4	85	(Alizadeh et al., 2017)
3D-GO	BPA	n-Hexane	5	90.3	(Wang et al., 2019)
GO-AC-CS	ACP	Methanol	5	70–80	(Delhiraja et al., 2019)
GO-PVPP	2,4,6-TCP	Methanol/water	5	95	(Lv and Li, 2020)
SBMGO	Cu(II)	HCl	5	86	(Anush et al., 2020)
GO-IL	SMZ	Ethanol	7	75	(Lawal et al., 2020)
COPYGO	Pb(II)	HCl	5	91.2	(Anuma et al., 2021)
P(AAm/IA)/GO-PEI	CV	HCl & NaOH	5	84	(Tamer et al., 2021)
RGO-βCD-ECH	Phenol	HNO ₃	5	73.98	(Rout and Jena, 2022d)
PVA/PHPAm/GO	MB	HCl	5	70	(Rahmatpour et al., 2022)
GO-MF	RhB	Ethanol	7	88.1	(Vo and Vo, 2022)
GO-S-La ₂ O ₃ (CO ₃)	MG	HCl	5	85	(Eftekhari et al., 2022)
MAEGO	Amoxicillin	NaOH	5	74.1	(Moradi et al., 2022)
β-CD/rGO-MWCNTs	Naproxen	HCl	4	81.7	(Feng et al., 2022)

The utilization of incorrect thermodynamic constants, like K_d and other constants, for thermodynamic calculations in adsorption processes leads to obtaining erroneous values for thermodynamic parameters (Lima et al., 2019). Fortunately, such mistakes have been scrutinized and the most correct manner for calculation of thermodynamic parameters has been introduced (Lima et al., 2020; Lima et al., 2019). To calculate these parameters, the principles of chemical equilibrium should be considered and the correct thermodynamic equilibrium constant should be derived from isothermal studies (Lima et al., 2019).

5. Desorption and regeneration studies

An ideal adsorbent not only retain high amount of adsorption capacity, but also display excellent desorption and regeneration performance, which increases the efficiency of the adsorbent as well as reduces the cost of the process. As a result, desorption and regeneration are considered as imperative factors in adsorption, which can significantly decline the costs of the materials and the commercialization of graphene-based sorbents (Peng et al., 2017). It can be inferred that after removing various phenolic pollutants, dyes, organic pollutants, and heavy metals from water resources, the spent adsorbents could be separated from the solution, recycled, and finally regenerated for adsorption of these toxic pollutants. Various methods are available for separating spent adsorbents from the solution, such as cross-flow filtration, centrifugation, electric field, magnetic field, and filed flow fractionation (Ali et al., 2018). The separated spent adsorbents are regenerated by using an array of various eluents. Table 7 summarizes some of the eluent agents, which are used for the regeneration of spent adsorbents.

The authors have thoroughly reviewed various articles on the adsorptive removal of organic and inorganic pollutants utilizing graphene-based sorbents. It is found that different graphene-based adsorbents show different adsorption capacities towards different pollutants. The graphene-based magnetic composite is considered the best adsorbent for removing phenolic pollutants with a high sorption capacity of as high as 1548.78 mg/g for p-nitrophenol using Fe₃O₄@mSiO₂/GO composite (Liu et al., 2016). The advantage of magnetic composites is that they can be easily separated after adsorption from the clear solution, using an external magnet. The high value of adsorption capacity is due to the high specific surface area of GO which provides abundant active adsorption sites and presence of various functional groups which helps to bind the pollutants to be adsorbed onto the surface of adsorbent through intermolecular forces. For the adsorption of dyes, the authors have found out that graphene-based polymer composites have shown better adsorption performance. A novel P(AAm-IA)/GO-PEI double network nanocomposite was recruited for the adsorption of both cationic dye (CV) and anionic dye (DR23) (Tamer et al., 2021). The maximum adsorption capacity was 774.46 and 349.29 mg/g for CV and DR23, respectively, using only 100 mg/L as initial concentration. The adsorption capacity of cationic dye is higher due to more negative charge on the surface of adsorbent that attracts the positively charged pollutants. Increase in GO content from 0 to 0.3 wt% in the

composite enhances the adsorption capacity from 390.6 to 774.46 mg/g. The cyclodextrin-based adsorbents perform better adsorption for heavy-metal pollutants because of the host-guest inclusion complex, which adsorbs both positive and negative charged ions. A novel RGO- β CD-ECH composite was used for Cr(VI) removal, having 1321.01 mg/g adsorption capacity, using only 0.1 g/L adsorbent dosage (Ranjan Rout and Mohan Jena, 2022). Considering these results, the authors recommend that, for the adsorption of any specific type of pollutant (phenolic pollutants, dyes, or heavy metals), a suitable modification is required to enhance the adsorption performance.

6. Challenges and future studies and recommendations

Over the last decades, graphene-based materials as adsorbents for waters and wastewaters treatment purposes have been promising options, among other solid supports. Nevertheless, despite the “bright” perspectives and various advantages of graphene-based adsorbents, some serious challenges are associated with them. At present, there are various challenges, which exist in the way of treatment of waters and wastewaters using graphene-based adsorbents, such as;

(i) Although effective separation, regeneration, and reuse of graphene-based sorbents from the water after removing the toxic pollutants is possible, entering exhausted adsorbents into the natural environment cause secondary pollution through diffusion and migration of pollutant to water bodies and soil causes serious health and environmental risks.

(ii) Some synthesized graphene-based materials are single-layer adsorbents with less functional groups, limiting their enhancement and improvement for higher adsorption capacity.

(iii) The interaction mechanism between pollutants and adsorbents is still uncertain because of the great differences in the adsorbents surface properties.

(iv) Most research have been focused on synthetic lab-made solutions, while the real waters and wastewaters are complex and contains various organic and inorganic pollutants; hence, it is essential to analyze the competitions and synergetic mechanisms between graphene-based sorbents and heavy metals and/or organic compounds in real wastewater.

(v) Most of the studies are designed for batch-wise adsorption processes. However, using graphene-based materials for real treatment plants requires studying the performance of such materials in continuous adsorption processes.

(vi) In many studies, kinetic, equilibrium and thermodynamic studies have not been performed completely. In some cases, such studies are erroneous, because of using wrong equations or inferring wrong conclusions from the conducted studies. Such mistakes, in some cases, make it hard to judge about the feasibility of industrialization of using this class of adsorbents for real treatment plants.

(vii) Graphene-based adsorbents are being synthesized at a laboratory scale; however, for commercialization purposes, these adsorbents are encapsulated, which may lose their surface properties and high surface area and because of the formation of graphitic form.

Most of the articles reviewed in this paper have not discussed some of these criteria, which leaves important research gaps about the industrial applicability of novel graphene-based adsorbents. The future studies on exploiting the graphene-based adsorbents should be done more comprehensively, considering the challenges mentioned above. Also, there are some recommendations, concerns, and issues which should be noticed in the future studies, such as:

- (a) Although this review highlights some of the regeneration studies, the reusability study of various adsorbents needs to be determined systematically to evaluate each adsorbent's practical performance and efficiency.
- (b) In many cases, there are no cohesive conclusions regarding how the pollutants are adsorbed on the surface of these functionalized adsorbents. Therefore, some theoretical calculations are required, to obtain the relationship between pollutants and graphene-based sorbents as to how the sorption performance enhances.

- (c) DFT technique can be used to further analyze the adsorption mechanism, by measuring the sorption energy and electron cloud distribution betwixt adsorbates and adsorbents.
- (d) Further investigation is required to determine the internal relationship between the adsorption enhancement effect and the microstructure of the adsorbent.
- (e) Complete and correct modeling of equilibrium, kinetic, and thermodynamic aspects of adsorption process is essential for designing adsorption process for full-scale treatment plants. For the same reason, in the case of continuous adsorption process, correct and complete modeling of the effect of some parameters like the height of adsorbent column, effluent flow rate, etc. is necessary.
- (f) Finally, more studies are essential in future for designing and regulating graphene-based adsorbents, reusing them efficiently, reducing the environmental risks, improving the adsorption capacity, carrying out design optimization, exploring the interaction mechanism between pollutants and adsorbents, designing adsorption processes for real wastewater and water samples, and commercialization of graphene-based adsorbents.

7. Conclusions

This review paper highlights the removal of toxic organic and inorganic pollutants from wastewaters employing graphene-based adsorbents. In addition, the main adsorption parameters such as initial concentration, pH, temperature, and contact time are also discussed. The isotherm data are predominantly split between the Freundlich and Langmuir isotherm models and the maximum sorption capacity is calculated using Langmuir model. Moreover, in the adsorption kinetic section, PSO gives the best fit. Thermodynamic analysis of the adsorbents is also presented in this review. The interactive mechanism between pollutants and adsorbents is discussed in detail. The regeneration ability of some of the adsorbents has been discussed, which suggests these adsorbents can be effectively exploited without any significant reduction in their performances. The review suggests that these materials may be the best adsorbents, compared to other carbonaceous materials, as they can remove all types of pollutants. The results are highly encouraging in terms of adsorption capacity and removal efficiency of organic and inorganic pollutants. In this review, various challenges which exist in the way of treatment of waters and wastewaters by graphene-based adsorbents were implied. Also, a perspective for future studies was drawn and some recommendations were represented for complete and correct studies of the adsorption systems. Anyway, more studies involving real water samples and fixed-bed continuous column studies for commercialization of graphene-based adsorbents can be the next logical progression to pave the road to industrial exploitation of these valuable adsorbents in real waters and wastewaters plants.

CRediT authorship contribution statement

Dibya Ranjan Rout: Conceptualization; Methodology; Data analysis; Writing-Original draft preparation.

Hara Mohan Jena: Supervision; conceptualization; Investigation; Writing, Reviewing, and editing.

Omirserik Baigenzhenov: Writing, Reviewing, and editing.

Ahmad Hosseini-Bandegharaei: Writing, Reviewing, and editing.

Data availability

No data was used for the research described in the article.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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