Nanostructured Carbon-Based Materials for Adsorption of Organic Contaminants from Water

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Abstract Graphene is currently one of the most promising carbon-based materials being studied in the world due to its novel electronic, thermal and optical properties. Nowadays, graphene can be considered the basis for the whole family of carbon nanomaterials, except for diamond structure. Because of that, several methods of graphene production have been studied; however, such methods need to be improved and the scaling is still a bottleneck for the productive sector. This article presents the main way to produce graphene and some techniques to modify its surface. In addition, here we present a review about graphene and its derivatives in the adsorption from the aqueous medium of the most diverse types of organic contaminants in the environment, such as pharmaceuticals, dyes, surfactants, pesticides, etc. We have shown that graphene and its derivatives are efficient adsorbents for the removal of emerging organic pollutants from the environment.

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1 Introduction

The rapid growth of industrial and agricultural activities has led to a growing increase in the release of pollutants into the environment, such as persistent organic pollutants, for example, the industrial dyes [27, 122]. This has led to several environmental concerns, because the accumulations of toxic waste are potentially harmful to human health and the environment [17, 84, 119].

Therefore, efficient solutions are needed to lessen the effects caused by these pollutants in the environment. Thus, several methods have been used to remove these pollutants from the wastewater, where it is possible to highlight the adsorption, degradation, coagulation, flocculation, ion exchange, membrane filtration, electrochemical and catalytic oxidation, catalytic ozonization, all these technologies have limitations and restrictions [29, 75]. Among the remediation options, adsorption is one of the most used techniques due to its simplicity, ease of operation, low cost and efficient removal in low concentrations [121].

Among the materials used as adsorbents in the removal of organic compounds in wastewater, the carbon nanomaterials, such as graphene [49, 79, 99], which have recently been received special attention because of their specific surface area associated to relatively high adsorption capacity [21, 79, 107].

Therefore, graphene has been widely studied as an adsorbent for water decontamination because of its physico-chemical properties, which include, besides the high specific surface area, its mechanical, thermal and chemical stabilities [16, 36, 68, 120]. Therefore, these characteristics make graphene a potential material to be used in the treatment of effluents [35, 93].

Although recent studies have shown that graphene is being used as an adsorbent for emerging organic pollutants from the aquatic environment, there are few studies with this approach and there is a need for further studies and applicability on an industrial scale [33].

2 Graphene

The term "graphene" was first used in 1947, but the official definition was given by the International Union of Pure and Applied Chemistry (IUPAC) in 1994. In 1947, Walace in 1947 first studied to understand the structure of graphite, which consists of superimposed and weakly bonded graphene layers to each other, contrasting with the interatomic bonds in each plane, which are the strongest known bonds in a crystal [112].

In 2004, researchers were able to isolate small fragments exfoliated from graphite and after characterization verified that it was a single-layer structure of carbon atoms [77]. This material has attracted much attention from the scientific community because of its specific physical and chemical properties, large outer surface area, and

Table 1 Some of the main properties of graphene Huang et al [40, 52, 57]

Rupture force	~42 Nm^{-1}
Tensile strength (Young modulus)	1.0 TPa
Specific surface area	2630 m^2 g^{-1}
Intrinsic mobility	200 000 cm^2 V^{-1} s^{-1}
Thermal conductivity	~5000 W^{-1} K^{-1}

ease of modification [110]. Some of the main properties of graphene are shown in Table 1.

These properties provide graphene with properties that translate into greater mechanical strength than steel, higher electron mobility than silicon, higher thermal conductivity than copper, higher surface area than graphite and lighter material than many others [98].

2.1 Structure

Graphene is a two-dimensional (2D) network, composed of a hexagonal structure, which looks like a honeycomb [34]. Graphene has a sp^2 hybridization, where the carbon atoms form covalent bonds with each other (δ bonds), where the distances of the C–C bonds are approximately 1.42 Å, with a thickness of one carbon atom (approximately 1 Angstrom = 10^{-8} cm) (Fig. 1) [88].

In the graphene structure, the sp^2 hybrid orbital is a result of the bonding in the plane of the pure orbitals s, p_x and p_y, while the pure orbital p_z is free and perpendicular to the plane. This produces a sharing of sp^2 orbital hybridization of a carbon with three neighboring carbon atoms forming the hexagonal and 2D structure of graphene, as shown in Fig. 2 [105].

2.2 Synthesis of Graphene

Graphene production can be performed through two different strategies, which are designated as Top-Down and Bottom-Up [30].

2.2.1 Top Down Approach

The Top Dow strategy (top to bottom) is characterized by the attack of graphite powder, which will eventually separate its layer to generate graphene sheets [11]. Among Top Dow methods, we can highlight mechanical and chemical exfoliation and chemical reduction.

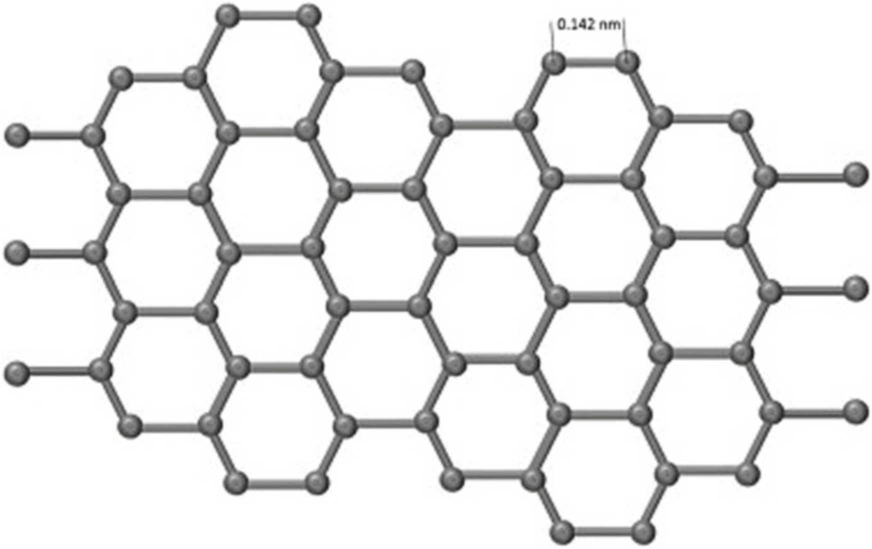

Fig. 1 Structure of a Graphene Blade. Reproduced with permission from Ref. [80]. Copyright: 2017 Elsevier

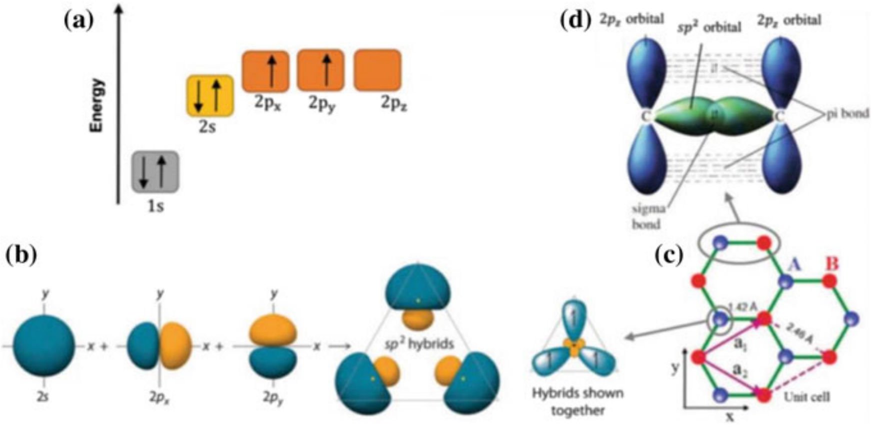

Fig. 2 **a** Energy levels of outer electrons in carbon atoms. **b** The formation of sp^2 hybrids. **c** The crystal lattice of graphene, where A and B are carbon atoms belonging to different sub-lattices, a_1 and a_2 are unit-cell vectors. **d** Sigma bond and pi bond formed by sp^2 hybridization. Reproduced with permission from Ref. [105]. Copyright: 2019 Elsevier

Mechanical Exfoliation

Graphite forms when the layers of mono-atomic graphene are stacked together by weak forces of van der Waals, the method of exfoliating the inverse of the stacking

[87, 125]. Hummers and Offman were the first to synthesize graphene in 1958, they obtained graphene through graphite exfoliation, although they did not obtain only carbon graphite as it is now known as graphene [41].

Andre Geim and Konstantin Novoselov reported in 2004, the synthesis of graphene nanosheets through the mechanical exfoliation. It was observed for the first time that it was possible to isolate a sheet of carbon atoms at room conditions [73]. Mechanical exfoliation is an ancient method and the most popular, since it was the process that led to the discovery of graphene [74].

This method involves exfoliating the graphite sheets until a single sheet is obtained. Exfoliation has the purpose of removing the graphite layers, this can be done using a variety of agents, such as adhesive tape [73], ultrasound [25] and electric field [58], and this technique does not require special equipment, but has a low performance disadvantage [100].

Chemical Exfoliation

Chemical exfoliation is the best route to be used to obtain graphene. This method consists in using the graphite to produce the graphene through the continuous reduction of the forces of Van der Waals that occurs through the insertion of special chemicals in the atomic planes of the graphite [113].

It is important to stress that chemical exfoliation is performed in two steps. Initially, occurs the reduction of the interlayer van der waals forces to produce compounds interlaced with graphenes [113]. Then, graphene is exfoliated with one or a few layers by rapid heating or sonication [6, 64].

Chemical Reduction of Graphite Oxide

In 1859, graphite oxide was first reported by Brodie, this one also presented the possibility of exfoliation, through the use of functional groups introduced in the oxidative graphite [14]. Graphite oxidation can be produced by the oxidation of graphite using oxidants such as concentrated sulfuric acid, nitric acid and potassium permanganate based on the method of Brodie [14], Staudenmaier method [102], Hummers method [41].

The oxidized graphite disperses easily in polar solvents, and the sonication process separates the leaves to obtain a smaller number of leaves than in graphite [7]. The number of leaves varies according to the experimental conditions of oxidation and sonication [24].

2.2.2 Bottom-Up Approach

The Bottom-Up strategy explore carbon dioxide to generate graphene [11]. Among the methods used in this strategy are: pyrolysis, epitaxial growth and CVD.

Pyrolysis

The graphene can be obtained through the pyrolysis of sodium ethoxide via sonication. This process improves the performance of graphene sheet detachment. Thus, the generated graphene sheets are measured up to 10 μm [22].

Epitaxial Growth

The term “epitaxy” derives from the Greek, the prefix epi means “on” and taxis means “order” or “agreement”. When deposition of a single crystalline film on a single crystalline substrate produces epitaxial film and the process is known as epitaxial growth [9]. In this process, graphene is produced in the substrate (semiconductor) and the growth process is followed by lithography to make electronic devices based on graphene [9, 114]. The graphene produced by this process is called epitaxial graphene that can be grown on various substrates, such as silicon carbide [31], iron (Fe) [71] and copper (Cu) [32].

A promising substrate used in the growth of epitaxial graphene is silicon carbide. The preparation of graphene can be accomplished by applying heat and cooling of a silicon crystal (SiC). Usually, on the Si face of the crystal, there will be single layer or double layer graphene, however, on face C, graphene of few layers is cultivated [18].

Chemical Vapor Deposition—CVD

Chemical vapor deposition (CVD) is defined as the placement of a solid on a heated surface from a chemical reaction in the vapor phase where the deposition species are atoms or molecules. The chemical energy required to initiate a specific chemical reaction is provided by heat, light or electric charge [56].

High quality graphene deposition from the CVD process is usually done on various transition metal substrates such as Ni [45], Cu [90] and Pd [22], where graphene growth by CVD has been produced mainly on copper and nickel substrates [108].

3 Modifications

One of the great limitations in the use of graphene is its low reactivity, which hinders its interaction with different chemical species. Thus, there is a constant search for techniques that can be used to increase the reactivity of graphene with the introduction of different functional groups, these groups can be added by functionalization, doping and defects [72].

Among these techniques, chemical functionalization has attracted attention due to the possibility of increasing the solubility, processability and interactions of graphene with organic polymers [48]. An example is the introduction of oxygen-containing groups (−COOH, −CO and −OH) on the surface of the graphene. These groups occupy up to 60% of the surface area of graphene oxide (GO) [92].

Graphene oxide (GO), an oxidized version of graphene, can be synthesized by the oxidation of natural graphite [38, 41, 96]. This reaction occurs through the oxidation and exfoliation of graphite, usually in aqueous solution. This produces carbon-based hydrophilic plates decorated with various oxygenated functional groups (hydroxyl, epoxide and carboxyl), as shown in Fig. 3 [66].

The continuous, atomically thin, two-dimensional (2D) arrangement of carbon atoms that is functionalized with epoxy and hydroxy groups in the basal carbon plane and carboxy groups around the edges is the most accepted structure of GO leaves [66]. The GO may be reduced, partially, to graphene-like sheets by withdrawing the oxygen-containing groups and causing the recovery of a conjugated structure. Reduced GO (rGO) sheets are generally considered as a chemically derived graphene type (Fig. 3) [76]. The reduction of the GO does not completely remove oxygenated functional groups, only promotes a significant reduction of them. One way to accomplish GO reduction is to use high temperature treatment or use chemical agents such as hydrazine to form rGO [66, 76].

When performing the oxidative removal of the functional groups of oxygen from the GO there is the formation of another derivative of the graphene, named of graphene acid. The experimental procedure is based on the multiple oxidation of graphite with potassium permanganate in acidic medium. This procedure leads to the formation of a graphene derivative with an approximate composition of carboxyl

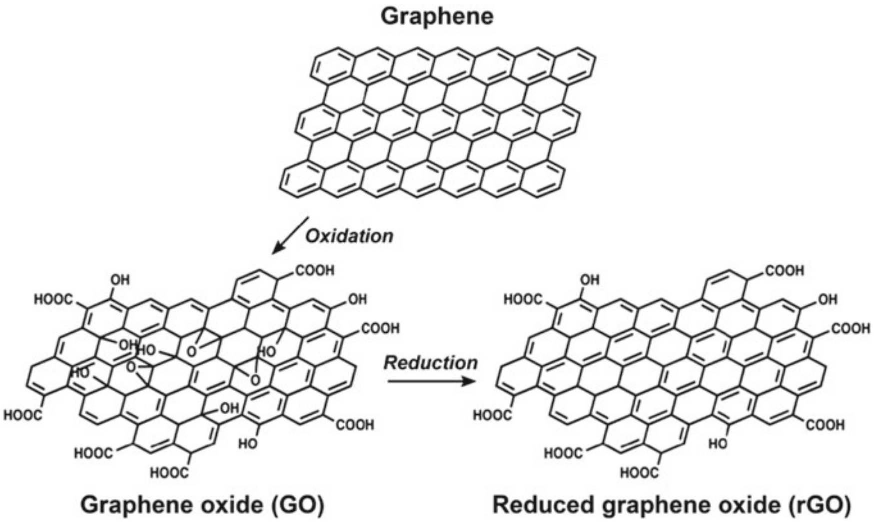

Fig. 3 Idealised structures of graphene, graphene oxide and reduced graphene oxide. Reproduced with permission from Ref. [66]. Copyright: 2019 Elsevier

groups, $[C_1(COOH)_1]_n$, of reaches 30 wt%, and simultaneously causing the oxidative elimination of other functional oxygen groups [42].

GO has a negative surface when in aqueous medium due to the formation of COO^-. Thus, when there is functionalization on the GO surface with a functional group which in aqueous medium produces a positive charge occurs the formation of the zwitterionic graphene oxide (ZGO). Zwitterionic compound containing both anionic and cationic groups would convert charge with the pH values. One way of producing ZGO is through the introduction of silane groups. For example, the preparation of the ZGO nanosheets with two silanes ((3-glycidyloxypropyl)trimethoxysilane (GPTMS) and (3-aminopropyl)triethoxysilane (APTES)), as shown in Fig. 4. Covalent bonds are responsible for grafting the silane molecules onto the GO surface and when the pH of the aqueous solution is changed from 12 to 2, there is also the variation of the potential (ζ) of ZGO of -29.0 mV to $+28.5$ mV [26].

Another important functionalization of graphene is the incorporation of thiol groups on its surface. An example of this reaction is shown in Fig. 5. From the Figure, it can be observed that, initially, the graphene is oxidized and forms graphene oxide (GO), which is then heated to above 400 °C in order to exfoliate the GO structure in layers in thermally reduced graphite oxide (TRGO) sheets. TRGO contains different oxygen groups directly bound to the carbon skeleton of a two-dimensional graphene-derived backbone (Fig. 5a). Soon after, The TRGO is placed to react with propylene sulfide forming the TRGO-SH, as shown in Fig. 5b [65].

Pristine graphene can be functionalized by organic functionalities such as free radicals and dienophiles. For example, sp^2 carbon atoms of graphene are easily attacked by a free radical generated by heating a diazonium salt, causing the formation of a covalent bond. The sulfonic groups ($-SO_3H$) can be incorporated into the graphene by this reaction. Figure 6 shows the sulfonation reaction of graphene using 4-sulfobenzenediazonium with added of the sodium dodecylbenzensulfonate (SDBS) to the graphene dispersion to perform surfactant wrapped graphene [85].

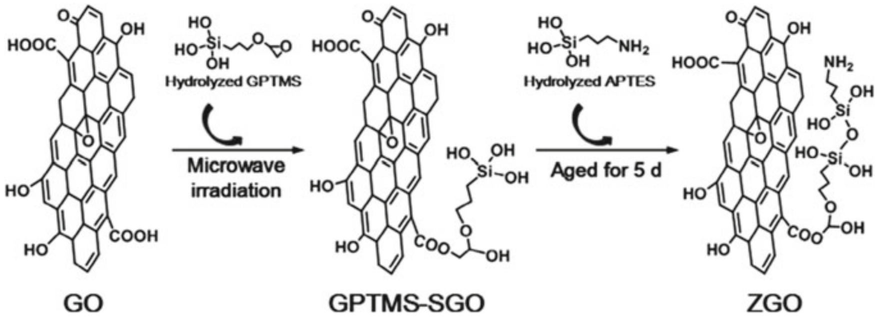

Fig. 4 Reaction scheme for the two steps silanization by GPTMS and APTES. Reproduced with permission from Ref. [26]. Copyright: 2018 Elsevier

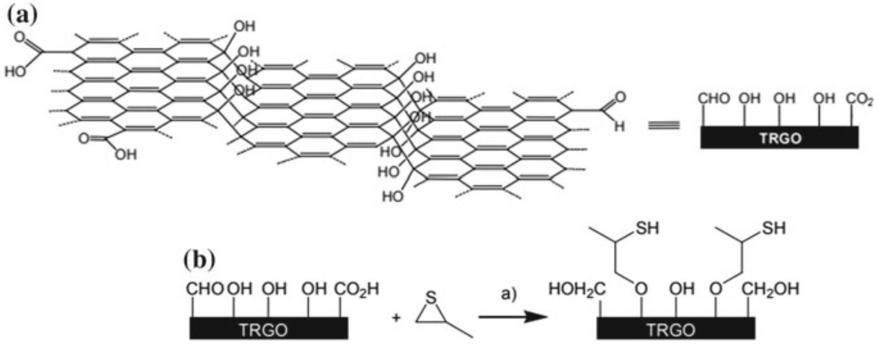

Fig. 5 **a** Schematic presentation of a model structure for thermally reduced graphite oxide (TRGO) with its functional carboxyl, aldehyde and especially hydroxyl groups according to recent studies. Reproduced with permission from Ref. [65]. Copyright: 2014 Elsevier. **b** Schematic presentation of the ring opening reaction of propylene sulfide (2-methylthiirane) with deprotonated hydroxyl groups of TRGO to yield the material TRGO-SH. Reproduced with permission from Ref. [65]. Copyright: 2014 Elsevier

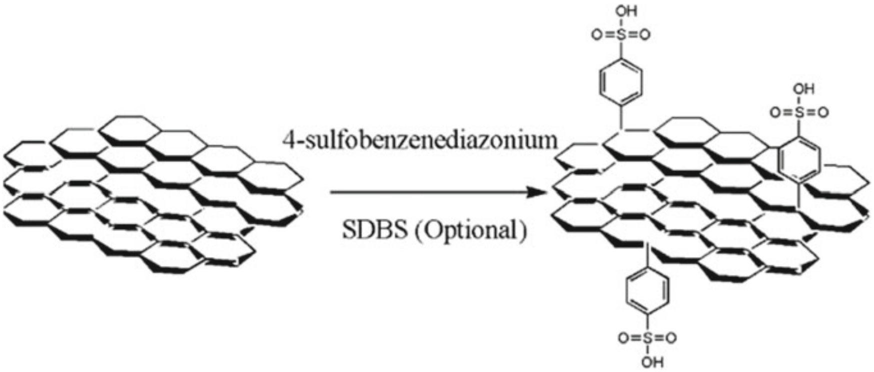

Fig. 6 The reaction of sulfonation of the graphene using 4-sulfobenzenediazonium. Reproduced with permission from Ref. [85]. Copyright: 2018 Elsevier

In addition, on the graphene surface can also be incorporated phosphate groups. One way to accomplish this incorporation is the phosphating of GO from the covalent attachment of triethylphosphite on the GO surface via the Arbuzov reaction (Fig. 7). This reaction occurs at about 150 °C and is characterized by the reaction of triethylphosphite with electrophilic site of graphene oxide like epoxide or near to carbonyl group. After the non-localized attack of the GO surface by the triethylphosphite is formed the diethyl phosphonate. Then the ethyl group reacts with the bromide obtained from the LiBr to form the ethyl bromide. This process is carried out until the formation of the phosphene oxide graphene. Finally, hydrolyzing the ethyl groups present in the phosphonated GO is carried out to give hydroxyl groups and to form the phosphated graphene oxide (PGO) [2].

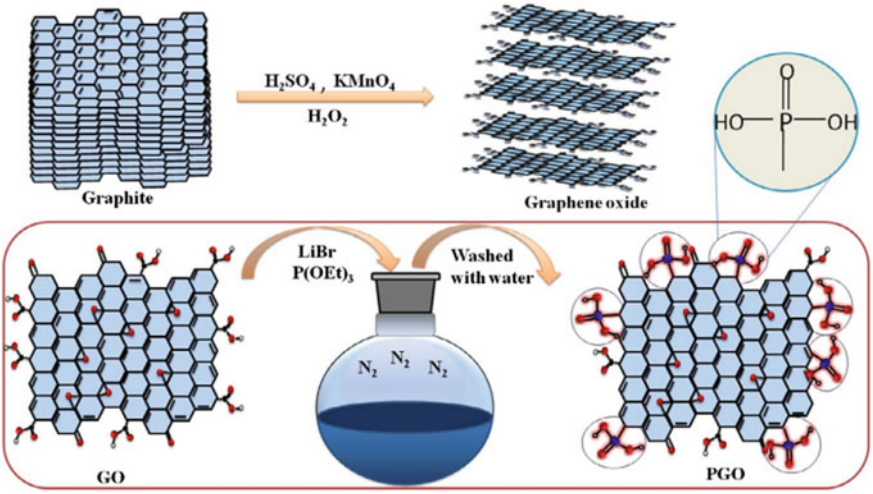

Fig. 7 Schematic diagram for the synthesis of PGO. Reproduced with permission from Ref. [2]. Copyright: 2018 Elsevier

4 Graphene Nanocomposites

The development of nanotechnology has attracted the interest of researchers to improve the performance of composites by introducing nanomaterials to them [54]. Graphene and its derivatives are considered promising candidates as nanomaterials that can be used to enhance composites, due to its excellent properties such as high mechanical and chemical stability [54, 55, 117].

Thus, various materials are used together with graphene and its derivatives for the production of composites for the most diverse applications. For example, one study showed a production of GO/bentonite (BG) compounds, prepared from GO interspersed with an intermediate layer of bentonite, as shown in Fig. 8. In these composites, it can be observed that after the addition of the GO there was an increase of the BET surface area, because the presence of GO between the BG layers formed an exfoliated structure. In addition, BG composites exhibited a greater adsorption capacity of toluidine blue dye (TB) from aqueous solutions than normal bentonite due to the synergistic effect between bentonite and GO. Finally, it was concluded that the adsorption of TB in BG composites occurs mainly through ion exchange, electrostatic interaction and intermolecular interactions (Fig. 8) [116].

The GO may also be introduced onto the surface of silica gel to decorate/functionalize GO through specific functional groups. To prepare this composite (SiO_2@GO–PO_3H_2) four steps are required which are schematically presented in Fig. 9. (i) Silica gel (SG) is grafted using 3-aminopropyltriethoxysilane (APTS) producing the compound SG-APTS. (ii) The GO is added to the surface of the SG-APTS forming SiO_2@GO. (iii) An aminosilane group is added to the surface of the SiO_2@GO generating the SiO_2@GO-NH_2. (iv) The vinylphosphonic acid is added

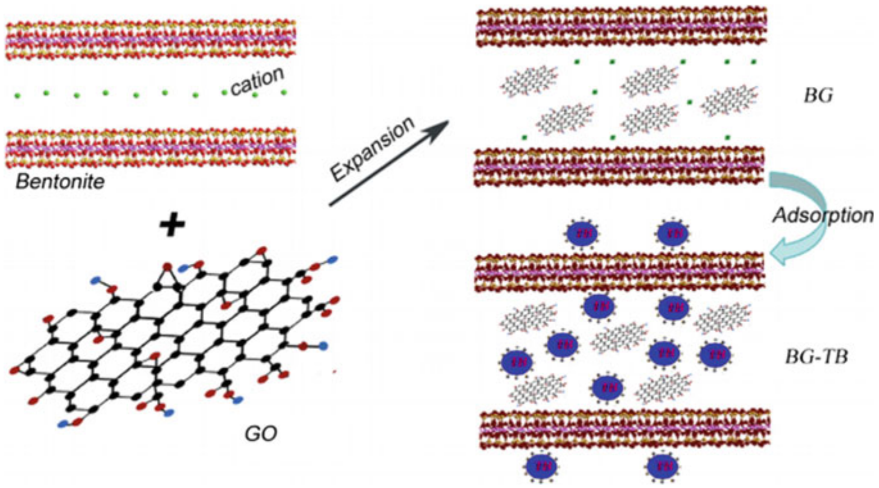

Fig. 8 Illustration of the synthesis of BG composites and TB adsorption using BG composites. Reproduced with permission from Ref. [116]. Copyright: 2019 Elsevier

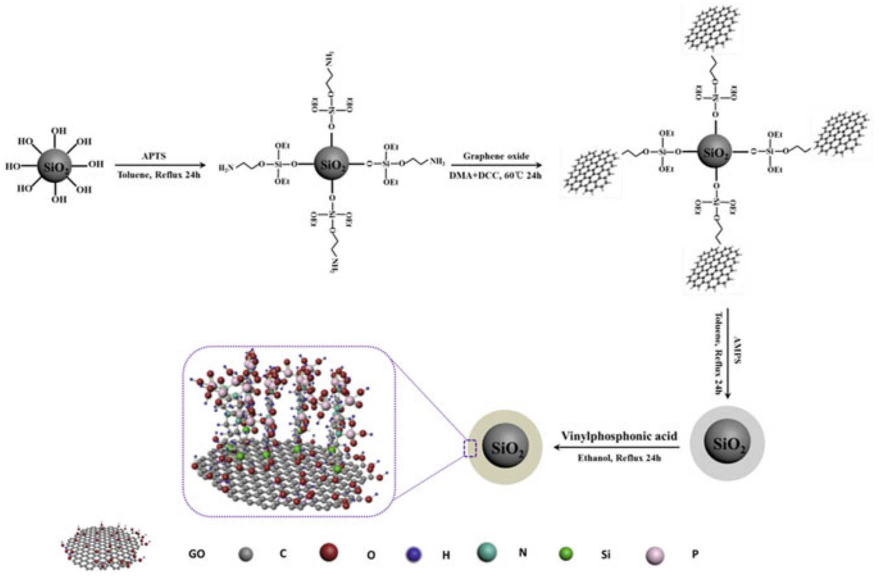

Fig. 9 The scheme for preparation of SiO_2@GO–PO_3H_2. Reproduced with permission from Ref. [53]. Copyright: 2019 Elsevier

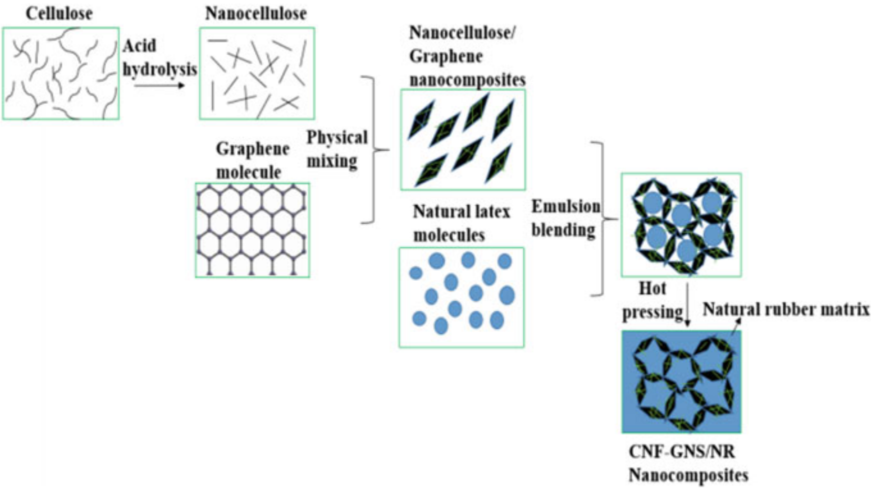

Fig. 10 Schematic of the CNF-GNS/NR fabrication process. Reproduced with permission from Ref. [115]. Copyright: 2019 Elsevier

on the SiO_2@GO-NH_2 forming the SiO_2@GO–PO_3H_{2}- composite and the incorporation of the phosphate group is confirmed by the appearance of the peaks at 2325 and 1695 cm^{-1}, which were assigned to P(O)-OH stretching vibration. The adsorption of ln (III) ions on the surface of SiO_2@GO–PO_3H_2 occurs by a chemical adsorption process, due to the coordination of the ln (III) ions to the element P, present on the surface of the adsorbent, generating a lnP bond [53].

In addition, some researchers have prepared composite materials from of graphene and polymeric materials. For example, a recent study prepared a nanocomposite (CNF-GNS/NR) using cellulose nanofibrils (CNF), graphene (GNS) and natural rubber (NR). The CNF-GNS/NR nanocomposite was produced through the formation of a three-dimensional multilayer network structure generated by the dispersion and overlap of CNF and GNS in NR (Fig. 10). The results showed that the incorporation of CNF increased the electrical conductivity of the composite GNS/NR, in addition, the addition of CNF reduced the percolation threshold of the composites. This confirms that using the CNF to construct a multi-layer multi-layer conductive network in NR is effective to promote the increase of the electrical conductivity of these composites [115].

Another polymer widely used in the production of composites with graphene is chitosan (CS). As an example, it may be mentioned a research recent which produced a composite using CS and graphene. For the production of this composite SiO_2 was used to improve the dispersibility of the grafene in chitosan suspensions. The CS/SiO_2-loaded graphene composite beads were cross-linked with ethylene glycol diglycidyl ether (EGDE) and prepared by the phase inversion method (Fig. 11). The results showed that the spheres Cs and Cs/graphene-SiO_2 presented spherical

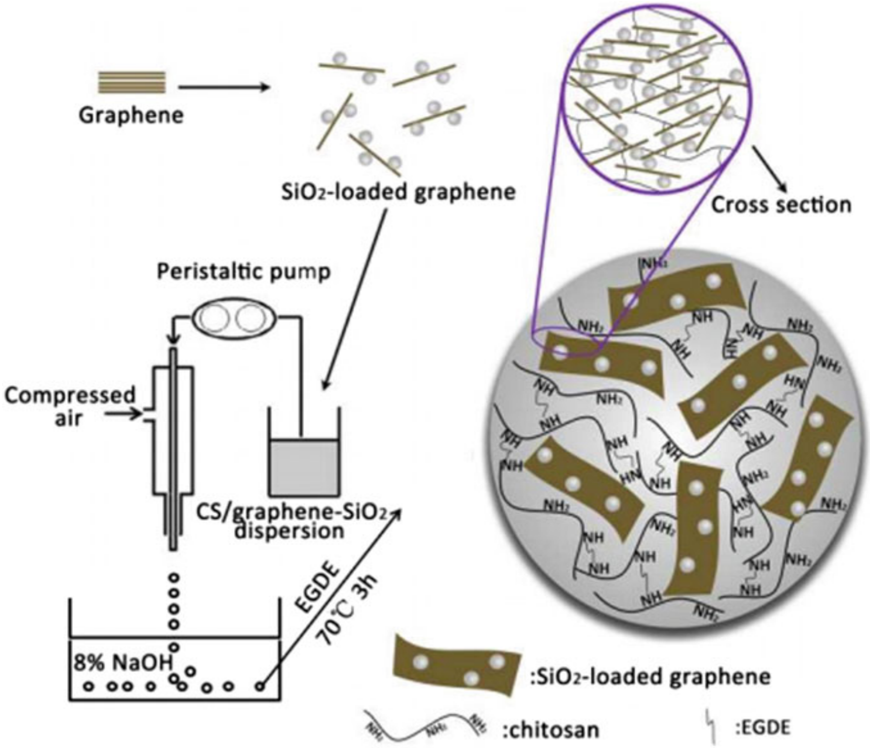

Fig. 11 Schematic illustration of the preparation of CS/graphene-SiO_2 composite beads. Reproduced with permission from Ref. [19]. Copyright: 2019 Elsevier

shapes and the incorporation of graphene improved the mechanical strength of the composites compared to the CS spheres [19].

In addition to studies related to graphene/polymer composites, research related to metal matrix graphene composites (CMMs) has also gained prominence. An example is the graphene/Cu composites, these composites attracted attention because of their electrical, thermal and mechanical properties, which made them promising materials for a wide range of applications [23].

The two main difficulties in the production of reinforced copper based graphene composites are the non-uniform dispersion of the graphene flakes inside the copper matrix and the low bond strength of the graphene/Cu matrix interface. An effective preparing approach of graphene-strengthening copper-based composites is an easy electrochemical deposition and atmosphere sintering. Figure 12 shows the schematic of preparation of graphene-nanoplatelets/copper (GNP/Cu) composite by electrochemical deposition and atmosphere sintering. The results showed that when the graphene content is 1.8 wt%, it is dispersed homogeneously in the matrix and forms a coherent interface in the GNP/Cu composites. In addition, it is observed that Cu-O-C bond formation is promoted by nickel (Ni) in the formation of graphene nanoplatelets

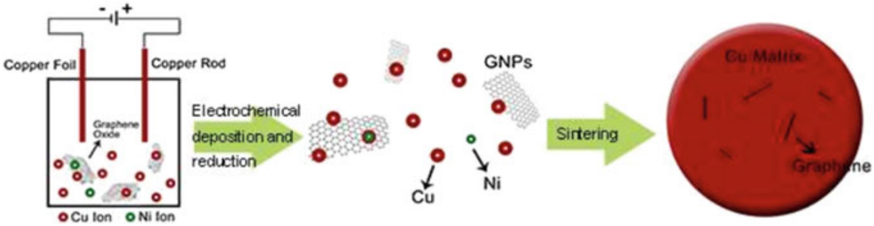

Fig. 12 Schematic of preparation of GNP/Cu composite. Reproduced with permission from Ref. [126]. Copyright: 2018 Elsevier

(Ni-GNPs) during electrochemical deposition. Finally, the results showed that oxygen mediates the formation of the Cu-O-C bond during the electrochemical deposition process and that this bond modifies the interstitial oxygen atoms by combining them with ionic or covalent bonding in the crystal lattice of copper [126].

Another interesting example of graphene/metal composites are graphene composites reinforced with aluminum (graphene/Al). These composites when dispersed uniformly in graphene show an improvement in their properties related to strength and stiffness [43]. A way to prepare the graphene/Al composite is to use the pressure infiltration method. The schematic preparation process of the GNPs/Al composites is given in Fig. 13. Initially, graphene nanoplates (GNPs) are mixed with pure aluminum powder (Al) using a planetary mill at a speed of rotation. Soon after, the mixture is placed in a steel mold up to a defined height to prepare the preforms. This step is performed with addition of pressure to the defined height. The infiltration of molten Al is carried out at low temperature and with higher pressure (15 MPa) to inhibit the reaction and overcome the poor wettability between the graphene and the Al matrix. No Al_4C_3 phase was detected in the composites, while GNPs have been well bonded with the Al matrix. It is also suggested that the use of graphene with less defect may inhibit the reaction between the pure Al matrix and graphene. In addition, it has been found that the addition of graphene significantly improves the mechanical properties of the composites [118].

5 Adsorption of Organic Compounds

In recent years, graphene-based nanomaterials have sparked great interest into potential applications in a wide range of industrial or agricultural fields. Among these applications, it is possible to mention the adsorption of polluting organic compounds from aqueous medium. These materials can interact with organic pollutants and alter the transport, fate and bioavailability of these contaminants in the environment [91].

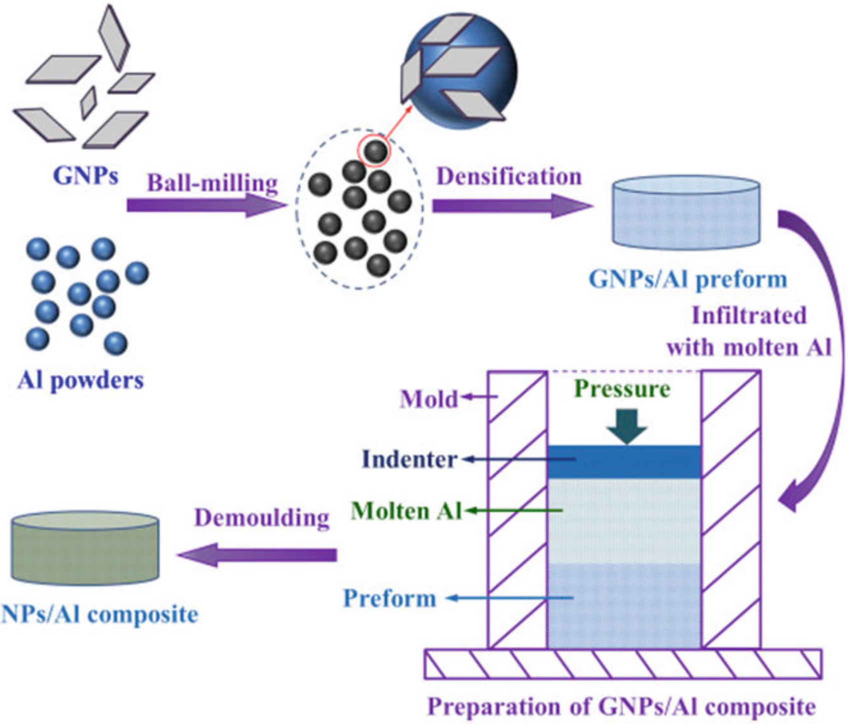

Fig. 13 The schematic preparation process of the GNPs/Al composites. Reproduced with permission from Ref. [118]. Copyright: 2018 Elsevier

5.1 *Pharmaceutical Drugs*

Pharmaceutical drugs are organic pollutants that have attracted increasing attention from recent research. These pollutants are resistant and have become a hazard to the aquatic ecosystem. An example of this type of contaminant is the antibiotic ciprofloxacin (CIP), a type of quinolone. Recent research has produced a hydrogen and graphene adsorbent (GH) from a hydrothermal reduction for the removal of CIP from the aqueous medium. In the adsorption process of CIP on GH, The interactions responsible for the adsorption process were based on the π–π interaction of electron donor-receptor (EDA), which are proven interactions as responsible for the adsorption of organic pollutants with benzene rings on carbon materials [103].

Another example of organic pollutants of pharmaceutical origin are the substances that can affect the endocrine system, called endocrine disrupting chemicals (EDCs). These contaminants can generate serious environmental and health problems. In recent years, EDCs have been found in effluents from different sources, which makes their removal an important issue. Thus, the process of removal of this contaminant type has been well reported in the literature. For example, researchers performed the adsorption of endocrine disrupting chemicals (EDCs), 17α-ethynyl estradiol and β-estradiol, sp^2 hybridized GO sheets. The study showed that 17α-ethynylestradiol and β-estradiol molecules interacted with GO through hydrogen bonds and electrostatic interactions. These interactions originate through the GO-containing oxygen groups and the OH groups of the 17α-ethynyloestradiol molecules as β-estradiol. In addition, there are also the π–π interactions between the π electrons of the GO and the aromatic rings of the molecules of the pollutants. Finally, it was verified that the adsorption process was more efficient in acid medium, with a maximum adsorption of 98.46% and 97.19% for 17α-ethinyl estradiol and β-estradiol, respectively [12].

Another pollutant drug detected in water due to incomplete treatment is diclofenac. This is a pharmaceutical compound with analgesic and antipyretic properties, categorised under the therapeutic class of non-steroidal anti-inflammatory drug (NSAID). The toxicity of diclofenac has been documented in the literature, indicating the adverse effects of this compound on both the environment and terrestrial organisms. A recent research has developed a three-dimensional rGO aerogel (rGOA) for the removal of diclofenac in aqueous solution. The production of rGOA occurred by reducing the GO using a reducing environment (L-ascorbic acid). The highest adsorption capacity of diclofenac on this adsorbent was 596.71 mg under the conditions of: dosage of 0.25 g/L, initial concentration of 325 mg/L, adsorption velocity of 200 rpm and temperature of 30 °C. The pH strongly influenced the adsorption process of diclofenac on rGOA. This study showed that the highest amount of diclofenac adsorbed on rGOA occurred in acid medium, with an amount of 96% of adsorbed drug at $pH < pKa$ and adsorption mechanisms based on hydrophobic attraction, π–π EDA and precipitation. Under basic conditions, it was observed that the amount of drug adsorbed decreased to 81% when the pH reached the value of 9. In this medium, hydrogen bonds and hydrophobic interactions are responsible for the removal of diclofenac using rGOA [37]. Table 2 shows other pharmaceutical pollutants that are removed through graphene and its derivatives.

5.2 *Organic Dyes*

In addition of drugs, dyes are also found in the wastewater. The dyes present high biological toxicity, decrease the transparency of the water and consumption of high quantity of oxygen. This causes a reduction in the capacity of water bodies to perform self-purification, in addition to affecting the growth of water organisms and microorganisms. Like this, the removal of the dyes from the aqueous medium is necessary to reduce water pollution. This can be done using the adsorption process which is one of the most effective ways to turn polluted water into clean water. The use of graphene and its derivatives as adsorbents for dyes has been reported in recent research. For example, researchers prepared graphene-tannic acid hydrogel using GO and tannic acid (TA) through one-step hydrothermal method, as shown in Fig. 14 [106].

The hydrogels produced from graphene were used in adsorption of the organic dye methylene blue (MB). The adsorption process was improved by the presence of

Table 2 Types of pharmaceutical organic pollutants removed using graphene and its derivatives

Adsorbent	Adsorbate	Maximum adsorbed amount (mg g^{-1})	pH	Type of interaction	References
MnO_2/graphene nanocomposite	Tetracycline	168	5	Electrostatic interaction, H-bonding, coordination effect and π–π interactions	[101]
Graphene nanoplatelets (GNPs)	Aspirin Caffeine	12.98 19.72	8	Non-electrostatic interactions	[4]
Phosphorous-doped microporous carbonous material (PPhA)	Ibuprofen Carbamazepine	22.04 17.91	6–7	H-bonding, π–π and n–π electron donor–acceptor interactions	[97]
Nitrogen-doped reduced graphene oxide/Fe_3O_4 nanocoposite	Norfloxacin Ketoprofen	158.1 468	10	Electrostatic attraction, π–π interaction and hydrophobic interaction	[78]
Graphene oxide nanosheet (GOS)	Doxycycline	117	6–7	Cation–π bonding and π–π interaction	[94]
Double-oxidized graphene oxide (DGO)	Acetaminophen	704	8	Hydrophobic interactions	[69]
Graphene oxide (GhO)	Atenolol Propranolol	116 67	2	Electrostatic forces, pi–pi interactions and van der Waals forces	[50]
Graphene oxide nanosheet (GOS)	Sulfamethoxazole	122	6	Electrostatic interaction	[95]
Reduced graphene oxides (rGO)	Sulfapyridine Sulfathiazole	117 142	5	Hydrophobic interaction, π–π EDA interaction and electrostatic interaction	[62]
Magnetic graphene nanoplatelets (M-GNPs)	Amoxicillin	106.38	5	π–π stacking and electrostatic interaction	[44]
Graphene oxide (GO)-based composite	Triclosan	14.5	4	hydrogen bonding, electrostatic, and π–π interactions	[28]

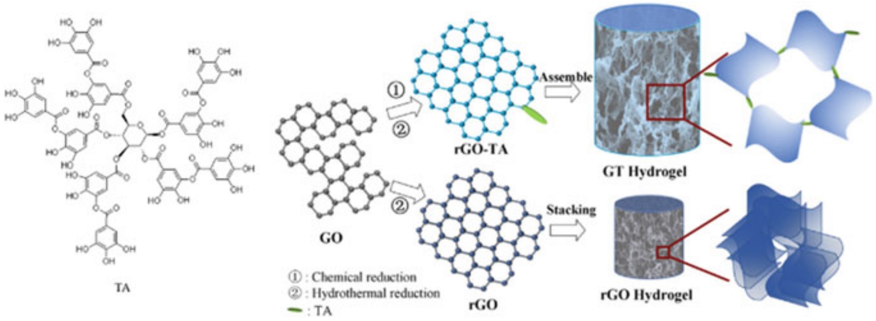

Fig. 14 Structure of TA molecule and formation of the hydrogels. Reproduced with permission from Ref. Tang et al. [106]. Copyright: 2018 Elsevier

tanic acid on the surface of the graphene sheets and microstructures of the hydrogels. In addition, the results showed that the adsorption of the dye on the geis occurs more effectively at alkaline pH. The main mechanism of adsorption of the dye on the surface of the hydrogels is the electrostatic attraction, which increases with increasing pH, reaching a maximum value in pH 10 (the maximum adsorption capacity = 563 mg g^{-1}), due to the presence of tanic acid on the surface of the hydrogels [106]. Thus, graphene and its derivatives can be used as adsorbents for removal of dyes from the aqueous medium. Table 3 shows other examples of dyes removed by graphens and their derivatives.

5.3 Surfactants

Surfactants play a key role in many industrial processes and are chemical substances with The presence of surfactants in aquatic environment is also a major public health concern. the most varied applications. These compounds being biodegraded generate by-products that have been found in aquatic sediments, groundwater, surface water and drinking water. Thus, the adsorption process is also used in the removal of these contaminants from the aqueous medium. Among the adsorbents that can be used in these adsorption processes are compounds derived from graphene, such as GO and rGO. Recently, the GO and rGO were used in the adsorption of the non-ionic surfactant Triton X-100 (TX-100) from water. The adsorption process of TX-100 on rGO was based on hydrophobic interactions and π-stacking. In addition, GO and rGO revealed superior removal capabilities when compared to other adsorbents [82]

Table 3 Examples of dyes removed from aqueous medium using graphene and its derivatives

Adsorbent	Adsorbate	Maximum adsorbed amount	pH	Type of interaction	References
Graphene oxide	Rhodamine B	88%	Not included	Electrostatic interactions	[67]
Graphene nanosheets	Methyl orange	22%	neutral pH	Van der Waals interactions	[5]
Partly reduced graphene oxide aerogels induced by proanthocyanidins	Neutral red Amino black Congo red	382.40 mg g^{-1} 313.37 mg g^{-1} 308.86 mg g^{-1}	Not included	Interaction force hydrophilic	[59]
Graphene oxide intercalated montmorillonite nanocomposite	Crystal violet	575 mg g^{-1}	6.2	Interactions π–π and hydrogen bonding	[83]
Poly(methyl methacrylate)/graphene oxide-Fe_3O_4 magnetic nanocomposite	Malachite green	92%	12	Electrostatic interaction	[86]
Graphene oxide	Proflavine	~90%	9	Electrostatic interaction	[10]
Graphene oxide-doped nano-hydroxyapatite	Trypan Blue	~100%	pH < 11	Electrostatic and π–π interactions	[81]
Modified magnetic graphene oxide by metformin	Methyl violet Acid red 88	239 mg g^{-1} 173 mg g^{-1}	7 4	Electrostatic and π–π interactions	[1]
Graphene oxide modified with polystyrene	Reactive Blue 19 Direct Red 81 Acid Blue 92	13.13 mg g^{-1} 19.84 mg g^{-1} 15.44 mg g^{-1}	7	Not included	[8]
Graphene oxide	Basic Yellow 28 Basic Red 46	64.50 mg g^{-1} 81.40 mg g^{-1}	11	Electrostatic interactions, π–π interactions and hydrogen bonds	[46]
Graphene oxide/chitosan aerogel	Metanil yellow	430.99 mg g^{-1}	~6.8	Electrostatic attraction, π–π stacking and hydrogen bonding	[51]

(continued)

Table 3 (continued)

Adsorbent	Adsorbate	Maximum adsorbed amount	pH	Type of interaction	References
Graphene oxide (GO)	Acid Orange 8 Direct Red 23	27.80 mg g^{-1} 23.30 mg g^{-1}	3	Electrostatic interaction, H-bonding and π–π stacking interactions	[47]
Graphene oxide (GO)	Basic Red 12	56.30 mg g^{-1}	9	Electrostatic interactions	[68]
Polypyrrole/ Chitosan/Graphene oxide (PPy/CS/GO) nanocomposite	Ponceau 4R	6.27 mg g^{-1}	2	Electrostatic interactions, hydrophobic effect and π–π bonds	[15]
dithiocarbamate-functionalized graphene oxide	Basic Blue 41	~80%	4.5	Electrostatic interactions	[63]

5.4 *Pesticides*

In addition, another serious environmental problem is the contamination of water with pesticides. Pesticides are classified according to their biological function and target organism (herbicides, fungicides, rodenticides, insecticides, etc.). The presence of pesticides in the environment can cause serious damage to human health, such as headaches and nausea to chronic impacts such as cancer, reproductive damage and endocrine disruption. The pesticides are very soluble and cause adverse effects even at levels of µg/L and are therefore considered primary pollutants for aquatic ecosystems. An efficient process for the removal of pesticides from the aqueous medium is to use graphene based nanocomposites as adsorbent through the adsorption process. For example, a study used Fe_3O_4/rGO nanocomposite for the adsorption of the pesticide ametryn in an aqueous medium. The adsorption process of this pesticide on the Fe_3O_4/rGO nanocomposite showed was efficient of the 93.61% due to electrostatic, hydrophobic and π–π interactions of composite towards the heterocyclic conjugation of pesticide molecule [13].

Another organic pollutant in the waters is bisphenol A (BPA). BPA is an example of biphenol compounds (BCs) being one of the most produced in the world. BCs exhibit various adverse effects, such as endocrine disruption, cytotoxicity, genotoxicity, reproductive toxicity, dioxin-like effects, and neurotoxicity. These effects caused several materials to be used for the removal of BPA from the aqueous medium, among them we can mention the adsorption process using nanomaterials derived from graphene. For example, a study showed which the graphite (GP), GO and rGO can be used as adsorbents for BPA. The rGO has the highest adsorption capacity

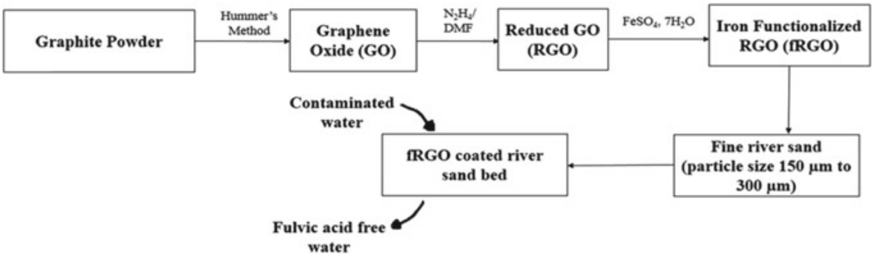

Fig. 15 Flow diagram of fulvic acid removal by iron-functionalized reduced graphene oxide (fRGO). Reproduced with permission from Ref. [89]. Copyright: 2017 Royal Society of Chemistry

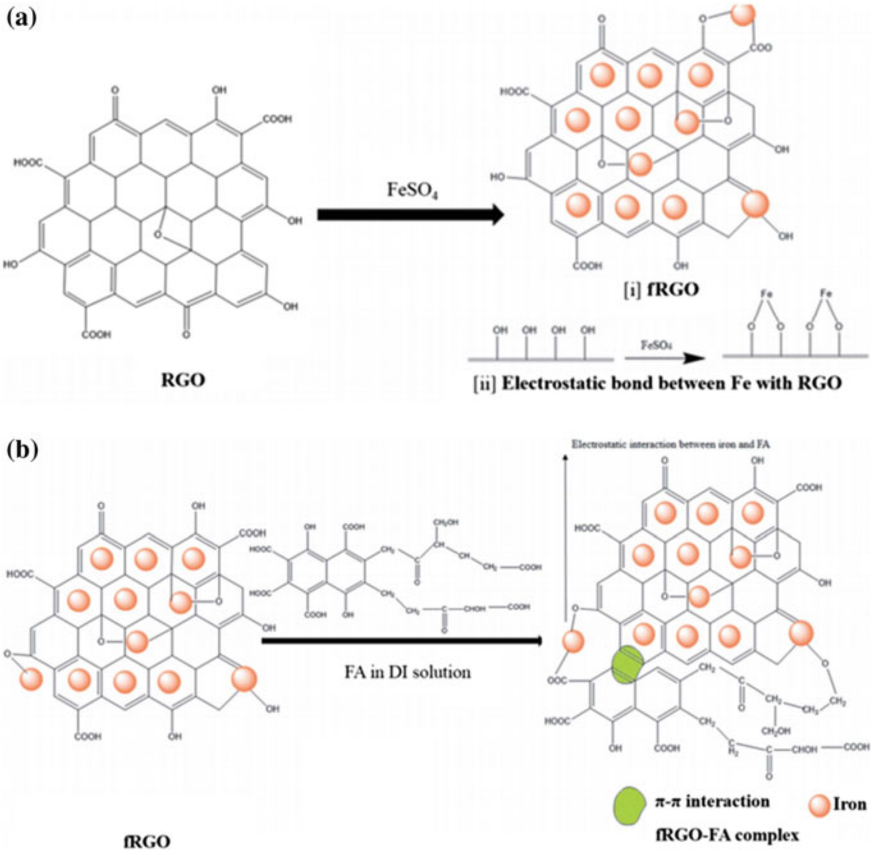

Fig. 16 **a** RGO to fRGO conversion by adding $FeSO_4$ **b** Proposed FA-fRGO interactions complex. Reproduced with permission from Ref. [89]. Copyright: 2017 Royal Society of Chemistry

for BPA than GO and GP. The study showed that the interactions reponsible for the adsorption of BPA on the GP are the hydrophobic interactions and on the rGO were the π–π interactions [109].

In addition to these pollutants, there is also natural organic matter (NOM) which is a complex of organic substances that are dangerous to the environment and have been found in surface water [3]. One way to remove this type of pollutant is to use the adsorption process with adsorbents derived from graphene. For example, recently, a research prepared an iron-functionalized rGO (frGO)-coated and was that used for the adsorption of natural organic matter, such as fulvic acid (FA), from synthetic water. The production process of the iron-functionalized frGO is shown in Fig. 15.

The study indicated that iron-functionalized frGO can be used as an effective adsorbent material for the removal of contaminants such as fulvic acid. The pH was a variable that influenced the adsorption process of the FA on the fRGO, being that the greater adsorption occurred in low pH. The adsorption mechanism was based both by electrostatic interactions and π–π interactions (Fig. 16) [89].

5.5 *Other Organic Pollutants*

Other organic molecules that are not include in the different categories defined before, are also considered extremely dangerous for aquatic ecosystems. Table 4 presents other examples of organic pollutants removed from aqueous medium using graphene and its derivatives.

Table 4 Other examples of organic pollutants removed from aqueous medium using graphene and its derivatives

Adsorbent	Adsorbate	Maximum adsorbed amount	pH	Type of interaction	References
Graphene oxide	Dodecylamine Hydrochloride	∼1150 mg g^{-1}	Not included	Electrostatic interaction and hydrogen bonding	[20]
Magnetic chemically-reduced graphene (MCRG)	Phenanthrene	∼29 mg g^{-1}	5	π–π interactions	[39]
Graphene-metal-organic framework (MOF)	Benzene	24.50 mmol g^{-1}	Not included	π–π interactions	[104]
Chemically reduced graphene (CRG)	Naphthalene 1-Naphthol	∼142 ∼247 mg g^{-1}	5 5	Hydrophobic effect, π–π interaction and Sieving effect π–π interaction, n-π EDA interaction, H-bonding and Lewis acid-base interaction	[111]

(continued)

Table 4 (continued)

Adsorbent	Adsorbate	Maximum adsorbed amount	pH	Type of interaction	References
Graphene oxide/montmorillonite nanocomposite	p-Nitrophenol	15.54 mg g^{-1}	6	Not included	[123]
Defective graphene oxide (GO-COOH)	Nicotine	~125 mg g^{-1}	8	π–π interaction and cation-π bonding	[60]
Sodium bisulfite reduced graphene oxide aerogels	Tetrabromo bisphenol A	128.37 mg g^{-1}	7	π–π interaction	[124]
Graphene oxide–silver nanocomposite	Ethyl violet	39.59 mg g^{-1}	9	Electrostatic attractions	[70]
Fe_4O_3–graphene oxide (GO)–β-cyclodextrin (β-CD) nanocomposite	Thiamethoxam Imidacloprid Acetamiprid Nitenpyram Dinotefuran Clothianidin Thiacloprid	2.88 mg g^{-1} 2.96 mg g^{-1} 2.88 mg g^{-1} 2.56 mg g^{-1} 1.77 mg g^{-1} 2.88 mg g^{-1} 3.11 mg g^{-1}	Not included	Hydrogen bonding, hydrophobic interactions, electrostatic interactions, and π–π stacking/interactions	[61]
Graphene oxide (GO)	Metformin	~47 mg g^{-1}	6	π–π interactions and hydrogen bonds	[127]

5.6 Conclusions

Thus, it can be observed that there are several ways of producing graphene and an extremely versatile nanomaterial. This versatility causes graphene to undergo various chemical modifications on its surface to improve its physical, chemical and mechanical properties. In addition, graphene can form several composites with a myriad of materials (clays, polymers, metals, etc.). Finally, it can be concluded that graphene and its derivatives have been used as efficient adsorbents in the removal of emerging organic contaminants (pharmaceuticals, dyes, surfactants, pestiscides, etc.) from the aqueous medium, and nanomaterials have become promising for the decontamination of this pollutants of the environment.

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