FUNCTIONALIZED GRAPHENE-BASED MATERIALS AS INNOVATIVE ADSORBENTS OF ORGANIC POLLUTANTS: A CONCISE OVERVIEW

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Abstract - The functionalization of graphene nanosheets is the cutting edge of materials sciences nowadays. Such research promotes the development of innovative, low cost and highly capable sorbents. This review article aims to assemble the available information on functionalized graphene used for the adsorption of organic pollutants and establishes a critical comparison between the data reported in the literature. Various optimal experimental conditions (pH, temperature, contact time, adsorbent dosage) and adsorbent characterization methods (FTIR, Raman, XPS spectra, XRD, TEM and AFM) have been listed to enlighten adsorption mechanisms, capacity and limiting aspects. Moreover, adsorption isotherms, kinetics and thermodynamic data of different functionalized graphene-based materials towards a wide range of organic pollutants were analyzed and tabulated. In each evaluation topic, environmental and human health protection is subject for discussion, as well as the scientific breakthrough works available in high impact journals in the field.

Keywords: Adsorption; Graphene; Functionalization; Atmospheric; Wastewater; Organic pollutants.

INTRODUCTION

The development of new graphene-based engineering materials is at the cutting edge among recent research in chemical and materials engineering. There are two ways to insert functional groups on the graphene nanosheet surface via chemical routes: by covalent or non-covalent functionalization. Graphene covalent chemical functionalization creates covalent bonds by converting sp² into sp³ orbitals (Daukiya et al., 2017; Vecera et al., 2017); however, surface enhancement can also be achieved by non-covalent functionalization, in which there are weak intermolecular interactions between the ligand and graphene structural elements, such as dipole-dipole and van der Waals forces (Punetha et al., 2017).

The functionalization of graphene or graphene oxide (GO) nanosheets confers specific properties to the composites, e.g., their chemical selectiveness, solubility, thermal and electronic conductivity (Bueno et al., 2017; Xiang et al., 2016). Such enhancement allows the employment of functionalized graphene-based materials in several fields, such as chemistry and catalysis (Yé et al., 2018; Rana and Jonnalagadda, 2017), biomedicine (Kenry et al., 2018; Yu et al., 2018; Zeng et al., 2017), electronics (Scidà et al., 2018; Gevaerd et al., 2018; Chiu et al., 2017; Zhao et al., 2017), energy (Li and Zhi, 2018; Sadri et al., 2017) and environmental sciences and technologies (Ren et al., 2018; Othman et al., 2018; Khurana et al., 2018). Due to their large specific surface area and rich porous structure, carbonaceous materials usually show
high adsorption capacity and have been successfully employed as adsorbents of organic pollutants (Zhang et al., 2017). Functional moieties distributed on the graphene surface and edges facilitate sorbent-sorbate specific interactions, which depend on the pollutant structure. In this sense, discovering the nature of the forces involved is crucial for enhancing the adsorbent selectiveness and performance (Kyhl et al., 2018). The most reported interactions are π−π stacking, electrostatic, van der Waals forces and H-bonds (Xue et al., 2018; Das et al., 2017; Wang et al., 2017a).

The most toxic and dangerous organic pollutants discharged into the environment, which have been object of study for adsorption onto graphene-based nanomaterials, are listed as follows: organic dyes (Das et al., 2018; Ganesan et al., 2018), polycyclic aromatic hydrocarbons (Yang et al., 2015), pharmaceuticals (Akpotu and Moodley, 2018; Rostamian and Behnejad, 2018), pesticides (Zhang et al., 2015; Maliyekkal et al., 2013), herbicides (Liu et al., 2016; Wu et al., 2015), oil-derived products (Huang and Yan, 2018; Xia et al., 2018; Xiao et al., 2018) and volatile organic compounds (VOCs) (Chen and Chen, 2015). These compounds frequently present aromatic rings in their structure, hence they have the property to degrade and deliver carcinogenic and mutagenic products in water bodies and the atmosphere (Zhang et al., 2017; Carvalhlo et al., 2016). Furthermore, the bioaccumulation of products such as pharmaceuticals, pesticides, plasticizers, hormones and their by-products in water bodies may also generates microbial drug resistance (Sophia and Lima, 2018; Andersson and Hughes, 2012; Merlin et al., 2011). Modified graphene has also been tested as gatekeepers for several chiral molecules, many of them with bioactive and toxic properties (Hauser et al., 2014). Among the advantages of employing functionalization processes on graphene and graphene oxide nanosheets, it can be cited: increase of sorbent selectivity towards specific classes of pollutants (Lazarevic-Pasti et al., 2018; Shrivas et al., 2017); outstanding adsorption performance in terms of capacity and high recoverability (Suo et al. 2018; Nodeh et al., 2015; Zhao and Liu, 2014); unlimited possibilities of functionalization, oftentimes by using the same reactant (Wanjeri et al., 2018; Bueno et al., 2017); some non-covalent functionalization can be reversed by non-aggressive methods (McCoy et al. 2015); functionalization routes can be developed by using bio and ecofriendly compounds, such as amino acids, wood extracts, chitosan, etc. (Cobos et al., 2018; Xue et al., 2018; Wang et al., 2017b; Wang et al., 2016b). Therefore, some disadvantages can also be pinpointed: high investment and synthesis costs, specific reactants may be needed to perform functionalization and certain operational conditions necessary, increasing the consumption of energy and other resources (Mahmoud et al., 2018); extensive reaction time is pointed out by some articles as a considerable obstacle in chemical functionalization, which increases its costs (Sainsbury et al., 2016); covalent functionalization generally is physically irreversible, hence reactants and graphene structures becomes irrecoverable (Feng et al., 2013); despite graphene itself being reported as non-toxic by some works (Lazarevic-Pasti et al., 2018; Mahmoud et al., 2018), functionalized graphene may releases by-products in the form of gases and ionic species during its synthesis reaction and washing; since their toxicity and harm to human health are not yet entirely known, their disposal in the environment may be treated as a liability (Yang et al., 2013a; Hu and Zhou, 2013); some functionalized graphenes are rather difficult to separate after the adsorptive process, requiring elevated energy consumption and complex operations, such as centrifugation, nanofiltration, decantation and precipitation in large tanks, which demands elevated costs of assembly, operation and maintenance (Yao et al., 2017; Zou et al. 2016a), depending on the adsorption nature.

This paper has the objective to provide a critical review of the state of art referring to recent research works with functionalized graphene used as adsorbents of a wide class of organic pollutants. The environmental impacts of these pollutants, as well as the benefits of the treatment techniques employed have been widely explored.

**GRAPHENE AND ITS DERIVATIVES OVER HISTORY**

The first physical method by which single sheets of graphene were obtained with a certain degree of purity was developed by Novoselov et al. (2004), in which a Scotch-type tape was used to separate the graphene layers from graphite crystals by mechanical exfoliation. In the authors’ words: “Graphene is the name given to a single layer of carbon atoms densely packed into a benzene-ring structure”. This discovery guaranteed him the Nobel Prize in 2010. As a consequence of this breakthrough research, the classical methods of obtaining graphene and GO have been improved through the use of new routes such as oxidation, chemical reduction, electrochemical deposition, ultrasonic exfoliation, among others (De Silva et al., 2017; Yusuf et al., 2015).

Brodie (1980), Staudenmaier (1898), and Hummers and Offeman (1958) were pioneers in developing efficient chemical routes to oxidize graphite. The most widespread method was Hummers’, which consists of a strong oxidative attack on the sp² carbons present in the structural plane by sulfuric acid and potassium permanganate (Figure 1a), followed by a finishing reaction with hydrogen peroxide (Hummers and
Offeman, 1958). Over the years, Hummers’ method has been optimized by the changing some variables, such as reaction time, process temperature, reactant nature and dosages (Muzyka et al., 2017). Nowadays, these synthetic procedures are named “modified Hummers’ method”; however, they keep the original Hummers’ method core steps. The exfoliation of graphite oxide is the next step to obtain pure and single layered graphene oxide (GO) (Figure 1b). These material properties are efficiently achieved by a sonication process (Velasco-Sotto et al., 2015; Pan and Aksay, 2011; Dreyer et al., 2010); however, other techniques, such as thermal exfoliation (You et al., 2013; Brodie, 1860) and the innovative directional freezing (Ogino et al., 2014) have been undertaken to obtain sonication-free GO nanosheets.

Following the exfoliation of GO, the materials can be modified according to their final application. In this sense, graphene-based nanomaterials have been widely used in several fields of the knowledge. One of these stages is the reduction of GO; reduced graphene oxides (r-GO) (Figure 1e) can be obtained by thermal reduction, through heating GO samples to temperatures varying from 250ºC (Lavin-Lopez et al., 2017) to above 800ºC (McAllister et al., 2007). Besides, a chemical reduction of GO can be achieved by adding reducing agents, whose choice depends mainly on avoiding parallel reactions, the cost of synthesis and also the aggressiveness of these compounds to the environment (De Silva et al., 2017). Hydrazine hydrate and dimethylhydrazine (Stankovich et al., 2006; Kovtyukhova et al., 1999) are the most used chemical reductants for GO; however, many ecofriendly substances have been researched to achieve this goal. Among these agents, it is possible to find ascorbic acid (Cobos et al., 2018; Begum et al., 2017; Ahmed et al., 2016), amino acids (Wang et al., 2017c; Ma et al., 2013a), proteins (Sheng et al., 2013; Liu et al., 2010) and microorganisms (Chouhan et al., 2016; Gurunathan et al., 2013; Akhavan and Ghaderi, 2012) reported in the literature.

**FUNCTIONALIZATION OF GRAPHENE AND ITS DERIVATIVES**

The covalent functionalization of graphene (Figure 1c) is characterized by the presence of functional groups bound to the basal plane structure by intense intermolecular forces, with high binding energy. This is typical of covalent bonds, which usually change the sp² hybridization of its G networks, resulting in the formation of defects and loss of electronic properties (Vecera et al., 2017). Doubtless, the most common type of functionalization is the introduction of oxygen-containing groups on the nanosheet surface and it happens in graphite oxidation, with the formation of COO, COOH, CO and OH moieties (Wang et al., 2017d). Organic covalent functionalization reactions of graphene include two general routes: (a) the formation of covalent bonds between free radicals or dienophiles and C═C bonds of pristine graphene and (b) the formation of covalent bonds between organic functional groups and the oxygen groups of GO (Georgakilas et al., 2012). Characteristic of these...
processes are the presence of carbonyl, hydroxyl and carboxyl groups (resulting from the oxidation of graphite itself by the Hummers method); nevertheless, functional moieties, such as amines (Wanjeri et al., 2018; Bueno et al., 2017), amides (Ahmed and Kim, 2017; Mrlik et al., 2016), nitro (Begum et al., 2017), thio-compounds (Mahmoodi et al., 2017; Cai and Larese-Casanova, 2016), carbene cycloaddition (Zan, 2014), among others, can be chemically added to the carbon plane edges and surface. Within the covalent routes, a functionalizing group, such as thionyl, can replace the hydroxyl groups that form on the graphene surface after oxidation (Cai and Larese-Casanova, 2016). The covalent bonding of dibromocarbene groups results in the re-hybridization of the carbon atoms through the formation of cyclopropyl groups, whose degree of defect in the covalent functional group can be confirmed by the Raman spectroscopy after the functionalization of graphene through carbene (Sainsbury et al., 2016).

Graphene or GO can also be functionalized through non-covalent routes, which involve the presence of functional moieties based on weak interactions between them and the structure of the graphene, such as π-π stacking interactions, van der Waals forces and electrostatic interactions (Eigler and Hirsch, 2014). Generally, ionic, metallic or organometallic compounds such as Al⁺³, Mn²⁺, Cu₂⁺, Fe₄O₇, MnFeO₂⁺ (Bisht et al., 2017; Zheng et al., 2016; Muralikrishna et al., 2015), ionic and poly-ionic liquids, such as polyvinylimidazolium, polyvinylpyrrolidone, triphenylenes, pyrene derivatives, among others are employed in non-covalent functionalization synthesis (Cai et al., 2016; Tamilarasan and Ramaprabhu, 2015; Parviz et al., 2012). Ionic (IL) and polymerized ionic liquids (PIL), such as imidazolium (Figure 1d) and vinylimidazolium, confer versatility to graphene-derived nanomaterials, enhancing their adsorption capacity for gaseous pollutants, such as CO, CO₂, NO and SO₂. According to Wang and Wang (2016) and Plechkova and Seddon (2008), although several chemical and physical properties of ILs and PILs have yet to be discovered, these ionic species possess distinct properties, including negligible volatility, high stability, high ionic conductivity, high polarity, and good solubility. Hence, they have been applied to carbon engineered nanocomposites, in innovative synthesis processes, and used as CO₂ blockers with elevated capacity of capture in the form of photocatalysts, mixed-matrix membranes (MMMs), bubble column additives, gaseous adsorbents, among others (Sarfraz and Ba-Shammakh, 2018; Tamilarasan and Ramaprabhu, 2015). Organic polymeric compounds are also applied in both covalent and non-covalent functionalization; though it depends on the strength and nature of their bonds to the graphene basal planes (Xiang et al., 2016; Yang et al., 2013b).

**FUNCTIONALIZED GRAPHENE, ITS INTERACTIONS AND CHARACTERIZATION**

Graphene oxide naturally has hydrophilic properties, physically showing colloidal suspension (Saleem et al., 2018); graphene, on the other hand, shows hydrophobicity, hence easily forms agglomerates irreversibly or even restacks to form graphite via van der Waals interactions in aqueous solutions (Ren et al., 2018; Petosa et al., 2010). The capacity of graphene derivatives to form π-π interactions with adsorbate molecules deserves special attention, which depends on some factors: the occurrence of π electrons in the two interacting species, their molecular geometry and the level of covalent functionalization, from which the graphene π structure retention derives (Bottari et al., 2017; Georgakilas et al., 2012). In this sense, the presence of aromatic rings in the adsorbate molecule contributes highly to π-π interactions with graphene-based adsorbents. Hydrogen bonds and electrostatic interactions are the dominant heteroaggregation mechanism of GO with layered double hydroxides and oxides, such as TiO₂, MgO, ZnO, and positively charged mineral clays (Wang et al., 2017c; Wang et al., 2016a; Zou et al., 2016b). Moreover, electrostatic interactions govern the adsorption of ionic species, such as metals and some small dyes, which frequently are used in their ionized form. Meanwhile, the presence of OH, COOH functional groups on the GO surface can enhance H-bonds and van der Waals forces, which are reported in the adsorption of nitrogen and chlorinated species, such as pesticides and pharmaceuticals. In order to evaluate quantitative information of the nature of the interactions between the adsorbent and the adsorbate, many authors have applied Density Functional Theory (DFT), which allows the determination of significant parameters in the main interactions, such as activation energy, enthalpy of adsorption and intermolecular distances (Li et al., 2017; Zou et al., 2016b). This has been possible through mathematical modeling and phenomenological simulations, performed by molecular dynamics software, such as Gaussian 09 and ORCA 3.3 (Im et al., 2017). Larijani et al. (2015) verified that non-covalent interactions (van der Waals forces) were present in order to stabilize the amino acid-graphene configuration in aqueous medium, information based in theoretical adsorption energies, calculated as -4.8 kcal/mol.

Characterization techniques must be thoroughly chosen according to the functionalized graphene application and desired properties; nevertheless, they consist of a key step in the research of nanocarbon materials as adsorbents. The most used nowadays are Fourier-transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), Raman spectroscopy,
magnetization and transmission electronic microscopy (TEM). The presence of functional groups linked to the graphene structure is easily detected by FTIR (Figure 2a) and XPS, where new peaks appear at different frequencies (cm⁻¹) compared to the previous spectrum (graphene or GO before functionalization). As an example, Figure 2a shows the infrared spectra of the GO before and after functionalization with magnetite and silica. Moreover, the oxidation of graphite and further functionalization increases its interlayer space as a consequence of the carbon plane re-hybridization (Eigler and Hirsch, 2014). Such changes in graphite morphology are detected through electron transmission microscopy (TEM), combined with other analyses, XRD and Raman spectroscopy, and are responsible for facilitating the diffusion of the adsorbate molecules between the adsorbent layers, or even increasing the availability of active sites of this adsorbent. According to Yusuf et al. (2015), TEM is a powerful tool by which high resolution images can be obtained and generates numerous statistical data that make it possible to calculate the thickness between layers. Several data found in the literature evidence that graphene functionalization tends to introduce defects into graphene, such as vacancies and dislocations; however, defect-free structures can be found, especially in non-covalent functionalized graphene (Wu et al., 2018; Tkalya et al., 2014; Becerril et al, 2008). Magnetization techniques can be used to reveal the saturation point of the ferromagnetism and if the functionalized graphene shows diamagnetism or paramagnetism characteristics, which is important if the graphene is functionalized with magnetic nanoparticles, such as α-Fe₂O₃, Fe₃O₄, Mg-Fe₂O₄, among others (Liu et al., 2013; Ai et al., 2011).

Finally, Atomic Force Microscopy (AFM) is another technique commonly used to unravel significant morphological characteristics of graphene-derived nanomaterials (Figure 2e-f). By AFM, graphene layer thickness, the number of graphene layers and the space between these layers can be determined. Moreover, some defects resulting from functionalization are clearly observed, and measured by AFM technique, which can give important data to describe surface phenomena. Wrinkles, folds and layers stacking might be indicative of interactions between functional groups over different graphene layers. Wrinkles can also be consequence of fast “explosion” that the GO is submitted to during reduction or even aggregation of two or more nanosheets (Ghislandi et al. 2015). Thicknesses were between 1 and 3 nm for more than 90% of chemically reduced graphene oxide (Chem-rGO), according to the authors. Moreover, unremoved functional groups, or surfactants on Chem-rGO treated...
surfaces can be easily detect by AFM technique through the appearance of roughness and wrinkles. Nanoparticles anchoring on graphene plane, such as magnetic α-Fe$_2$O$_3$, Fe$_3$O$_4$, MgO, SiO$_2$, among others, are also detected by AFM topographies; particles with very different heights and sizes can be observed and measured through AFM images (Muñoz et al., 2018).

**ADSORPTION OF WATER POLLUTANTS**

Several works reported in the literature, which have explored the use of graphene based nanomaterials as adsorbent of water pollutants, have highlighted that functionalization increased their adsorption efficiency in comparison to their predecessors (Wu et al., 2016; Shi and Ye, 2015). Another remarkable characteristic of functionalized graphenes in comparison to GO is their elevated recyclability, which allows their reuse even after more than ten adsorption-desorption cycles (Wanjeri et al., 2018; Nodeh et al., 2015) as summarized in Table 1. However, the functionalization route must be carefully chosen according to the newly-developed adsorbent and adsorbate properties, as well as the operating conditions of the adsorptive process. Furthermore, functionalization gives the graphene a high specificity, which can make it limited when used for different types of adsorbates.

Recent works have reported that GO and aggregated graphene may cause severe and continuous injury to the lungs after direct inhalation and ingestion, leading to inflammation of pulmonary cells, edema and granuloma formation, among other pathologies (Li et al., 2017; Wang et al., 2017d; Yusuf et al., 2015). GO is also reported as be toxic to bacteria and mammalian cells (Li et al., 2015); therefore, more in depth studies are needed to reach conclusions about the damages caused by functionalized graphene and graphene oxide on human and animals health.

Despite the reported advantages, one key point to be thoroughly considered when working with functionalized graphene as adsorbent is their difficulty of separation. It becomes a major challenge when it comes to operating on large scale. Nanofiltration with filters of Teflon or PTFE, vacuum filtration and centrifugation are employed nowadays to separate graphene-derived nanomaterials from aqueous media, however, this increases operational costs. Therefore, coagulation agents, such as ZnO and MgO, should be employed after adsorption in order to ease its separation from adsorbate and minimize graphene’s adverse influences on the environmental balance after its release (Wang et al., 2017d; Yao et al., 2017). On the other hand, many researchers have applied magnetic nanoparticles successfully to the graphene basal plane via non-covalent functionalization (Shi and Ye, 2015) as an alternative for aggregation and ultra-coagulation, processes which add new chemicals after pollutant removal. Magnetite nanoparticles (Fe$_3$O$_4$) are the most preferred due to their facility, low cost of production and large availability of FeCl$_3$. Magnetite nanoparticles, such as Fe$_3$O$_4$ or α-Fe$_2$O$_3$, are reported to be responsible for conferring ferromagnetic properties to functionalized graphene nanosheets (Cai et al., 2016; Liu et al., 2013), leading to an easy recovery of the adsorbent after the incidence of a magnetic field on the solution by external magnets (Boruah et al., 2017). However, the energy costs of this application must be carefully analyzed to compare its viability with other separation process.

**Aromatic organic pollutants**

Aromatic compounds are the major part of the research involving organic pollutants; hence, their removal processes are particularly benefited by adsorption onto functionalized graphene or reduced graphene oxide, due to their very large delocalized π-electron systems, which provides strong π-π stacking interaction with the aromatic rings of organic compounds (Yang, 2003; Dreyer et al., 2010; Zhu et al., 2010).

Paul et al. (2016) proposed a one-pot hydrothermal synthesis of a composite of Ag/Fe$_2$O$_3$, anchored on reduced graphene oxide (Ag/α-Fe$_2$O$_3$-rGO) via homogeneous chemical precipitation of Fe(OH)$_3$ and simultaneous reduction of Ag(I). The adsorbent was used to remove nitroarenes from aqueous solution. The Raman spectra of Ag/α-Fe$_2$O$_3$-rGO showed two characteristic peaks of rGO, at 1352 and 1590 cm$^{-1}$, corresponding to the D and G band; BET analysis showed high specific surface area and pore volume, of 772.65 m$^2$·g$^{-1}$ and 1.47 cm$^3$·g$^{-1}$, respectively; VSM analysis showed that the magnetization of Ag/α-Fe$_2$O$_3$-rGO is 57.2 emu·g$^{-1}$. The synthesized Ag/Fe$_2$O$_3$-rGO nanocomposite was used as magnetically recoverable sorbent for room-temperature chemoselective reduction of aromatic nitro groups to the corresponding amines. The adsorbent was tested with 10 species of nitroarenes and the average yield and time of reaction evaluated were 95.9% and 41.5 min respectively; the Ag/α-Fe$_2$O$_3$-rGO showed selectivity higher than 99% with all nitroarene species.

Chavez-Sumarriva et al. (2016) employed reduced graphene oxide (r-GO) to remove dodecylbenzene sulfonate from aqueous solution at the optimum conditions of temperature, 25°C, and contact time. A satisfactory adsorption capacity of 546.90 mg·g$^{-1}$ was achieved; however, kinetic data showed that the system reached the equilibrium state after a long time (30 h), with initial concentration of 700 mg·L$^{-1}$. The pseudo-second-order model fitted the kinetic data better, and the Langmuir isotherm is the one which best
represented the adsorption. Moreover, hydrophobic interactions, hydrogen bonding, and π-π interactions were pointed out by the authors as being the most representative according to a study of the pH influence on the adsorptive process.

Another type of metal-graphene oxide functionalization was synthesized by Shi and Ye (2015) to adsorb sulfamides from environmental water body samples. The functionalization of GO was performed at mild temperature (70°C) and anionic medium, under vigorous stirring. The porphyrin-functionalized Fe₃O₄-graphene oxide (TCPP-Fe₃O₄-GO) nanocomposite was used in the adsorption of aromatic sulfanilamides, sulfaguanidine, sulfapyridine, sulfamethoxazole, sulfadiazine, sulfadimethoxine and sulfadimidine. TEM techniques can successfully depict the presence of metallic elements, such as aluminum, impregnated over graphene surfaces (Figure 3f). Such observation can be facilitated when a comparative basis between precursor, metal and functionalized graphene is established (Figure 3d and e). Moreover, TEM images exhibited the presence of magnetic Fe₃O₄ nanoparticles in both Fe₃O₄-GO and TCPP-Fe₃O₄-GO, and a disaggregation of these nanoparticles after the functionalization (Shi and Ye, 2015). However, the values of interlayer spaces before and after the TCPP addition are not presented in the work, which could give substantive information to explain the sulfonamide sorption mechanism. Adsorption results presented satisfactory water treatment efficiency and recovery, between the range 83.7% - 116.7% for sulfamethoxazole and from 84 to 272 mg·g⁻¹ for Sulfadimethoxine. The adsorption mechanism of the prepared TCPP-Fe₃O₄-GO material was investigated and predicted through ion chromatography, pH evaluation and charge balance on the adsorbent surface. The π-π stacking and electrostatic attraction between the positively charged analytes and the negatively charged porphyrin-functionalized Fe₃O₄-GO accelerated the electron transfer between the materials. This is evidenced by the higher adsorption capacity obtained at acid pH.

Figure 3. (a) Synthesis of partially reduced GO via PIL functionalization (PrGO-PIL) (reproduced from Bhunia et al. (2012), with permission from the Royal Society of Chemistry, Copyright 2018); (b) General structure of imidazolium ILs and imidazolylidene NHCs (reproduced from Wang and Wang (2016), with permission from John Wiley and Sons, Copyright 2018); (c) reaction between imidazolium amine-functionalized TSIL and CO₂ (reproduced from Wang and Wang (2016), with permission from John Wiley and Sons, Copyright 2018); TEM images for: (d) metallic aluminum framework; (e) reduced graphene oxide; (f) metallic aluminum-graphene oxide (MA-rGO) nanocomposite (reproduced from Wu et al. (2016), with permission from Springer Nature, Copyright 2018).
Ionic liquid functionalized graphene and coated with magnetic nanoparticles have been successfully used as adsorbent for the extraction of polycyclic aromatic hydrocarbons (Pena et al., 2009). In that sense, magnetic poly-ionic liquid functionalized graphene (PGO-MILN) has been applied as adsorbent of chlorophenols by Cai et al. (2016). The magnetic solid-phase extraction (MSPE) technique was applied to extract chlorophenols from aqueous solution, with recoveries from 85.3 to 99.3%. This result confirmed that PGO-MILN was a kind of highly effective MSPE material used to remove traces of chlorophenols in environmental water. Furthermore, tetrabromobisphenol A (TTBBA), an organic pollutant with capacity to promote the disruption of endocrine function, cytotoxicity and neurotoxicity, was submitted to adsorption by poly(tert-butyl acrylate)-GO (PtBA-GO) (Zhao and Liu, 2014; Lilienthal et al., 2008). π–π interactions were pointed out to be the dominant mechanism of the adsorption, due to the attraction forces generated between π-electrons in graphene C=C bonds and benzene rings of the pollutant and the π-electrons on the basal plane of the adsorbent. Raman spectra showed that the sp²-hybridized carbon G-band (at 1583 cm⁻¹) shifted to 1609 cm⁻¹ after the adsorption, indicating that the adsorption occurred via π–π stacking interactions between TBBPA and the aromatic structure on PtBA-GO (Ma et al., 2013b). π-electron bonds are detected in FTIR spectra, by the revelation of peaks at 1453 and 1369 cm⁻¹, due to the symmetrical deformation vibration of the tertiary butyl groups in tert-butyl acrylate. In the studies of adsorption kinetics and equilibrium, performed by Zhao and Liu (2014), PtBA-GO presented maximum adsorption capacity of 54.17 mg·g⁻¹ at 293 K, and the Freundlich model adjusted better to the experimental data (R², 0.9916). Moreover, the system reached the equilibrium state after 170 min and pseudo-second-order was the most representative model for kinetic data (R², 0.9956). Desorption evaluation showed that PtBA-GO possesses an incredible potential of recyclability, since after six cycles, PtBA-GO adsorption capacity reduced 3.0%. Bhunia et al. (2013) synthetized PIL-GO nanosheets through a simple reaction with 1-(3-aminopropyl)-3-methyl imidazolium bromide (IL-NH₃(Br)) at homogeneous dispersion in polar aprotic organic solvents medium (Figure 3a). Moreover, this reaction took place at low temperatures (50°C), which leads to a major cost saving in the process in comparison to many functionalization routes. Some of the most applied ionic liquids (ILs) are the imidazolium and the imidazolidene (Figure 3b), both compounds can be used to amine-functionalize ILs to enhance their capture properties towards CO₂ (Figure 3c), as performed by Wang and Wang (2016). GO can be systematically functionalized by these PILs and increase their sorption properties to adsorb metallic ions and also organic compounds (Cai et al. 2016).

**Aliphatic organic species**

Fe-Mn-thiol-functionalized graphene oxide (GO-Fe-Mn/S) was applied to remove methylmercury (CH₃Hg⁺) from aqueous solution by Huang et al. (2017). In the adsorbent synthesis, 3-mercaptopropyltrimethoxysilane (3-MPTS) was used as a silanizing reagent after the electrochemical method to obtain GO-Fe-Mn. Three different precursor methods were used to sulphonate the composite: acetic acid method (GO/Fe-Mn-ac), neutral method (GO/Fe-Mn-ne), and ammonium hydroxide method (GO/Fe-Mn-am) (Hakami et al., 2012; Gupta et al., 2014; He et al., 2012) and the maximum adsorption capacity was evaluated for the adsorbent obtained by each method. FTIR spectra revealed stretching vibrations at 673 cm⁻¹, 671 cm⁻¹ and 679 cm⁻¹, indicating the presence of a C-S bond in SGO/Fe-Mn-Ac, SGO/Fe-Mn-ne and SGO/Fe-Mn-am, respectively; and stretching vibrations at 1043 cm⁻¹, 1059 cm⁻¹, and 1047 cm⁻¹, corresponding to C=O/Si-O-M, where M is Si, Fe, or Mn metal ligands. Raman spectra showed no changes in the spectra after the functionalization, indicating that there were no defect occurrences. Similar results were reported by Luo et al. (2017), when compared GO aerogel sponge and grafted GO-polyurethane composite (Figure 4b). XPS spectra revealed a peak at 282.9 eV, which corresponds to a C-Fe bond, hence indicating that the Fe-functionalization had been successful. The BET surface area of SGO/Fe-Mn-am was 2.79 m²·g⁻¹, noticeably smaller than 153.00 m²·g⁻¹ for GO/Fe-Mn. However, the maximum surface area of GO in water is accessible only at concentrations below 35.00 µg·mL⁻¹ (Eigler and Hirsch, 2014; Montes-Navajas et al., 2013). Accordingly, the specific surface area and pores distributions of functionalized graphene adsorbents are not a major factor influencing in the adsorption performance, yet the combination of structural properties of adsorbents and adsorbates defines the adsorption of organic species, such as organophosphorus pesticides, biomedical compounds and many classes of dyes (Lazarevic-Pasti et al., 2018; Yusufl et al., 2015; Kyzas et al., 2014). This is reflected in the adsorption parameters obtained: 33.36 mg·g⁻¹, 28.00 mg·g⁻¹ and 43.88 mg·g⁻¹ for SGO/Fe-Mn-ac, SGO/Fe-Mn-ne and SGO/Fe-Mn-am, respectively. It is clear that the differences in surface area between the three adsorbents did not influence their adsorption capacities. Kinetics studies showed that the uptake of all adsorbents reached the equilibrium state after 500 min. The pseudo-second-order and Langmuir models fitted better the kinetic and equilibrium experimental data, respectively. The study suggested the potential viability of SGO/Fe-Mn for enhanced immobilization of CH₃Hg⁺.
Figure 4. (a) FTIR spectra of GO, functionalized polyurethane-GO and for both samples after adsorption of aqueous organic wastes (reproduced from Fan et al. (2017), with permission from Springer Nature, Copyright 2018); (b) Raman spectra of GO aerogel and polyuretane-GO composite (reproduced from Luo et al. (2017), with permission from Springer Nature, Copyright 2018); (c) TGA analysis of copper-mesh and polymeric-GO (reproduced from Fan et al., 2017); (d) XPS spectra of GO and PGO (reproduced from Fan et al. (2017), with permission from Springer Nature, Copyright 2018).

Aqueous organic waste disposal is a major concern when they are not correctly treated. These organic wastes have the potential to degrade into several compounds that can cause severe diseases in people who consume from this contaminated water body. To minimize the impact of organic matters, Fan et al. (2017) synthesized GO-anchored bio-functional polymer to remove N,N-dimethylformamide (DMF) from wastewater. FTIR spectra (Figure 4a) exhibited an intense peak at 1720 cm⁻¹, which may be attributed to C=O stretching vibration; moreover, increase of peaks at 1384 cm⁻¹ indicated the strong bond of O=C-O, which revealed that the polymers were grafted on GO successfully. XPS spectra of O1s (Figure 4d) revealed that the intensity of the peak at 533 eV, attributed to O=C-O, showed a significant increase after polymerization when compared with GO, which is an indicative that copper-mesh polymer was successfully grafted on GO. TGA (Figure 4c) showed a slight decrease on GO-polymer mass at 190°C, which might be an indicative of low degree of graphite oxidation. Thus, there is no satisfactory discussion by the authors on these analyses.

Pesticides

Pesticides are widely used in agriculture, livestock and pest control; moreover, they have also been used by ordinary people in household gardening and veterinary practice. Many pesticides have aromatic rings in their structure, which leads to carcinogenic diseases, neurotoxicity and other pathologies (Wanjeri et al., 2018). Moreover, organophosphorus pesticide toxicity lies in the fact that these substances are inhibitors of the enzymes acetylcholinesterase, which leads to nervous system malfunction (Lazarevic-Pasti et al., 2018; Heidari and Razmi, 2012). The current main techniques employed to treat pesticides are advanced oxidation and chemical-microbial degradation of the compound. Adsorption onto several different materials has also been used as an end of pipe treatment (Suo et al., 2018; Zheng et al., 2016) Many researchers nowadays have been studying the adsorption of pesticides by graphene-derived nanomaterials due to their selectiveness, versatility, strong mechanical and other key surface properties (Lazarevic-Pasti et al., 2018; Chinthakindi et al., 2015). Table 1 summarizes the results of several functionalized graphene and GO nanocomposites employed as adsorbent of different classes of pesticides and herbicides found in the literature. For most of the functionalized graphene-based materials evaluated in this work, applied as adsorbents of pesticides, their adsorption was fitted by the Langmuir model, which assumes that the adsorption occurs in specific sites located on the sorbent homogeneous surface (Ruthven, 1984). Freundlich model, on the other hand, is characteristic of a heterogeneous surface and is usually applied for intermediate concentration systems (Ray et al., 2017). The pseudo-second-order kinetic model (PSO), that provides a better correlation for systems over a long period (Ho and McKay, 1999), is the one which fit the adsorption kinetics in the major works evaluated, as shown in Table 1. High recyclability (average of 10 cycles) of graphene-based adsorbents is pointed out as an outstanding advantage, since they can be re-applied in the treatment process.

The adsorption of the toxic triazine pesticide Ametryn was studied by Zhang et al. (2015), who used cellulose-GO as adsorbent. The maximum sorption capacity obtained at pH 9.0 and 298 K was 8.53 mg·g⁻¹; however, it is 7 times lower than that achieved by Boruah et al. (2017), who applied Fe₃O₄-GO in the adsorption of the same pesticide at pH 5.0. The electrostatic interactions provoked by the positively charge surface of the adsorbent, which was employed below the sorbent pHₚₑₙ₅₅ (5.5), were responsible for its elevated efficiency. According to Zhang et al. (2015), the ionic charges govern the adsorption of Ametryn onto cellulose-GO; nevertheless, the point of zero charge analysis was not performed for this adsorbent.
This lack of information leads to the assumption that interactions of different natures are involved in the adsorption mechanism.

Wanjeri et al. (2018) used the polymeric magnetic functionalized GO (2-PEA-Fe$_3$O$_4$-GO) to remove three types of chlorinated pesticides, Chlorpyrifos, Parathion and Malathion. Excellent adsorption capacity was obtained for Parathion adsorption (135.00 mg·g$^{-1}$); all experiments were conducted at pH 10 and environmental temperature. The isotherm which best fitted the adsorption for the three pesticides was the Sips model, although the Langmuir model also gave a good fitting. According to the data found in the literature, shown in Table 1, the adsorption fittings of Chlorpyrifos are contradictory; thus, there are experimental data better adjusted by Langmuir (Su et al., 2018; Nodeh et al., 2015), Freundlich (Lazarevic-Past et al., 2018) and Sips (Wanjeri et al., 2018) models.

### Bio and pharmacologic compounds

Kyzas et al. (2015a) and most recently, Hiew et al. (2018) made a systematic and detailed overview

### Table 1. Comparative study for adsorption of pesticides and organic compounds onto functionalized graphene derivatives.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>$S_{BET}$ cm$^2$g$^{-1}$</th>
<th>Adsorbate</th>
<th>Isotherm model</th>
<th>$q_{m}$ mg·g$^{-1}$</th>
<th>Eq. time, min</th>
<th>Kinetic model</th>
<th>pH</th>
<th>Reg. cycles</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CM-P(GO)</td>
<td>-</td>
<td>DMF</td>
<td>Langmuir</td>
<td>95.03</td>
<td>660</td>
<td>PFO</td>
<td>-</td>
<td>3</td>
<td>Fan et al. (2017)</td>
</tr>
<tr>
<td>GNP</td>
<td>-</td>
<td>Chlorpyrifos</td>
<td>Freundlich</td>
<td>140</td>
<td>1440</td>
<td>-</td>
<td>6.0</td>
<td>-</td>
<td>Lazarevic-Past et al., 2018</td>
</tr>
<tr>
<td>2-PEA-Fe$_3$O$_4$-GO</td>
<td>133.00</td>
<td>Chlorpyrifos</td>
<td>Sips</td>
<td>25.60</td>
<td>20</td>
<td>PSO</td>
<td>7.0</td>
<td>10</td>
<td>Wanjeri et al. (2018)</td>
</tr>
<tr>
<td>corn straw cellulose-GO</td>
<td>160.37</td>
<td>Chlorpyrifos</td>
<td>Langmuir</td>
<td>120.48</td>
<td>-</td>
<td>PSO</td>
<td>1.0-7.0</td>
<td>8</td>
<td>Suo et al. (2018)</td>
</tr>
<tr>
<td>SiO$_2$-Fe$_3$O$_4$-graphene</td>
<td>-</td>
<td>Chlorpyrifos</td>
<td>Langmuir</td>
<td>16.58</td>
<td>-</td>
<td>-</td>
<td>6.5</td>
<td>15</td>
<td>Nodeh et al. (2015)</td>
</tr>
<tr>
<td>β-CD-Fe$_3$O$_4$-GO</td>
<td>250.33</td>
<td>Thiacloprid</td>
<td>Langmuir</td>
<td>3.11</td>
<td>60</td>
<td>PSO</td>
<td>-</td>
<td>Liu et al. (2017)</td>
<td></td>
</tr>
<tr>
<td>β-CD-Fe$_3$O$_4$-GO</td>
<td>250.33</td>
<td>Thiamethoxam</td>
<td>Freundlich</td>
<td>0.66</td>
<td>60</td>
<td>PSO</td>
<td>-</td>
<td>Liu et al. (2017)</td>
<td></td>
</tr>
<tr>
<td>β-CD-Fe$_3$O$_4$-GO</td>
<td>250.33</td>
<td>Imidacloprid</td>
<td>Freundlich</td>
<td>1.42</td>
<td>60</td>
<td>PSO</td>
<td>-</td>
<td>Liu et al. (2017)</td>
<td></td>
</tr>
<tr>
<td>2-PEA-Fe$_3$O$_4$-GO</td>
<td>133.00</td>
<td>Parathion</td>
<td>Sips</td>
<td>135.00</td>
<td>40</td>
<td>PSO</td>
<td>11.0</td>
<td>10</td>
<td>Wanjeri et al. (2018)</td>
</tr>
<tr>
<td>2-PEA-Fe$_3$O$_4$-GO</td>
<td>133.00</td>
<td>Malathion</td>
<td>Sips</td>
<td>61.90</td>
<td>20</td>
<td>PSO</td>
<td>3.0</td>
<td>10</td>
<td>Wanjeri et al. (2018)</td>
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<tr>
<td>Fe$_3$O$_4$-r-GO</td>
<td>-</td>
<td>Ametryn</td>
<td>Langmuir</td>
<td>60.90</td>
<td>70</td>
<td>PSO</td>
<td>5.0</td>
<td>7</td>
<td>Borah et al. (2017)</td>
</tr>
<tr>
<td>SiO$_2$-Fe$_3$O$_4$-graphene</td>
<td>-</td>
<td>Lindane</td>
<td>Langmuir</td>
<td>13.04</td>
<td>-</td>
<td>-</td>
<td>6.5</td>
<td>15</td>
<td>Nodeh et al. (2015)</td>
</tr>
<tr>
<td>Ag-r-GO</td>
<td>1123.0</td>
<td>Lindane</td>
<td>-</td>
<td>827.00</td>
<td>15</td>
<td>-</td>
<td>3.0-9.0</td>
<td>5</td>
<td>Gupta et al. (2015)</td>
</tr>
<tr>
<td>SiO$_2$-Fe$_3$O$_4$-graphene</td>
<td>-</td>
<td>Hexaconazole</td>
<td>Langmuir</td>
<td>18.69</td>
<td>-</td>
<td>-</td>
<td>6.5</td>
<td>15</td>
<td>Nodeh et al. (2015)</td>
</tr>
<tr>
<td>SiO$_2$-Fe$_3$O$_4$-graphene</td>
<td>-</td>
<td>Azaconazole</td>
<td>Langmuir</td>
<td>15.35</td>
<td>-</td>
<td>-</td>
<td>6.5</td>
<td>15</td>
<td>Nodeh et al. (2015)</td>
</tr>
<tr>
<td>Fe$_3$O$_4$-GO</td>
<td>-</td>
<td>Endrin</td>
<td>Langmuir</td>
<td>99.00</td>
<td>30</td>
<td>PFO</td>
<td>4.0</td>
<td>-</td>
<td>Shrivas et al. (2017)</td>
</tr>
<tr>
<td>Fe$_3$O$_4$-GO</td>
<td>-</td>
<td>Dieldrin</td>
<td>Langmuir</td>
<td>1.00</td>
<td>30</td>
<td>PFO</td>
<td>4.0</td>
<td>-</td>
<td>Shrivas et al. (2017)</td>
</tr>
<tr>
<td>Graphene quantum dots</td>
<td>1221.0</td>
<td>Oxamyl</td>
<td>Langmuir</td>
<td>70.12</td>
<td>25</td>
<td>PSO</td>
<td>8.0</td>
<td>-</td>
<td>Agarwal et al. (2016)</td>
</tr>
</tbody>
</table>
of several pharmaceutical compound treatments via adsorption, their increasing consumption by humans and animals, and the dangerous passive derived from the discharge of pharmaceutical active compounds in the environment. According to the data presented in the literature, about 30-90% of the pharmaceuticals remain undegradable in humans and animal bodies and are excreted as active compounds in the environment (Khan et al., 2017; Rivera-Utrilla et al., 2013).

Understanding the mechanisms of pharmaceutical adsorption onto graphene and GO is a key-step to optimize the adsorption. In this sense, Khan et al. (2017) evaluated different adsorbent-adsorbate interaction behaviors involving pharmaceuticals. Pharmacological compounds, such as levofloxacín (Sun et al. 2018; Dong et al., 2015), ciprofloxacin (Rostamian and Behnejad, 2018; Wang et al., 2016b; Fei et al., 2016; Ma et al., 2015), dorzolamide (Kyzas et al., 2014), tetracycline (Zhu et al., 2018; Lin et al., 2013; Ghadim et al., 2013), ibuprofen (Banerjee et al., 2016), paracetamol (Shan et al., 2017), aspirin (Akpotu and Moodley, 2018; Al-Khateeb et al., 2014), amoxicillin (Kerkez-Kuyumcu et al. 2016), among others, have had their adsorption onto graphene-based nanomaterials evaluated in several studies reported in the literature, as shown in Table 2.

Different interaction natures between pharmaceuticals and GO are shown in Figure 6 and Figure 7a-d. π−π interactions, hydrogen bonding and hydrophobic interactions are present in the mechanisms of several compounds. The abundance of π-electrons in the G and GO structures, together with large electron clouds due to the aromatic rings in the molecules of the pharmaceuticals, tends to favor π−π interactions (Yu et al., 2015; Eigler and Hirsch, 2014). Moreover, there are plenty of research articles in the literature regarding the use of Density Functional Theory (DFT) to investigate the mechanisms and energetic aspects on the interaction between biomolecules and graphene-derived adsorbents, e.g., amino acids and GO. DOS curves and total density map showed that weak interactions occurred between delocalized π electrons of aromatic rings and the lone-pair electrons of oxygen atoms, distributed on the GO surface. Non-covalent interactions are also detected by these tools, as a consequence of weak but numerous van der Waals forces between the molecules (Larijani et al., 2015). The addition of certain charged functional groups on the surface of the graphene basal plane can change the balance of charges, which tends to attract the ionic compounds of opposite charge via electrostatic attraction; such mechanism was observed by Cai and Larese-Casanova (2016), they evaluated the influence of pH on the adsorption of the cationic atenolol and the anionic ibuprofen by ethylenediamine functionalized GO. In that sense, the adsorption of pharmaceuticals is favored by a cationic attraction when the pK_a is higher than the solution pH, as depicted in Figure 6; the opposite phenomenon drives the adsorption via anionic attraction (Khan et al., 2017). Hydrogen bonds, weak interactions that form between a hydrogen with a partial positive charge and a more electronegative atom such as oxygen, fluorine or chlorine, can be formed between the hydrogen atoms present in the functional moieties and the partially negative charged atoms of the adsorbate molecule. Moreover, an undesirable effect is generated when the molecules of water form hydrogen bonds with the oxygen electronic pair present in the COOH, OH and COC groups. This tends to occupy the GO active sites, and consequently decrease the adsorption of tetracyclines (Khan et al., 2017). However, the adsorption of tetracycline onto graphene nanosheets is reported to be mainly governed by π−π interactions (Yu et al., 2015).

Functionalized graphene has been studied as an adsorbent of pharmacologic-nature contaminants in wastewater, as proposed by Cai and Larese-Casanova (2016). Graphene oxide was functionalized with ethylenediamine (ED-GO) through an acyl chlorination and amidation process that gave a net positive surface charge at pH < 8.1. ED-G had greater sorption capacity for anionic ibuprofen compared to cationic atenolol and neutral carbachazepine. ED-GO XRD diffractograms present an enlargement of the characteristic graphite peak at 2θ = 27°, besides the disappearance of the characteristic peak for GO at 2θ = 8.5°, which is caused by the presence of oxygen functional groups between the layers (Cai and Larese-Casanova, 2016). FTIR spectra for ED-GO reveal the replacement of most O groups with N groups and confirms ethylenediamine functionalization, which is characterized by the following stretchings: 1168 cm⁻¹ (C-N), 1560 cm⁻¹ (N-H) and 1678 cm⁻¹ (N=C=O) (Velickovic et al., 2013; Vukovic et al., 2010; Ramanathan et al., 2005). Ma et al. (2015) evaluated the adsorption of bisphenol-A (BPA)
Table 2. Comparative study of the data found in the literature for adsorption of pharmacological compounds onto functionalized graphene.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Adsorbate</th>
<th>Isotherm model</th>
<th>q_{eq} (mg.g^{-1})</th>
<th>Equ. time, min</th>
<th>Kinetic model</th>
<th>pH</th>
<th>Reference</th>
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<tr>
<td>GO</td>
<td>Metformin</td>
<td>Freundlich</td>
<td>96.75</td>
<td>40</td>
<td>PSO</td>
<td>6.0</td>
<td>Zhu et al. (2017)</td>
</tr>
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<td>β-CD-PL-graphene</td>
<td>17-β-estradiol</td>
<td>Langmuir</td>
<td>85.80</td>
<td>480</td>
<td>PSO</td>
<td>4.2</td>
<td>Jiang et al. (2017b)</td>
</tr>
<tr>
<td>DFB20-GO</td>
<td>Paracetamol</td>
<td>Freundlich</td>
<td>0.10</td>
<td>2160</td>
<td>-</td>
<td>6.0</td>
<td>Shan et al. (2017)</td>
</tr>
<tr>
<td>Ethylenediamine-GO</td>
<td>Ibuprofen</td>
<td>Freundlich</td>
<td>36.00</td>
<td>240</td>
<td>PSO</td>
<td>&lt;4.0</td>
<td>Cai and Larese-Casanova (2016)</td>
</tr>
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<td>GNP</td>
<td>Ibuprofen</td>
<td>Langmuir</td>
<td>3.72</td>
<td>60</td>
<td>PSO</td>
<td>6.0</td>
<td>Banerjee et al. (2016)</td>
</tr>
<tr>
<td>Double-oxidized GO</td>
<td>Acetaminophen</td>
<td>Langmuir</td>
<td>704.00</td>
<td>100</td>
<td>PSO</td>
<td>&lt;8.0</td>
<td>Moussavi et al. (2016)</td>
</tr>
<tr>
<td>FeO_{2}-GNP</td>
<td>Amoxicillin</td>
<td>Temkin</td>
<td>14.10</td>
<td>175</td>
<td>PSO</td>
<td>3.0</td>
<td>Kerkez-Kuyumcu et al. (2016)</td>
</tr>
<tr>
<td>FeO_{2}-GO</td>
<td>Tetracycline</td>
<td>Langmuir</td>
<td>39.10</td>
<td>20</td>
<td>PSO</td>
<td>&gt;5.0</td>
<td>Lin et al. (2013)</td>
</tr>
<tr>
<td>CH_{2}N\text{N}-FeO_{2}-GO</td>
<td>Tetracycline</td>
<td>Langmuir</td>
<td>1233.00</td>
<td>2000</td>
<td>PSO</td>
<td>4.0</td>
<td>Yang et al. (2017)</td>
</tr>
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<td>Ca^{2+} alginate-GO</td>
<td>Tetracycline</td>
<td>Freundlich</td>
<td>131.57</td>
<td>780</td>
<td>PSO</td>
<td>6.0</td>
<td>Zhu et al. (2018)</td>
</tr>
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<td>poly(acrylic acid)-chitosan-GO</td>
<td>Dorzolamide</td>
<td>Langmuir-Freundlich</td>
<td>175.00</td>
<td>1440</td>
<td>PSO</td>
<td>3.0</td>
<td>Kyzas et al. (2014)</td>
</tr>
<tr>
<td>GO</td>
<td>Ciprofloxacin</td>
<td>Langmuir</td>
<td>409.00</td>
<td>120</td>
<td>-</td>
<td>7.0</td>
<td>Sun et al. (2018)</td>
</tr>
<tr>
<td>r-GO</td>
<td>Ciprofloxacin</td>
<td>Langmuir</td>
<td>235.64</td>
<td>120</td>
<td>PSO</td>
<td>8.0</td>
<td>Ma et al. (2015)</td>
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<tr>
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<td>Ciprofloxacin</td>
<td>Langmuir</td>
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<td>700</td>
<td>PSO</td>
<td>6.5</td>
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<td>Levofloxacin</td>
<td>Langmuir</td>
<td>303.00</td>
<td>120</td>
<td>-</td>
<td>7.0</td>
<td>Sun et al. (2018)</td>
</tr>
<tr>
<td>FeO_{2}-r-GO</td>
<td>Norfloxacin</td>
<td>Temkin</td>
<td>22.20</td>
<td>700</td>
<td>PSO</td>
<td>4.5</td>
<td>Tang et al. (2013)</td>
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<tr>
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<td>-</td>
<td>12.98</td>
<td>30</td>
<td>PSO</td>
<td>8.0</td>
<td>Al-Khateeb et al. (2014)</td>
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<td>MCM-41-graphene</td>
<td>Aspirin</td>
<td>Freundlich</td>
<td>769.20</td>
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<td>PSO</td>
<td>2.0</td>
<td>Akpotu and Moodley (2018)</td>
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<td>Diclofenac</td>
<td>Langmuir</td>
<td>500.00</td>
<td>360</td>
<td>-</td>
<td>11.0</td>
<td>Nam et al. (2015)</td>
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<tr>
<td>Single-layered-GO</td>
<td>Sulfa-methoxazole</td>
<td>Langmuir</td>
<td>3709.00</td>
<td>360</td>
<td>-</td>
<td>11.0</td>
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<tr>
<td>GO</td>
<td>Propanolol</td>
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<td>67.00</td>
<td>180</td>
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<td>Kyzas et al. (2015b)</td>
</tr>
<tr>
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<td>Atenolol</td>
<td>Langmuir-Freundlich</td>
<td>116.00</td>
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<td>2.0</td>
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<td>Bisphenol-A</td>
<td>Langmuir</td>
<td>182.00</td>
<td>360</td>
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<td>2.0</td>
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<td>Bisphenol-A</td>
<td>Langmuir</td>
<td>59.60</td>
<td>240</td>
<td>PSO</td>
<td>6.0</td>
<td>Ragavan and Rastogi (2017)</td>
</tr>
</tbody>
</table>

* For the kinetic models, PFO means pseudo-first-order; PSO, pseudo-second-order; and IPD, intraparticle diffusion.

onto graphene and found that many new peaks had been introduced in the FTIR spectrum of graphene after BPA adsorption (Figure 7b). These new peaks at 2800-3000 cm\(^{-1}\) and 400-1800 cm\(^{-1}\) are in accord with the peaks of the FTIR spectrum of BPA and appeared at significant intensities, which indicated that a large amount of BPA molecules had been adsorbed on the surface of graphene. A dual-compound adsorption process was performed to evaluate the effect of adsorbate-adsorbate interactions on each single compound adsorption efficiency; the presence of dual sorbates diminished the sorption extent for each compound compared to sorption in single sorbate experiments. The Freundlich isotherm model fitted better the adsorption of ibuprofen and other pharmaceutical pollutants onto ED-GO (Table 2). These results are in disagreement with other ibuprofen data reported in the literature (Banerjee et al., 2016), though they can be explained by the elevated BET surface area (771 m\(^2\)∙g\(^{-1}\)) of ED-GO in comparison to the other adsorbents, evidencing a greater availability of heterogeneous sites on ED-GO surface (Ruthven, 1984). Furthermore, the Freundlich constants (K\(_{f}\)) obtained for ibuprofen, carbamazepine and atenolol were 291, 129 and 100, respectively.

The reported data for the adsorption of tetracycline by magnetite-GO showed an outstanding increase in the adsorption capacity by comparison to Fe\(_3\)O\(_4\)-GO (Lin et al., 2013) and thiourea-dioxide functionalized...
GO through forming strong $\pi-\pi$ and hydrophobic interactions with the tetracycline molecule, as observed by the endothermic thermodynamic parameters ($\Delta H^\circ = 6.65$ kJ mol$^{-1}$) and the very long time for the system to reach the equilibrium state, 2160 min, in comparison to Fe$_3$O$_4$-GO. The data point to a chemical nature of the adsorption of tetracycline on CH$_2$N$_2$S-Fe$_3$O$_4$-GO and the formation of near-covalent bonds between sorbent and sorbate. However, the lower regeneration capacity of this new adsorbent can be a drawback, since its adsorption capacity decreased from 148 to 52 mg g$^{-1}$ after five cycles. Different from the reported data, Zhu et al. (2018) reported that the Freundlich model better fitted the adsorption of tetracycline onto Ca-alginate-GO, described as a heterogeneous surface adsorbent. Yet, both Langmuir and Freundlich models were tested and the coefficients of determination were almost equal, 0.9938 and 0.9986, respectively. Moreover, the authors showed no sufficient evidences of the heterogeneous arrangement of active sites on Ca-alginate-GO surface, and a more focused study should be performed to unravel this mechanism.

The adsorption of pharmacological hormones (17$\beta$-estradiol and 17$\alpha$-ethynyl estradiol) onto carbonaceous adsorbents was performed by Jiang et al.
(2017a), who tested different carbon-based adsorbents, including multi-walled carbon nanotubes (MWCNT) and graphene oxide nanosheets, and made a comparison between the adsorption capacity reached with each adsorbent. Equilibrium studies were performed and the Freundlich isotherm was applied to obtain the adsorption parameters. The results showed an adsorption capacity for GO of 64.39 mg·g\(^{-1}\). The study of a pre-loading of Natural Organic Matter (NOM) before the adsorption process showed that the competition of NOM decreased the estrogen adsorption by all adsorbents evaluated. Previous kinetic studies showed that the system reached the equilibrium after 1440 min for all adsorbents (Jiang et al., 2016). Then, β-cyclodextrin/poly(L-glutamic acid) supported magnetic-GO was synthetized to adsorb 17β-estradiol and equilibrium experiments presented higher maximum adsorption capacity, 85.80 mg·g\(^{-1}\) (298 K, with Langmuir’s and pseudo-second-order models fitted better), an increase of 33.25% in comparison to the result obtained for GO.

The summarized data revealed that adsorptions of pharmaceutical compounds are better fitted by the models of Langmuir for equilibrium and pseudo-second-order for kinetics. The data presented in Table 2 show that, unlike activated carbons and clay-based adsorbents, the specific surface area does not have a major influence in the adsorption efficiency nor in the adsorbent capacity, since the surface interactions play a major role in the adsorption mechanisms (Eigler and Hirsch, 2014; Kyzas et al., 2014).

**Oil and its derivatives**

Due to the substantial increase of crude oil exploration, as well as the scale-up of production of petroleum derivatives, their main and related activities have caused detrimental and long-term degradation of different ecosystems (Ge et al., 2016; Gu et al., 2014). The adsorption of oil emulsions onto graphene-based materials has been growing in concern and successfully explored in recent studies, showing outstanding adsorption capacities. Newly developed cutting-edge adsorbents consist of functionalized graphene-decorated sponges (Figure 8a-d), hydrogels (Figure 8e) and xerogels; many of them are decorated with magnetic metallic nanospheres and generally present high recyclability (Nguyen et al., 2012).

![Figure 8](image-url)

**Figure 8.** (a) Schematic illustration of the mechanism of formation of graphene/iron oxide hydrogels (reproduced from Ge et al. (2016), with permission from John Wiley and Sons, Copyright 2018); (b) wide scale synthetized oilphilic graphene sponge (reproduced from Nguyen et al. (2012), with permission from the Royal Society of Chemistry, Copyright 2018); (c) SEM images of the bare sponge (d) and the graphene-coated sponge; (e) SEM image of the ice-template growing graphene hydrogel (reproduced from Nguyen et al. (2012), with permission from the Royal Society of Chemistry, Copyright 2018); (f) absorption and desorption mechanism with UV-responsive wettability and air-bubble flow (adapted from Kim et al. (2015), with permission from Springer Nature, Copyright 2018).
Crude oil removal from wastewater by adsorption onto N-doped-reduced-GO presented a maximum adsorption capacity of 210000 mg·g⁻¹ (Rahmani et al., 2018). Samples containing diesel oil emulsion showed maximum adsorption capacity of 25000 mg·g⁻¹ and 733 mg·g⁻¹, for GO (Huang and Yan, 2018) and thermally-reduced GO (T-rGO) (Diraki et al., 2018), respectively; moreover, the Freundlich isotherm model fitted the experimental data better for both GO and T-rGO, confirming the highly heterogeneity of the adsorption sites. Kinetic experiments showed that the oil emulsion reached the equilibrium state after 45 min when adsorbed by GO, with the pseudo-second-order model presenting better adjustment to experimental kinetic data (Huang and Yan, 2018); the adsorption onto T-rGO was noticeably faster, when 90% of oil emulsion reached the equilibrium state after 10 minutes (Diraki et al., 2018). For GO sorption evaluation, kinetic experiments were performed at different temperatures and showed that the adsorption capacity increased with the increase of temperature, while thermodynamic parameters pointed to a spontaneous physisorption process (Huang and Yan, 2018). The intermolecular interactions showed that π−London and van der Waals forces govern the adsorption mechanisms, since the hydrocarbon molecules do not present chemisorption groups (Diraki et al., 2018). The adsorbent high oil selectivity was the reason for the highly efficient separation of the emulsified diesel oil present in the oil-water emulsion from the graphene aerogel. Furthermore, the sorbent recyclability was evaluated as being one of the remarkable characteristics of graphene aerogel. The tests were performed under compressive strain-stress and showed high adsorption capacity after 10 cycles. External O₂ bubble flow may be added to the system (Figure 8f) in order to accelerate the oil desorption process, since it may take too much time only with UV irradiation (Kim et al., 2015).

Volatile Organic Compounds (VOC)

According to the World Health Organization, a large variety of volatile organic compounds (VOCs) are responsible for development of cancer in people all over the world. To minimize the damage caused by VOCs in the environment and human health, GO based materials have been recently employed by several researchers for VOCs treatment (Chabot et al., 2014). VOCs adsorption is strongly influenced by the temperature and the presence of water vapor. Moreover, the presence of oxygen-content groups on the surface of GO (such as hydroxide, carboxyl, phenol, among others) gives it a high hydrophilicity. In this sense, the removal of these groups generates more sp² carbon atoms on the adsorbent, that would weaken the reaction between water vapor and the adsorbent, leading to an increase of the adsorption of VOCs onto GO based adsorbents (Zhang et al., 2017; Asai et al., 2011).

In order to detect the presence of VOCs in the air, Nag et al. (2014) evaluated six types of r-GO based sensors. It was observed that cyclodextrin-functionalized rGO (CD-rGO) had a major non-polar interaction and low disconnection capability, which tended to be used as reference. Van der Waals interactions between the chemical groups present in the conductive cyclodextrin nanocomposites and the VOC can be correlated to the amplitude of their chemoresistive response; in this sense, CD-rGO showed high sensitivity to detect VOC presence in air and water (Kumar et al., 2012; Feller and Grohens, 2004).

The use of reduced graphene oxide (rGO) as absorbent of benzene and toluene was studied by Yu et al. (2017). A good adsorption capacity was obtained for these two toxic and carcinogenic pollutants, 276.4 and 304.4 mg·g⁻¹ for benzene and toluene, respectively. Adsorption dynamics showed that the functional groups on the rGO surface played a significant role in benzene and toluene adsorption; π−π and hydrophobic interactions govern the adsorption mechanisms; moreover, the methyl group of toluene can interact with the O-containing groups at the surface of rGO through hydrogen bonding, which can enhance the interaction between toluene and rGO.

ATMOSPHERIC POLLUTANTS

In face of the advance of industrial power, gaseous pollutants emissions have been substantially increased over the decades and have become one of the most important challenges of the modern society. CO₂ is the atmospheric pollutant which generates major concern nowadays because of its widespread emission from the combustion from automobiles, forest fires and industrial processes. Its capacity to block the infrared radiation in the stratospheric layer aggravates the greenhouse effect and, consequently, global warming (Haque et al., 2017). Another chemical species which causes severe damage to the atmosphere is chlorofluorocarbon (CFC), a gas used in freezers, refrigerators and air-conditioners. CFC has the property to react with O₃ and cause damage to the ozone layer even in residual volumes, responsible for filtering the sunlight UV irradiation (Zhao et al., 2011). Moreover, gaseous inorganic pollutants, such as SO₂ and NOₓ, can react with water vapor present in the air and clouds, causing the acid rain phenomenon (Babu et al., 2016). The environmental consequences of acid rain in big cities are observed in monument and building damages, flora destruction, lowering of soil pH, water body contamination and human diseases; nevertheless, it is rather difficult to quantify them economically (Singh and Agrawal, 2008).
Between the treatments indicated to avoid emissions of gaseous pollutants into the atmosphere, one can cite: gas-liquid absorption (Li et al., 2013; Horikawa et al., 2004), photocatalytic reduction (Wang and Wang, 2016; Sakakura et al., 2007), gas washing (Xiao et al., 2014; Liao and Siddoway, 1996), bio-, micro- and nanofiltration (Serfraz and Bashamkhal, 2018; Soreau et al., 2013; Montebello et al., 2012) and gas-solid adsorption (Yuan et al., 2018; Lalitha et al., 2017). However, gas-liquid absorption is one of the most effective processes to treat gaseous pollutants and decrease the emission of greenhouse effect gases in the atmosphere. Such treatments are widely employed in oil refineries worldwide to degas mercaptans, thiocompounds and SO_x, NO_x compounds which have strong potential to cause acid rain. Develop an alternative to overcome the drawbacks of the use of the classical monoethylenamine and diethylenamine (MEA/DEA) as capture agent for CO_2 and other atmospheric pollutants has been pursued by many researchers. Among the candidates to substitute or to be used as enhancers of liquid-amine-based aqueous solutions, numerous alternative solid absorbents have been designed and investigated, such as zeolites, metal-organic frameworks, mesoporous silicas, hydroaluminas, activated carbons, etc. (Bae et al., 2013; Zhang et al., 2014; Drese et al., 2009; Quang et al., 2016; Gao et al., 2013; Dutta et al., 2014; Zhou et al., 2014). Furthermore, carbon nanomaterials including carbon nanotubes, graphene and graphene oxides have been extensively investigated for CO_2 adsorption (Tamilarasan and Ramaprabhu, 2015; Su et al., 2014; Mishra and Ramaprabhu, 2014; Shen et al., 2015; Chowdhury and Balasubramanian, 2016). The application of functionalized graphene or graphene oxide as adsorbent of air pollutants has been studied and new mechanisms for enhancing the removal efficiency, as well as adsorbent improvements have been proposed (Chowdhury and Balasubramanian, 2016).

**Gaseous pollutants capture**

It is rather difficult to find scientific works about experimental *in situ* adsorption of gaseous pollutants in the literature, the majority of them being related to adsorption simulation and molecular dynamics theoretical studies (such as DFT) (Razmkhah et al., 2018; Kumar et al., 2017; Faye et al., 2016). Computational simulation with mathematical models is helpful to predict and understand the sorbent-sorbate interactions, adsorption mechanisms and the influence of graphene structural properties on the nanoscale (Kumar et al., 2017). Yet, among the papers reporting real gaseous compound removal, a great part is divided between liquid-solid absorption and gas-solid adsorption. Among the last ones, the adsorption of CO_2 and CH_4 are the overwhelming majority nowadays, as summarized in Table 3.

Tamilarasan and Ramaprabhu (2015) evaluated the gain in efficiency of CO_2 adsorption onto polymerized ionic liquid (PIL) functionalized graphene. An ionic liquid (IL) or polymerized ionic liquid (PIL) was integrated with graphene to achieve enhanced carbon dioxide adsorption properties. Graphene was non-covalently functionalized by IL or PIL, and the carbon dioxide adsorption and desorption properties were determined at pressures below 100 kPa. Upon functionalization, IL uniformly covers the graphene surface, while PIL forms highly distributed porous nanoparticles. The PIL functionalized graphene shows 22% higher adsorption capacity than graphene, but lower than amino functionalized carbon nanotubes (CNT-APTS) in a TVSA dual column process, applied by Su et al. (2014); moreover, IL functionalization improves CO_2 capture only by 2%. Interestingly, the adsorption capacities of the integrated systems are higher than those of the individual constituents (either graphene or IL or PIL). It is found that PIL functionalization offers more favorable adsorption and higher adsorbate retention with high adsorption energy, with adsorption capacities of graphene, graphene-IL and graphene-PIL of 695, 710 and 794 mmol·g⁻¹, respectively. Isosteric heats of adsorption are calculated to be in the range of 18-28 kJ·mol⁻¹, suggesting an ease of adsorbent regeneration. These results encourage the integration of PIL with other high surface area nanostructures for further improvement in the adsorption capacity. Table 3 summarizes different functionalized graphene nanocomposites employed as adsorbents of gaseous pollutants.

Song et al. (2017) synthetized melamine-functionalized graphene as additive in the CO_2 gas-liquid absorption process. Monoethanolamine (MEA) was used in aqueous solution as the basic CO_2 absorbent; the absorbance performance of CO_2 in the (MEL-GO)-MEA-H_2O solid-liquid hybrid absorbent for different mass concentrations of MEL-GO in 30 wt% MEA aqueous solution was investigated. FTIR spectra exhibited several bands in the regions 3469 - 3130 cm⁻¹, corresponding to the melamine spectrum and due to intermolecular hydrogen bonding. There are several strong peaks in the 1652-1437 cm⁻² region attributable to the C-N stretching and NH₃ bending vibrations (Mirescu et al., 2012); other characteristic peaks indicate the existence of hydroxyl, carboxyl, and epoxide groups in GO; the MEL-GO spectra, compared with GO, showed that the peaks at 1727 cm⁻¹ and 1384 cm⁻¹ practically disappeared (Chatterjee et al., 2013; Liu et al., 2015). Experimental results showed that the (MEL-GO) solid absorbent can enhance the solubility of CO_2 at lower mass concentrations of MEL-GO in MEA aqueous solution. This is attributed to the effect
of the special two-dimensional structure of the solid absorbent, together with many amine parts from both solid and liquid absorbent. CO$_2$ capture efficiency increased 10% when MEL-GO was used to enhance the absorption process. Despite the good results regarding gas-liquid absorption, MEL-GO was not yet tested as absorbent of liquid pollutants; however, this may be achieved in a further study. CdS nanoparticles were imprinted by amino-functionalized reduced graphene oxide (Figure 9c) and have been successfully tested in the catalytic reduction of CO$_2$ by Cho et al. (2017) (Figure 9b). CO$_2$ was converted into methane via photocatalytic reaction. Suggested mechanism for the amine functionalization of graphene oxide is presented in Figure 9a. Moreover, SEM photographs showed well defined sphere formats for CdS nanoparticles, which was reproduced even after the amino-functionalized GO anchoring (Figure 9e). TEM images exhibited CdS nanoparticles covering by amino-reduced graphene oxide (Amino-G) nanolayers (Figure 9f). Additionally high methane formation rate (1.62 μmol/(g h)) was observed for Amino-G/CdS under CO$_2$ at low pressure (0.1 bar) and visible light, result 20 times higher than GO grafted on CdS surface.

Table 3. Comparative study between the experimental data in the literature for adsorption of gaseous pollutants onto functionalized graphene.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>BET surface area (cm$^2$·g$^{-1}$)</th>
<th>Adsorbate</th>
<th>q$_m$ (mmol·g$^{-1}$)</th>
<th>Operation pressure (kPa)</th>
<th>T (K)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>3D mesoporous graphene</td>
<td>477</td>
<td>CO$_2$</td>
<td>0.68</td>
<td>106.6</td>
<td>273</td>
<td>Wang et al. (2011)</td>
</tr>
<tr>
<td>Graphene nanosheets</td>
<td>-</td>
<td>CO$_2$</td>
<td>75</td>
<td>1,100</td>
<td>298</td>
<td>Mishra and Ramaprabhu (2012)</td>
</tr>
<tr>
<td>Carbon Hollow fibers-Graphene</td>
<td>-</td>
<td>CO$_2$</td>
<td>76</td>
<td>140</td>
<td>298</td>
<td>El sabawy and Fallatah (2018)</td>
</tr>
<tr>
<td>Amine-CdS- graphene</td>
<td>-</td>
<td>CO$_2$</td>
<td>0.08</td>
<td>10</td>
<td>298</td>
<td>Cho et al. (2017)</td>
</tr>
<tr>
<td>Azido-Terpyridine-r-GO</td>
<td>440</td>
<td>CO$_2$</td>
<td>2.66</td>
<td>100</td>
<td>273</td>
<td>Zhou et al. (2014)</td>
</tr>
<tr>
<td>Polyethyleneimine-SiO$_2$-Graphene</td>
<td>32</td>
<td>CO$_2$</td>
<td>4.32</td>
<td>&lt; 100</td>
<td>348</td>
<td>Yang et al. (2013b)</td>
</tr>
<tr>
<td>Polyaniline-graphene</td>
<td>-</td>
<td>CO$_2$</td>
<td>75</td>
<td>1,100</td>
<td>298</td>
<td>Mishra and Ramaprabhu (2012)</td>
</tr>
<tr>
<td>Fe$_3$O$_4$-Graphene</td>
<td>98.2</td>
<td>CO$_2$</td>
<td>60</td>
<td>1,100</td>
<td>298</td>
<td>Mishra and Ramaprabhu (2014)</td>
</tr>
<tr>
<td>H$_2$-r-GO</td>
<td>344</td>
<td>CO$_2$</td>
<td>1.23</td>
<td>100</td>
<td>283</td>
<td>Tamilarasan and Ramaprabhu (2015)</td>
</tr>
<tr>
<td>MIL-101-GO</td>
<td>2950</td>
<td>CO$_2$</td>
<td>22.40</td>
<td>2,500</td>
<td>298</td>
<td>Zhou et al. (2015)</td>
</tr>
<tr>
<td>[ButylMethylimidazolium][BF$_4$]-r-GO</td>
<td>-</td>
<td>CO$_2$</td>
<td>1.10</td>
<td>100</td>
<td>283</td>
<td>Tamilarasan and Ramaprabhu (2015)</td>
</tr>
<tr>
<td>Poly(methylimidazolium)[BF$_4$]-r-GO</td>
<td>-</td>
<td>CO$_2$</td>
<td>1.05</td>
<td>100</td>
<td>283</td>
<td>Tamilarasan and Ramaprabhu (2015)</td>
</tr>
<tr>
<td>3D-graphene</td>
<td>3000</td>
<td>CH$_4$</td>
<td>12.40</td>
<td>3,600</td>
<td>298</td>
<td>Mahmoudian et al. (2016)</td>
</tr>
<tr>
<td>O-nanocarbon</td>
<td>699</td>
<td>CH$_4$</td>
<td>2.27</td>
<td>100</td>
<td>273</td>
<td>Wang et al. (2015)</td>
</tr>
<tr>
<td>MIL-101-GO</td>
<td>2950</td>
<td>CH$_4$</td>
<td>7.50</td>
<td>2,500</td>
<td>298</td>
<td>Zhu et al. (2015)</td>
</tr>
<tr>
<td>Cu-BTC-GO</td>
<td>1677</td>
<td>CH$_4$</td>
<td>1.30</td>
<td>100</td>
<td>273</td>
<td>Huang et al. (2014)</td>
</tr>
<tr>
<td>Graphene nanosheets</td>
<td>300</td>
<td>CH$_4$</td>
<td>3.24</td>
<td>20,000</td>
<td>253</td>
<td>Zhu and Zheng (2016)</td>
</tr>
<tr>
<td>GO-MOF-Cu</td>
<td>-</td>
<td>NH$_3$</td>
<td>2.64</td>
<td>-</td>
<td>298</td>
<td>Petit et al. (2010)</td>
</tr>
<tr>
<td>GO-Cu</td>
<td>8</td>
<td>H$_2$S</td>
<td>0.80</td>
<td>-</td>
<td>298</td>
<td>Mabayoje et al. (2012)</td>
</tr>
<tr>
<td>GO</td>
<td>268</td>
<td>SO$_2$</td>
<td>2.43</td>
<td>101.3</td>
<td>298</td>
<td>Babu et al. (2016)</td>
</tr>
</tbody>
</table>
The operational conditions of temperature and pressure in which the adsorption process takes place have fundamental importance, not only in terms of performance, but also in terms of operational costs. For adsorption of CO$_2$ (Table 3), graphene nanosheets reached 76.00 mmol·g$^{-1}$ of adsorption capacity (Mishra and Ramaprabhu, 2012); however, the carbon fiber-graphene composite obtained 75.00 mmol·g$^{-1}$ with a pressure eight times lower (Elsabawy and Fallatah, 2018). Table 3 also evidences that the adsorption capacity increases with the operational pressure; it is highlighted for CO$_2$ data. This is an effect of the saturation of the adsorbent, which happens at medium and high pressures; this behavior is with regard to the gas-solid interactions, hence microporous structure contributes only at the level of an increase of the specific area of the adsorbent (Malbrunot et al., 1996). Zhu and Zheng (2016) evaluated the adsorption of methane onto graphene sheets and made a comparative study between the results obtained for graphene and the ones obtained for activated carbon and carbon black. Three kinds of carbon materials, graphene nanosheets, activated carbon and carbon black, showed specific surface areas of about 300 m$^2$·g$^{-1}$, 1118 m$^2$·g$^{-1}$ and 76 m$^2$·g$^{-1}$ and were selected for adsorption equilibrium tests within the temperature-pressure range from 253.15 K to 293.15 K and 0 to 8 MPa. Their maximum adsorption capacities at 293 K were 2.17, 11.54 and 1.15 mmol·g$^{-1}$, for graphene nanosheets, activated carbon and carbon black, respectively. This behavior follows a tendency of increasing the adsorbed amount of gaseous pollutants with the increase of the sorbent specific surface area (Georgakilas et al., 2012), unlike adsorption in the liquid phase involving functionalized graphene, where the surface interactions are more determinant than the adsorbent porous structure (Yusuf

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et al., 2015). The Langmuir-Freundlich equation and a lattice theory based adsorption model were employed to determine the isosteric heat of adsorption and the molecular interaction energy between adsorbates, which presented the following values: 16.32-20.26 kJ·mol⁻¹, 15.75-19.05 kJ·mol⁻¹ and 11.91-12.35 kJ·mol⁻¹ for activated carbon, the graphene nanosheets and carbon black, respectively.

Babu et al. (2016) first studied the adsorption of pure SO₂ on graphene oxide (GO) activated with N₂, and compared with thermally treated GO at 150°C and 300°C. The BET measured specific surface area for GO was 268 m²·g⁻¹ following the BET N₂ adsorption method. Moreover, the N₂ isotherm showed type IV hysteresis, where no accentuated increase in N₂ adsorption occurs at low pressures, indicating the absence of extensive micropores (Ruthven, 1984), different from activated carbons. XPS spectra exhibited the characteristic GO C-O (286.1 eV) and O-C=O (288.3 eV) bonding energies; the main peak at 284.4 eV corresponds to the sp² bonded carbons (C-C bonds). The system quickly reached the equilibrium state (after 10 min), according to experimental kinetic data. The adsorption mechanism was found to be fundamentally different from conventional carbon materials such as activated carbon or carbon fibers. It was observed that GO binds SO₂ only by physisorption (ΔH ads 18.04 kJ·mol⁻¹) and still the adsorption capacity was found to be comparable to traditional adsorbents like activated carbon or carbon molecular sieves. The 2D layered morphology, as well as the absence of extensive micropores well known to promote SO₂ to SO₃ conversion is responsible for the observed physisorption characteristics. GO dosage effect analysis showed that SO₂ achieved its best adsorption capacity at 4.50 mmol·g⁻¹. This result was obtained at low operation pressure, in comparison to other reported data (Table 3), which required elevated pressure (up to 2000 kPa) to obtain similar adsorption capacities for CH₄ (Zhu and Zheng, 2016; Zhou et al., 2015).

**CONCLUSIONS AND FUTURE RESEARCH NEEDS**

The application of functionalized graphene and its derivatives as adsorbents towards different organic pollutants is cutting-edge research which have raised the interest of several researchers across the globe. Graphene versatility is pointed out as a characteristic which can be explored in the most varied fields. In this sense, functionalization of graphene plays an important role in the adsorption of aqueous and gaseous pollutants, due to remarkable increases in the adsorption performance. For a better understanding of this phenomenon, this review investigated the interaction mechanisms between functionalized graphene and organic compounds in adsorptive processes of liquid and gaseous systems.

Sorption mechanisms are strongly related to the graphene surface properties. Moreover, these are reported as being primarily responsible for the sorbent capacity; π–π interactions, electrostatic and van der Waals forces are depicted in several works as being the most representative for adsorption of several pollutants. Functional moieties can increase the availability of π-electrons in the system, contributing to the π-stacking interactions between the carbon basal plane and the aromatic structures of the adsorbate.

It was shown that the introduction of specific functional groups on carbonaceous nanomaterials surfaces and edges promoted relevant selectivity for the adsorption of some organic compounds. On the other hand, this new adsorbent may be inefficient towards other species of pollutants. Nevertheless the great sorption capacity, selectivity and high recyclability of functionalized graphene must be highlighted as strong points which motivate focused research.

Adsorption of gaseous pollutants, on the other hand, is described as more dependent on the adsorbent surface area, in comparison to liquid-solid adsorption. However, there are few in situ experimental works described in this field; hence, an in-depth study based on these observations is recommended.

Some challenges regarding the chemical functionalization must be faced by researchers worldwide, such as high production and operational costs, by-product release and their impact on the environment and human health, which are not entirely known. This is with no doubt a fertile field for further investigations. Nowadays few functionalized graphene-based nanomaterials have been tested and analyzed when compared to other well-known sorbents regarding toxicity. Thus, it is recommended that future studies evaluate the impact of the by-products on the environment and human health. Moreover, layered graphene nanosheets remain dispersed in aqueous media even after the adsorption, which makes it rather difficult to separate them from the adsorbate; separation process becomes a major concern from a large scale perspective. However, some works report that graphene dispersion effects can be minimized by introducing metallic oxides into the graphene and GO suspension, favoring their precipitation.

**NOMENCLATURE**

- DFT: Density functional theory
- BET: Brunauer, Emmett and Teller
- XRD: X-ray diffraction
- XPS: X-ray photoelectronic spectroscopy
- TEM: transmission electrons microscopy
- AFM: Atomic force microscopy
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