Water Remediation Using Graphene-Based Materials

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ABSTRACT

Graphene-based adsorbents with three-dimensional (3D) porous structure inherit the perfect carbon crystal structure of two-dimensional (2D) grapheme sheets and reveals many advantages such as high porosity, large surface area and extremely low density. Such exceptional properties enable diverse organic contaminants to easily enter and diffuse into 3D networks, and make these materials perfect adsorbents demonstrating outstanding adsorption and recyclability. The synthesis and use of graphene-based materials for water remediation by adsorptive removal of organic pollutants is an emerging field of research. Functionalization of graphene-based adsorbents have received widespread attention and are largely explored for water purification to get the benefit of their improved properties resulting from synergistic effects. This review deals with the recent trends and progress in the rapid developing field of wastewater purification using graphene-based adsorbents for the removal of toxic organic pollutants. This review highlights the targets achieved, the comparison of structural performance, challenges, limitations and future research directions.

Key words: Graphene, Adsorption, Organic pollutants, Wastewater

I. INTRODUCTION

Most of the water resources like lakes, rivers, groundwater, and even sea water are made impure by toxic organic contaminants such as organic solvents, spilled oil, dyes, pharmaceutical and personal care products and agrochemicals. Clean water is vital need to maintain human health as well as environmental sustainability but owing to the overuse of agrochemicals, industrialization growing at alarming rate and its byproducts have polluted water making it unfit for human consumption. It is to be noted that water pollution by toxic organic contaminants is complex in reality as one has to deal with the co-occurrence of diverse type of pollutants [1]. Water treatment is further hindered by imperfect water quality assessments and poor data compilation based on water purification techniques employed for removal of multipollutants in used water. Therefore, tactics to tackle these multipollutants is crucial challenge in water purification and thus there is need to develop efficient water purification technologies to remove these multipollutants from wastewater [1, 2]. Conventional water remediation techniques include physical, chemical and biological processes at preliminary, primary, secondary, and tertiary levels which are essential to purify wastewater containing several types of multipollutants [3]. Physical processes are such as filtration, adsorption, distillation, skimming and sedimentation; chemical

processes are oxidation, chlorination, precipitation, neutralization, hydrolysis, electrochemical, ultraviolet irradiation and ozonation and biological processes include either of the aerobic or anaerobic treatment conversions. In many of the existing water purification techniques there are several drawbacks such as high consumption of energy, huge operation cost, poor removal efficiency, production of toxic side products and secondary pollutants [3, 4]. Many of the carbon-based materials like charcoal, porous carbon, graphene, carbon nanotubes are widely used for the adsorptive removal of organic pollutants from wastewater [5, 6]. They have received great attention owing to their high surface area, low cost, remarkable affinity towards organic contaminants and ease of modification [7]. Among the existing carbon-based materials, graphene-based adsorbents have received notable attention in adsorptive removal of organic contaminants owing to their unique characteristics such as large surface area and diverse active sites for adsorption [8]. The adsorption performance of graphene-based adsorbents for the removal of organic pollutants is based on the interaction mechanisms between the pollutants and graphene-based materials and therefore understanding this correlation is crucial for the further development in the design of graphene-based functional materials to enhance their practical applications.

Graphene is made up from the 2D layer of sp^2 hybridized carbon atoms which are packed to form honeycomb type lattice [9]. 2D graphene is unique in terms of its dimensions because it can be enfolded to form 0D fullerene, rolled to form 1D-carbon nanotubes and further it can be stacked to form 3D graphite [10]. Graphene exhibits a very large theoretical surface area of 2630 m^2/g [11]. However, graphene has a property to generate restacking and irreversibly agglomerate because of van der Waals forces and strong π-π bonds that results into the lowering of its surface area than the theoretical value to a great extent and limits its practical use [12]. In order to effectively exploit the outstanding properties of graphene has become a major challenge and opportunity for researchers all over the world. To circumvent the above mentioned phenomenon, the promising strategy is employed, wherein 2D graphene sheets are converted into the assembly of 3D macroscopic structures. This conversion no way changes the fundamental exceptional properties of graphene sheets but further improves combined useful properties like high porosity, low density and notable mechanical and electronic properties [13, 14].

Graphene oxide (GO), one of the derivatives of graphene, has been largely used for the adsorption of several organic pollutants [15, 16]. But reduced graphene sheets and GO are different than that of pristine graphene in particular aspects. Pristine graphene has no oxygen in it whereas reduced graphene sheets and GO contain C:O ratio of 8:246 and 2:4, respectively. The Young modulus for pristine graphehe is 1000 GPa, whereas in GO it is largely compromised to 200 GPa and in the reduced GO (RGO) it is somewhat improved to 250 GPa. As compared to graphene, the production cost of RGO and GO is very low [17], which is one of the reasons for the wide use of GO. The oxygen functionality on GO renders a negative charge on its surface which aids to adsorb cationic organic dyes, electrostatically [18]. Thus the presence of oxygen in GO enables it for the adsorption purposes. Moreover, aromaticity of the GO also helps to interact, via the π-π interaction, with that of the aromatic groups on the organic pollutants. Owing to the presence of reactive species, functionalization of the GO is approachable [19]. Various reactive organic functionalities present on the GO are carboxylic acid, hydroxyl group and epoxy ring. The carboxylic acid functionality shows enhanced reactivity as it occupies the peripheral sites on the GO sheets. In order to get the functionalized GO the carboxylic group is activated by using thionyl chloride followed by the attack of nucleophile to generate the covalent bond linkage [20]. Functionalized GO can be obtained by using another reactive moiety, the hydroxyl group, which work as a nucleophile and smoothly attacks ketone to join the required ketone bearing functionality on the GO [21].

Lastly, the epoxy group on the GO can be smoothly opened by the attack of nucleophile to attain the functionalized GO [22]. Besides this, GO can also be functionalized using inorganic particles like metals, non-metals and their oxide nanoparticles [23].

II. REMOVAL OF ORGANIC POLLUTANTS

Albeit, there are several reviews available on graphene and its derivatives for water purification [24-27], this review focuses on the recent progress and strategies employed for the removal of organic dyes, pharmaceuticals, endocrine disrupting chemicals, brominated flame retardants (BFRs) and other organic compounds.

1.1. Organic dyes

Wastewater treatment and its reuse is a challenging approach for environmental sustainability. The large quantity of water utilized in the textile industry is just one side of this serious issue. Before the wastewater contaminates the other water sources, it must be treated properly for the efficient removal of dyes. Use of graphene and its derivatives is one of the best alternatives for the effective removal of dyes. This subsection highlights the representative examples for the graphene-based adsorptive removal of organic dyes. Organic dyes are colored macromolecules that are classified on the basis of molecular structure, solubility, charge or the chromophores residing in their structure [28, 29]. Several dyes such as direct, reactive, acid and base dyes are water-soluble dyes whereas disperse, azo, vat and sulphur dyes are water-insoluble dyes [30]. The aromatic rings present in their structures facilitates the interaction between the delocalized electrons on benzene ring and the delocalized π electrons present on the basal plane of the sheets via π- π and cationic- π interactions along with that of the hydrogen bonding and electronic interaction originating from the sp^3 domains of the graphene sheets. It is to be noted that functionalized graphene exhibits improved dye removal performance than the pristine graphene because of the charge groups present on the organic dyes. For example, GO with the negative charge on its surface exhibits improved performance for the adsorption of cationic dyes than that of anionic dyes while the latter are efficiently removed with the graphene modified using cationic functional groups like amine, chitosan and polyethyleneimine [31].

Organic dyes can be successfully removed from wastewater using the approaches that relies on the interaction between organic dyes and functionalized graphene. For instance, graphene sheets coated with polydopamine are fabricated for the effective removal of methylene blue, methyl violet and 4-nitrophenol via π-π and electrostatic interactions between organic dyes and polydopamine as the latter carries nitrogen and oxygen functional groups [32]. Sulphonated graphene nanosheets with $-SO_3H$, $-OH$ and $-COOH$ functional groups adsorb methylene blue mainly because of the electrostatic interaction apart from the slight contribution via π-π interaction [33]. A similar approach was demonstrated by GO/chitosan aerogel with dual functionality that exhibited electrostatic as well as π-π interactions between the cationic dyes and oxygen bearing groups on GO. The same functionalized GO shows adsorptive removal of anionic dyes because of the amino groups present on the chitosan chains [34]. Moreover, it was found that GO exhibits improved adsorption efficiency for methyl green with increase in temperature [35]. The highest adsorptive efficiency calculated by Langmuir was 5.496 mmol/g at pH 5.

Liu et al. prepared GO sponge by centrifugal vacuum evaporation method and this GO sponge exhibited higher adsorptive removal efficiency of 99.1% and 98.8% and that too in just 2 min for methylene blue and methyl violet, respectively [36]. Figure 1a shows a synthetic scheme for 3D GO sponge preparation. In the first step,

modified Hummers method was used to prepare the GO sheets. GO sponge was fabricated using a centrifugal vacuum system. Figure 1b confirms that the prepared GO sponge reveals high flexibility. It was found that the extruded GO sponge quickly recovered its original shape. Figure 1c and d represents SEM images for the GO sponge at low and high magnification. Figure 1c presents finely-assembled interconnected layers of GO sheets that construct a 3D network, while Figure 1d represents a fairly smooth organization of 3D linked graphene sheets that possesses an outstanding structural as well as mechanical stability to impart awesome adsorption capacity.
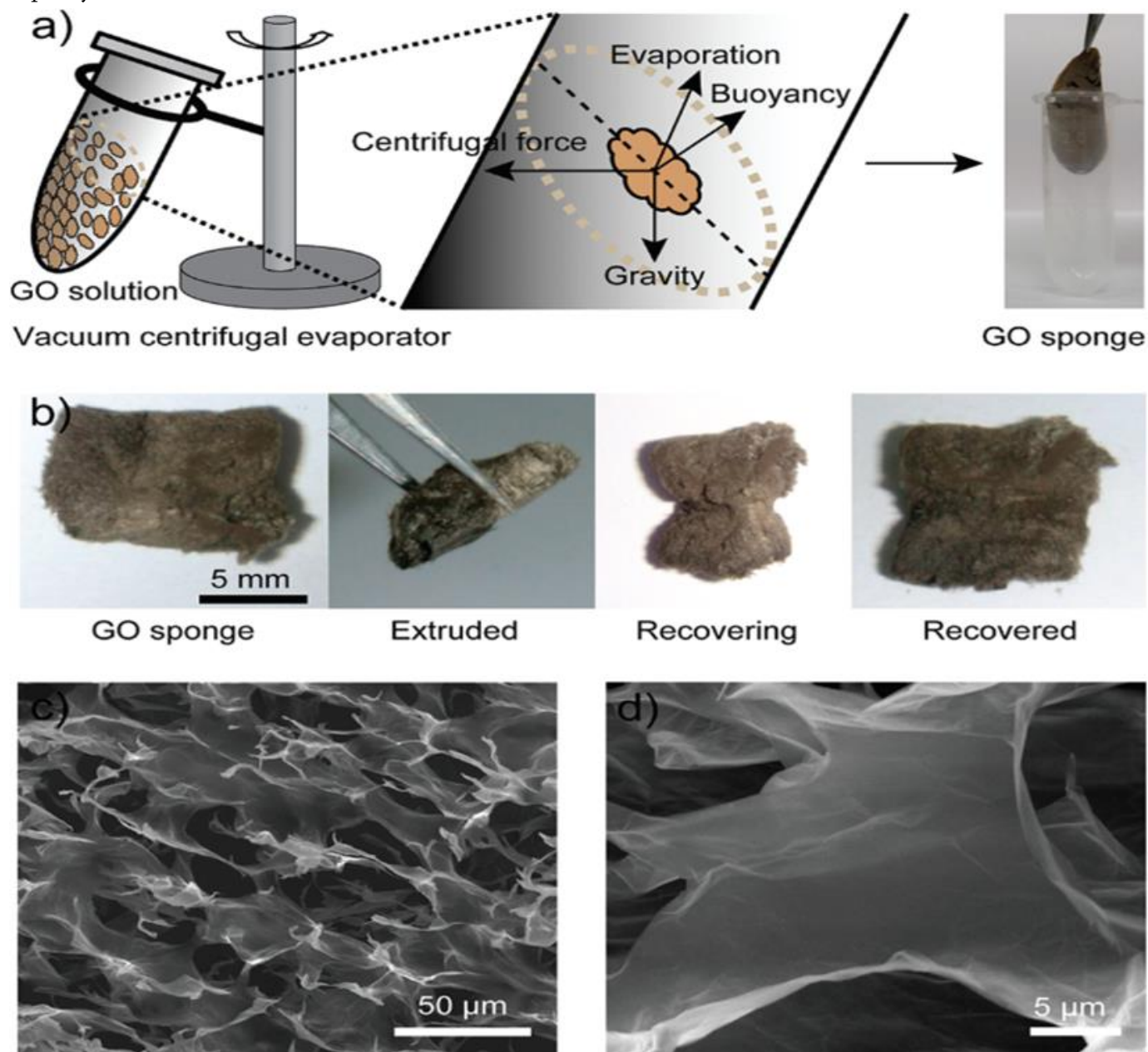

Figure 1. (a) Synthetic scheme of a 3D GO sponge. (b) Flexibility test of a GO sponge. (c) Low-magnification of SEM image for the GO sponge surface and (d) high-magnification of SEM image for the inner part of the 3D GO sponge [36]. Copyright © 2012, American Chemical Society.

Digital images of methylene blue adsorption on GO and SEM (Scanning Electron Microscope) images of the methylene blue adsorbed GO sponge are shown in Figure 2. The 3D GO sponge exhibits adsorption capacity as great as 397 and 467 mg/g for methylene blue and methyl violet, respectively. Here the adsorption of these dyes

on GO can be credited to endothermic chemical reaction that included π-π stacking and anion-cation interaction. The graphene-based adsorption for the removal of basic red 12 and methyl orange was reported using GO with the adsorptive efficiency of 63.69 mg/g and 16.83 mg/g, respectively, at pH 3 of the media [37]. The adsorption of dyes on GO was noticed to be endothermic in nature. Moreover, the degree of oxidation of GO also exhibits some effects on the dye removal process. Yan et al. reported that with the enhancement of the oxidation degrees of GO, its adsorptive removal efficiency for methylene blue also increases [38]. This is probably due to generation of higher number of active adsorption sites as well as increased exfoliation degree of the carbon planes. Le et al. showed that even the graphene based cathode exhibits improved performance for the adsorptive removal of dyes [39]. RGO over the carbon felt surface was successfully used as a cathode for the effective removal of acid orange 7. It was found that 94.3% of the dye was mineralized within 5 min. The cathode was completely stable even after 10 cycles with its mineralization ratio above 64%. Another report shows that GO/polyethylenimine (PEI) hydrogels exhibits improved performance for the adsorptive removal of methylene blue and Rhodamine B from water [40]. Here the advantage of using PEI hydrogels is that they can be easily separated from water after dye removal. It was reported that GO can be used as flocculants for the removal of several organic pollutants such as cationic yellow 7 GL dye, hematite, humic acid and kaolin [41].
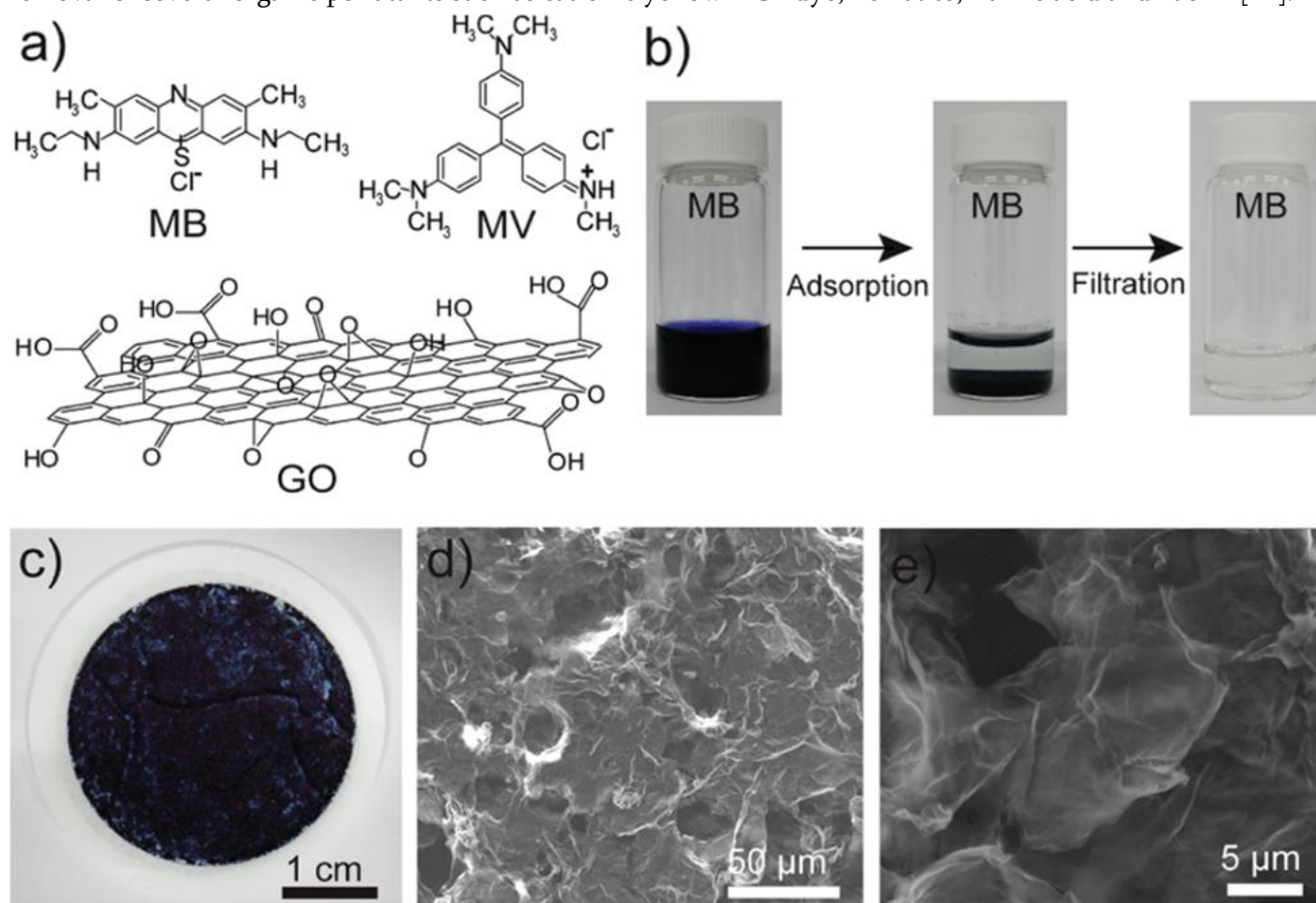

Figure 2. (a) Chemical structures of MB, MV, and GO. (b) Digital images of the original MB dye solution (left), the pale color solution with precipitated MB adsorbed GO sponges (middle), and the colorless water after filtering the MB adsorbed GO sponge (right). (c) Digital image of the filtered dye adsorbed GO sponges. SEM images of the MB adsorbed GO sponges with (d) low-magnification and (e) high-magnification [36]. Copyright © 2012, American Chemical Society.

Recently, GO and RGO were studied for the adsorptive removal of methylene blue via batch experiment method that involves various experimental factors such as pH (2-10), adsorbent dosage (0.5-2 g/L), contact time (0-1440 min), and initial methylene blue concentration (25-400 mg/L) [42]. Methylene blue removal was optimized for the GO and RGO adsorbents and it was found that increase in the initial concentration of methylene blue had positive effect on the adsorptive removal of methylene blue and similar effect was noticed for the amount of adsorbent employed and initial pH. The outstanding dye removal estimated was 99.11% after 240 min at optimal conditions. It was found that GO could be employed effectively for the adsorptive removal of methylene blue from wastewater. The adsorption data was obtained from the Langmuir isotherm (R^2: 0.999) and pseudo-second-order kinetic models (R^2: 0.999). The Langmuir isotherm was used with the consideration that the uniform surface of the GO adsorbent forms only a monolayer of the adsorbate. It is to be noted that along with physical adsorption, chemical adsorption also occurs here because the adsorption energy calculated by D-R (Dubinin-Radushkevich) model was found to be 9.38 kJ/mol.

Recently, it was found that adsorptive removal capacity for methylene blue was improved when agricultural waste was loaded with GO [43]. When corn straw core was loaded with 5 wt% GO, it exhibited the maximum adsorption capacity of 414.03 mg/g at 298 K, pH = 12 and methylene blue concentration of 1000 mg/L. It is to be noted that the adsorptive removal rate for methylene blue over corn straw core loaded with 5 wt% GO has improved by 21.62% compared to that of pure corn straw core (64.58%) and it has excellent recyclability (5 cycles) maintaining removal efficiency >90%. The adsorptive removal of organic pollutants get affected adversely by surface modification of graphene [44]. The difference in performances of graphene for the absorptive removal of Eriochrome Black T (EBT) was noted before and after acid modification with the maximum adsorption capacity of 102.04 mg/g before and 70.42 mg/g after acid modification. It was observed that EBT removal efficiency of acid modified graphene (80%) was lower than that of the pristine graphene (95%), at adsorbent dosage of 10 mg, pH 2, initial dye concentration of 10 mg/L and contact time of 3 h.

A GO based hydrogel, Fe_3O_4/RGO/PAM hydrogel, made from Fe_3O_4 nanoparticles, reduced graphene oxide (RGO) and polyacrylamide (PAM) could degrade 90% Rhodamine B (20 mg/L) within 1 h, under visible light irradiation, and it maintained same efficiency even after 10 cycles [45]. This GO based hydrogel could actually degrade sewage of fine chemical wastewater and it was found that chemical oxygen demand (COD) of wastewater decreased from 10400 to 2840 mg/L after visible irradiation of 1 h. Further, it can be concluded that this hydrogel provides new pathway because it has the capacity to remove organic pollutants and heavy metal ions, synchronously, from industrial wastewater, as evident from the 90% degradation of Rhodamine B (20 mg/L) under visible light irradiation for 20 min and 34.8%-66.3% removal rate for various metal ions after two days continuous adsorption. In another example it was found that when GO was incorporated into the other adsorbent such as sodium alginate (SA) to form SA/GO hydrogel beads, it improves the adsorptive removal efficiency of the latter for organic dyes like methylene blue, Rhodamine B, Vat Green 1 and methyl orange [46]. Such incorporation obviously decreases the pore size and swelling ratio of the hydrogel beads. The adsorption isotherm and kinetic studies of the SA/GO beads show that dye adsorption phenomenon consists of a series of diffusion and adsorption steps. The process starts with the diffusion of organic dyes through the GO macropores with subsequent saturation on the GO surface followed by intraparticle diffusion. The diffusion rate of the organic dyes reduces because of the pore shrinkage. The adsorption of dyes on GO surface involves π-π stacking and anion-cation interaction and is considered as endothermic chemical reaction. The adsorptive removal capacity can be further improved using magnetic graphene oxide (MGO). For instance orange G and methylene blue are successfully removed by using MGO because of the electrostatic interaction between the

organic dyes and negatively charged MGO surface as well as π-π interactions between π conjugation domain of MGO nanosheets and delocalised π electrons on the aromatic rings of the dyes [47].

1.2. Pharmaceuticals and endocrine disrupting chemicals

GO exhibits outstanding adsorptive removal of pharmaceuticals. For instance, GO shows adsorptive removal of 3709 and 500 mg/g for sulfamethoxazole and diclofenac, respectively in batch experiments [48]. The main binding mechanisms for the adsorption of sulfamethoxazole and diclofenac were hydrophobic and π-π electron donor-acceptor interactions. Both sulfamethoxazole and diclofenac were adsorbed over GO from the solution up to 12% and 35%, respectively within 6 h contact time and an increase in GO dosage resulted in the increment in the adsorption of diclofenac. This is because increase of GO dosage offers a larger adsorbable surface to the relatively more hydrophobic diclofenac, whereas sulfamethoxazole was inappropriate for hydrophobic adsorption owing to its hydrophilic nature. It is to be noted that the sonication of GO remarkably increased the adsorptive removal of drugs and removal of sulfamethoxazole and diclofenac increased with increasing intensity of sonication reaching maximum to 30% and 75%, respectively owing to the dispersion of exfoliated GO particles and the reduction in the density of oxygen-containing functional groups on GO surface. The oxygen-containing functional groups on GO surface produces electrical repulsion and inhibits the π-π electron donor-acceptor interactions with anionic compounds, limiting their adsorption. This modification causing reduction in the density of oxygen-containing functional groups and promoting dispersion of GO particles resulted in alleviation of electric repulsion and enlargement of adsorptive surface area and thus exhibited enhancement in the adsorption of these compounds on GO surface.

In another instance, 3D porous graphene hydrogel adsorbent demonstrated an outstanding adsorptive removal capacity of 235.6 mg/g for the antibiotic ciprofloxacin via combination of three adsorption interaction mechanisms viz. hydrogen bonding, π-π electron donor-acceptor interaction and hydrophobic interaction [49]. The size of graphene hydrogels also influences the adsorption process besides pH and NaCl ionic strength. It was investigated that reducing the size of graphene hydrogels considerably speed up the adsorption process and improves the adsorptive removal of organic pollutants from water. When three solvents namely water, methanol and ethanol were studied for knowing the ciprofloxacin removal mechanism over graphene hydrogel granules, it was found that the adsorptive removal followed the order water>methanol>ethanol. Hydrogen bonding by water molecules with that of ciprofloxacin might have contributed for the enhanced adsorptive removal, as compared with the remaining two solvents. Thus water with 99 wt% within graphene hydrogels demonstrated the major role in improving the adsorptive removal performance of ciprofloxacin. As graphene hydrogel revealed an outstanding adaptation to environmental factors, it stands as the promising adsorbent for the adsorptive removal of antibiotic pollutants from wastewater.

Another instance shows that SA/GO hydrogel beads can be used for the adsorptive elimination of endocrine disrupting chemicals like bisphenol A, a poisonous chemical, which may interfere the gene transformation and reproduction of human and animals [46]. SA/GO 1.0 wt% hydrogel beads demonstrates the outstanding adsorption capacity of 342.69 mg/g for bisphenol A, as computed from the Langmuir isotherm model. It can be observed that SA/GO hydrogel beads have a very promising adsorptive removal efficiency, wherein higher amount of bisphenol A molecules could be removed by the hydrogel beads in 6 h of contact time. On the other hand, the pristine SA exhibits a weaker adsorption capacity of 50 mg/g. Presence of GO enhanced the interactions between bisphenol A and hydrogel beads via hydrogen bonding, n-π stacking and π-π stacking. It was found that the adsorption of bisphenol A was enhanced with an increase in pH. At low pH, the successive

protons (H^+) were integrated to the carboxyl groups (COO^-) in the GO, obstructing the hydrogen bonding and n-π stacking between bisphenol A and hydrogel beads. When the pH was enhanced, there was the negatively charge on GO surface and higher number of carboxyl groups participated in the interactions resulting in the greater adsorption of bisphenol A. Thus, introducing GO in the hydrogel system give rise to higher number of carboxylic groups, the superior performance in the adsorption capacity can be noticed with SA/GO hydrogel beads.

In another instance, GO was used for the adsorptive elimination of other endocrine disrupting chemical, 17β-Estradiol, from aqueous solution through strong adsorptive interactions with adsorption capacity of 149.4 mg/g at 298 K and pH = 7 [50]. Go exhibited outstanding adsorption capacity even after several desorption/adsorption cycles. The adsorption mechanism was considered to be via hydrogen bonding and π-π interactions between GO and 17β-Estradiol. 17β-Estradiol is π electron rich owing to the numerous fused aromatic rings that can smoothly interact with the π electrons of GO. Besides, hydrogen bonding and π-π interactions between oxygen-based functionalities on GO and OH of 17β-Estradiol affect the adsorption process. The influence of background electrolyte cations such as KCl, NaCl, $CaCl_2$ and $MgCl_2$ was investigated for the 17β-Estradiol adsorption on GO and it was noticed that 17β-Estradiol revealed improved adsorptive removal capacity with the presence of monovalent cations K^+ and Na^+ than that of divalent cations Ca^{2+} and Mg^{2+}. This phenomenon is probably because of the squeezing out effect in the presence of cations. However, the background electrolyte anions such as Cl^-, NO_3^-, SO_4^{2-} and PO_4^{3-} exhibited no remarkably different effect for the adsorption of 17β-Estradiol on GO. But the presence of humic acid had an adverse effect on the adsorption of 17β-Estradiol adsorption on GO at pH = 7.

1.3. Removal of brominated flame retardants

GO can even be used for the adsorptive removal of brominated flame retardants. For instance, the sorption features of tetrabromobisphenol over GO were studied by carrying out batch experiments [51]. The highest adsorptive removal reported for tetrabromobisphenol over GO was 115.77 mg/g. Thermodynamic studies shows that sorption of tetrabromobisphenol over GO was a spontaneous as well as exothermic process. Sorption of tetrabromobisphenol over GO was studied to examine the influences of temperature, pH, concentration, coexisting anions and humic acid. The adsorption of tetrabromobisphenol over GO was comparatively more at pH < 6.0 owing to hydrophobic and π-π interaction, whereas it declined at pH >7.0 due to the weak π-π interactions manifested at higher pH. Besides, at higher pH, the functional groups of GO got deprotonated resulting in the creation of negative charge at the surface and thus the electrostatic repulsions lowered the adsorption capacity of GO for the negatively charged tetrabromobisphenol from its aqueous solution. The adsorption of tetrabromobisphenol over GO also gets affected by the anions such as NO_3^-, HCO_3^-, SO_4^{2-} and HPO_4^{2-}. The presence of HCO_3^- and HPO_4^{2-} can significantly lower the sorption of tetrabromobisphenol over GO, while NO_3^- and SO_4^{2-} have a minor influence on the sorption of tetrabromobisphenol. The influence of anions on the adsorption capacity of GO for tetrabromobisphenol is in the order $NO_3^- < SO_4^{2-} < HPO_4^{2-} < HCO_3^-$. The effect of humic acid on the adsorptive removal of tetrabromobisphenol over GO was also investigated and it was found that with increasing concentration of humic acid, the sorption of tetrabromobisphenol over GO got declined, probably because of the competition between humic acid and tetrabromobisphenol for the available sorption sites. Humic acid gets bonded on GO surface by the strong interaction of π conjugated structure of GO. Further, the oxygen bearing functional groups on GO gets bonded with amino and numerous

hydroxyl groups of humic acid via strong hydrogen bonding interaction, thus overall making humic acid as very strong competitor to lower the sorption of tetrabromobisphenol over GO.

1.4. Removal of other organic compounds

Graphene nanosheets (GNS) and GO were found to be even effective in the sorption of polycyclic aromatic hydrocarbons like pyrene, naphthalene and phenanthrene [52]. The experimental sorption capacity for naphthalene over graphene and GO nanosheets was reported to be 70.69 and 1.347 mg/g which was nearly equivalent to that calculated by using the pseudo-second-order model. Albeit, the isotherm models such as Dubinin-Ashtakhov, Langmuir and Freundlich could not appropriately clarify the adsorption of the polycyclic aromatic hydrocarbons over graphene and GO, particularly at lower concentrations, the Langmuir model clearly explained the adsorption of naphthalene and phenanthrene over GO. The sorption capacity of graphene nanosheets is greater for the polycyclic aromatic hydrocarbons compared to that of GO even if their surface areas are nearly equivalent. The SEM and TEM (Transmission Electron Microscope) images for phenanthrene adsorption over GNS and GO is shown in Figure 3. The π-π interaction is one of the mechanism responsible for the sorption of aromatic organic pollutants over graphene and its derivatives. The greater affinities of the polycyclic aromatic hydrocarbons to graphene nanosheets are owing to the π-π interactions to the flat surface besides the sieving effect of the potent groove regions generated by wrinkles on graphene surfaces. On the other hand, the sorption sites on GO altered to the carboxyl groups attached to the edges of GO since the groove regions died out and the surfaces of the polar nanosheets restricted the π-π interactions. The molecular sizes, hydrophobic properties of the polycyclic aromatic hydrocarbons and surface morphology of graphene and its derivatives also greatly affects their sorption capacity. For example, the sorption affinity of graphene was greater for smaller molecules compared to larger molecules. This implies that small molecules smoothly access many groove regions possessing greater surface energy sites. Moreover, sieving effect should also be regarded because molecules of different sizes could reach [53].
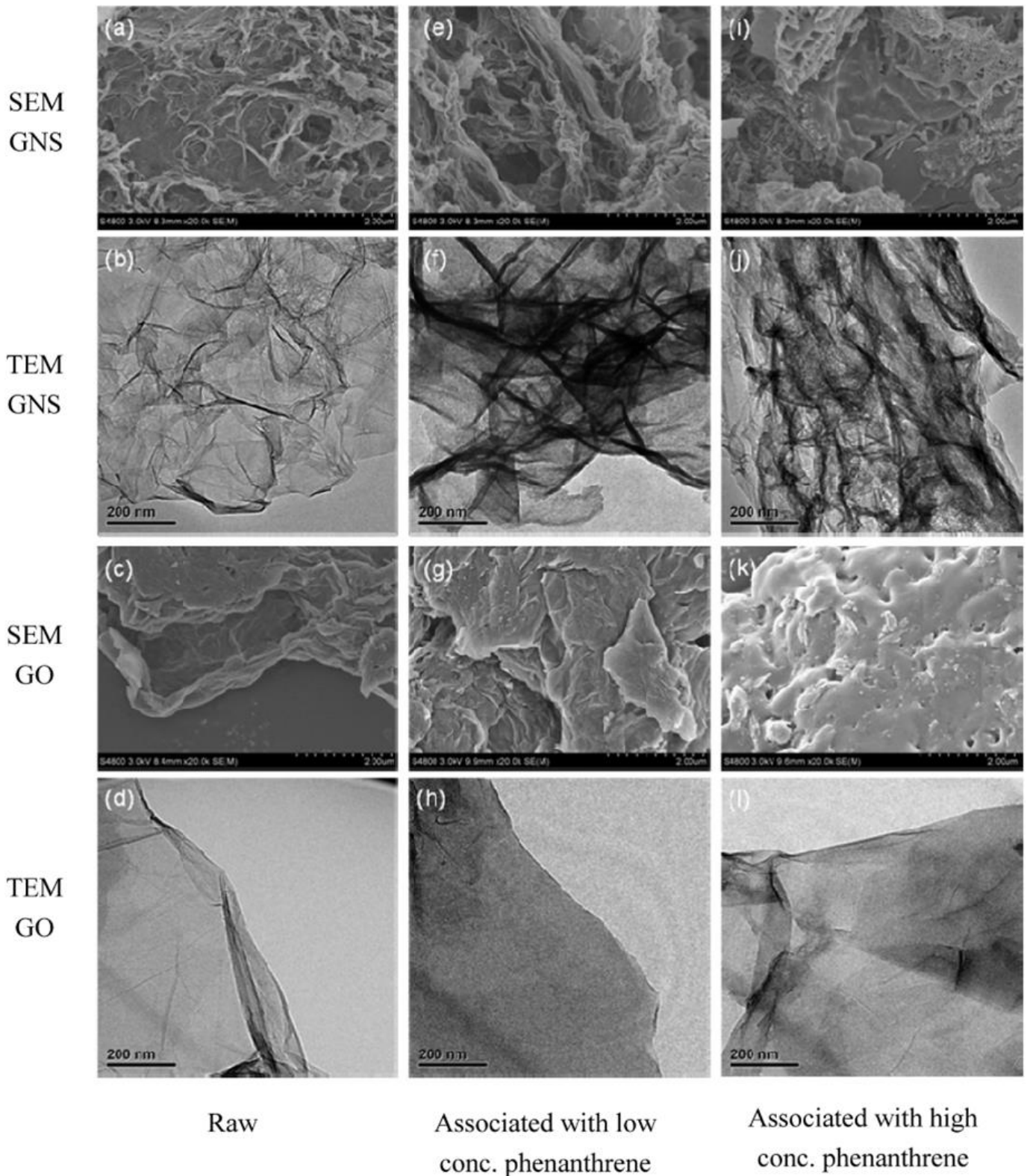
Figure 3. The SEM and TEM images of graphene (GNS) and graphene oxide (GO) before (the first column) and after association with phenanthrene at a low concentration (the second column) and at a high concentration (the third column) [52]. Copyright © 2014 American Chemical Society.

In another instance, graphene was found to be useful for the adsorptive removal of bisphenol A from aqueous solution [54]. The highest adsorption capacity demonstrated by graphene for bisphenol A was 182 mg/g at 302.15 K as computed from a Langmuir isotherm and it was among the maximum values of bisphenol A adsorption relative to the other carbonaceous adsorbents as per the reports of the literature. The probable reasons for the adsorption of bisphenol A on graphene were the π-π interactions and hydrogen bonding and that were even confirmed from the FTIR spectra of graphene. The π-π interactions occur between graphene and benzene ring in bisphenol A that favours the adsorption of bisphenol A, whereas the hydrogen bonding results from the interactions between bisphenol A and hydroxyl groups in graphene. Besides, the exceptional sp^2-hybridized single-atom-layer structure of graphene is accountable for its outstanding adsorption capacity. Thus graphene stands as a promising adsorbent for the adsorptive removal of bisphenol A from wastewater. The thermodynamic investigations suggests that the adsorption of bisphenol A is a spontaneous as well as exothermic process. Moreover, adding NaCl in the solution might favour the adsorption process, while high temperature and the basic pH range are regarded unfavourable.

Graphene and GO can even be used for the adsorptive removal of naphthalene, 2-naphthol, 1,2,4-trichlorobenzene and 2,4,6-trichlorophenol from aqueous solution [55]. Graphene demonstrates similar adsorptive removal efficiency for these four aromatic compounds at pH 5.0, although their chemical properties are different. However, at alkaline pH graphene exhibits greater adsorptive removal for 2-naphthol. It is because of the greater π-electron density on anionic 2-naphthol relative to that of neutral 2-naphthol, that favours π-π interaction with graphene. In case of GO, its adsorptive removal capacity for the four aromatic compounds is of the order naphthalene < 1,2,4-trichlorobenzene < 2,4,6-trichlorophenol < 2-naphthol. 2-naphthol, 1,2,4-trichlorobenzene and 2,4,6-trichlorophenol are adsorbed on graphene predominantly through π-π interaction, whereas 2-naphthol and 2,4,6-trichlorophenol are adsorbed on GO via hydrogen bonding between oxygen-containing functional groups on GO and hydroxyl groups on these two aromatic compounds.

Recently, graphene-based sponges were doped with atomic boron and nitrogen to use them for the electrochemical degradation of persistent organic contaminant, iopromide in one-pass, low-conductivity supporting electrolyte and by flow-through mode [56]. Nitrogen and Boron doping of graphene-based sponges improved their electrocatalytic activity. Graphene-based sponges were generated via low-priced, bottom-up method that permits effective introduction of dopants as well as the functionalization of the RGO coating and thus adaption of the material for the elimination of particular contaminants. The N-doped cathode and B-doped anode exhibited outstanding contaminant removal of >90% at the geometric anodic current density of 173 A/m². During the electrochemical degradation of iopromide, there was the direct electron transfer since the OH˙ radicals were formed via H_2O_2 decompositon (H_2O_2 produced at cathode) and O_3 was formed at the anode. The product formed from iopromide exhibits that the cleavage of all three C-I bonds on aromatic rings occurring at anode is favoured over the breaking of the alkyl side groups, which reveals the role of π-π interactions with graphene surface. Owing to the presence of sodium chloride, the productivity of chlorine was <0.04% and no chlorate and perchlorate were formed, which exhibits very poor electrocatalytic activity of the graphene-based sponge anode for chloride.

In another instance, the magnetic superhydrophobic polyurethane (PU) sponge loaded with Fe_3O_4@oleic acid@graphene oxide (Fe_3O_4@OA@GO) was used for the effective removal of oil from water [57]. Every year a lot of oil is released to water from industries. Therefore, there is need to develop superhydrophobic oil adsorbing material that can be potentially reused. To meet this demand, GO was coated with functionalized oleic acid, Fe_3O_4 nanoparticles and that was loaded on the three-dimensional microstructure of commercial

polyurethane sponge (Fe$_3$O$_4$@OA@GO-PU) via simple and low-priced dip coating method. To ensure the synthesis of modified polyurethane (M-PU) sponge characterization analysis was used. The M-PU sponge was eco-friendly and exhibited the superhydrophobicity that repelled water with contact angle of 158° and demonstrated selective adsorption for various oils and organic solvents from water with outstanding adsorption efficiency. Even the water quantity collected after distillation was <1%. It is to be noted that the M-PU sponge exhibited improved performance under the exposure of magnetic field with various intensities because of the increased surface area of the M-PU sponge. Moreover, the magnetic property of M-PU sponge contributed to recyclability of the material as it exhibited outstanding oil spill clean-up performance for 15 cycles without any notable decline in its adsorption efficiency. Further, uniqueness of M-PU sponge superhydrophobicity was the selective adsorption of contaminants from water at static and dynamic states. It is noteworthy that the M-PU sponge can be employed for practical application of separation of oil from oil-polluted water since, the M-PU sponge exhibits non-stop adsorption of oil from water when coupled with a peristaltic pump.

III. CONCLUSIONS

In this review article, the recent progress and strategies employed for the removal of organic dyes, pharmaceuticals, endocrine disrupting chemicals, brominated flame retardants (BFRs) and other organic compounds using graphene-based adsorbents have been summarized. To ensure the healthy sustainability of life, the problem of environmental pollution should be resolved smartly. Water purification technologies based on nanotechnology have received acceptance by industrial sectors as well as researchers. The art of converting carbon-based nanomaterials to efficient materials, especially for water purification applications, is nowadays a prime field of research. Carbon-based materials are widely used for removing the toxic contaminants owing to their porosity, easy availability and facile synthesis. Graphene and GO materials are optimal for the water treatment by adsorption owing to the desired tunability of these materials. Functionalization of graphene-based adsorbents through covalent and non-covalent interactions is one of the gainful steps to achieve the desired target.

To promote practical applications and future research more skilful efforts should be exerted. The basic problem after the adsorptive removal of target pollutant/s is the complete separation of graphene-based adsorbent from aqueous solution. The separation of these materials is essential as they have been already studied to have very toxic effects after inhalation, ingestion or even skin exposure [58]. It is not sensible to add another toxic substance while eliminating the other toxic contaminants. To meet these demands, appropriate and properly-managed design is needed to employ graphene and graphene-based adsorbents. Moreover, effective methods should be developed to recollect these adsorbents. It was found that ultracentrifugation separation is effective technique to separate graphene form water. But the major problem of this technique is consumption of high energy. An alternative option to this may be membrane filtration technique, but it has other problem like blockage of membrane pores that restricts its applications. Currently, the magnetic separation method is regarded as effective alternative for the separation of graphene and graphene-based adsorbents form water. The next challenge is the recreation of the graphene-based adsorbents. Occasionally, the adsorbed pollutants strongly stick to the surface and they cannot be separated, which remarkably affects their efficiency. Another challenge is associated with the engineering of these graphene-based adsorbents for suitable commercialization, because these adsorbents are tested in the laboratory setups. It may happen that these adsorbents after encapsulation may reduce their large surface area as they change into the graphitic form. In the current

scenario, the fresh 3D designs of graphene-based adsorbents are receiving attentions, wherein graphene sheets are ordered to get a 3D architecture of graphene that helps to prevent graphene agglomeration. Such architecture favours the adsorption as it provides better porosity and large surface area. The techniques to develop the design of graphene-based adsorbents are routes to the large-scale practical applications and commercialization.

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Conflict of Interest

The authors declare that there is no conflict of interest regarding the publication of this article.

IV. REFERENCES

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