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*Review Article*

# Qualitative and Quantitative Analysis of Graphene-Based Adsorbents in Wastewater Treatment

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Nowadays water bodies across the world are heavily polluted due to uncontrollable contamination of heavy metal particles, toxic dyes, and other harmful wastes discharged by emerging industries other than normal domestic wastages. This contamination needs sufficient control to protect the natural water bodies. There are various methodologies to be followed to perform wastewater treatment, in which the adsorption method of filtration is found to be efficient. The adsorption method is a high priority and preferable filtration method compared to other waste water treatment methods due to its peculiar characteristics. Considering the adsorption method, there are multiple options available in selecting material and methodology for the filtration process. In selecting the filtering material, there is much attraction towards graphene and its oxides, which have widespread range of differential applications in commercial industries because of their eco-friendly characteristic features. The importance of various graphene composites and their chemical properties is found to be significant in various fields. Analyzing the adsorbing properties of graphene widely, this article deeply reviews about the improvements and the technologies identified for using graphene and (GO) graphene oxide in wastewater treatment taken into discussion elaborately. Therefore, in this hard review, the advantages and demerits of using graphene for wastewater treatment as well as improving its properties to make it more suitable for wastewater treatment are detailed.

## 1. Introduction

Water in a suitable form is required for various purposes on Earth from survival to essential utilization. In olden days, the widespread natural water available on Earth was sufficient for usage, and the environmental cycle was tolerable to handle the water management. But considering recent scenarios, overcrowding of industries and man-made artificial things against natural environment introduces more contamination in water bodies. This uncontrollable intrusion of water contamination needs to be controlled, else it will affect the entire biodiversity leading to destruction of living and nonliving things on Earth. To control pollution, the major contaminating sources need to be narrowed down to avoid more effluence. Such identified water contaminating sources should take required measures to process their outputs by removing toxic and hazardous wastes from their sludge before it is discharged into the water bodies. This makes the water more suitable for household purposes, natural usages, groundwater recycling, and many other purposes.

The water treatment process involves removing or reducing the water contaminants so that it is suitable for natural uses. All water treatment methodologies involve the removal of solid materials, harmful microorganisms, and organic as well as inorganic compounds present in the wastewaters. A wastewater treatment usually has three levels: a primary level, which is mechanical, involves in removing solids from raw sewage through filtration as well as coagulation. This level itself would be capable of removing around half of the solids present in it. Then, in the consequent second level, beginning of biological treatment takes place. During this second level, removal of microorganisms escaping from the primary treatment is done. Here, a wide range of bacteria, fungi, and algae convert the sludge into carbon dioxide ($CO_2$) and water ($H_2O$). During this level, some amount of energy in terms of biogas production is generated. During the last treatment level, any impurities that are left out from the above two processes are removed, producing the water fit for environment and general purposes.

As water is very much important for all the living organisms and due to limited availability as well as high demand, the research community intends to bring novel methodologies that can ensure the sustainability of water resources. Some of the few novel methodologies established by the research community are listed below:

(1) There is a much attraction towards the use of nanomaterials on wastewater treatment. It has numerous potential merits, which includes high efficient treatment due to wide surface area and better chemical properties. In addition to that, less cost, high reusability, and availability of effective recovery of nanomaterials after their use made them more lucrative.Today, numerous researches aimed in exploiting the potential of nanomaterials [1] by using it in different forms such as nanotubes, nanoadsorbents, catalysts in Nano-sized, semi permeable membrane made from Nano fibers, Nanomaterials with magnetic properties, Nano flakes and Nano granules, etc. and recently reviewed the role of Nano science and nanotechnology on the treatment of wastewaters.

(2) Another research area in which much attention focused in recent years is membrane-based wastewater treatment. Today, researchers tested the efficacy of multiple ranges of membrane technologies, which include microfiltration, ultrafiltration, nanofiltration, and reverse osmosis. Microfiltration uses the membrane of pore size 0.04 to 0.1 microns while in ultrafiltration process, the membrane with pore size 0.01 to 0.02 microns is used for water purification processes. Microfiltration is also used in wastewater treatment but with larger pore sized (0.2 to 0.4 microns) membrane. However, microfiltration as well as ultrafiltration allows the flow of dissolved solids present in water. This can be eliminated with nanofiltration and reverse osmosis. Thus, microfiltration can be generously used as pretreatment to RO and nanofiltration. Thus, the membrane-based wastewater technologies are found to be more effective on eliminating suspended as well as dissolved solids in addition to removal of pathogens. However, they have a big limitation corresponding to cost incurred as they require very large amount of energy in comparison with conventional treatment methodologies.

Earlier, wastewater was considered as troublesome and more problematic, but today, wastewater is recycled and considered as renewable source of energy. The wastewater contains more than 4 times of energy required for treatment, and abundance of energy is present in wastewater in terms of chemical, thermal, and hydraulic energy. Among these, thermal energy stands first with about 80%, chemical energy availability attributes to about 20%, and hydraulic energy availability attributes to a negligible amount (<1%). Thus, implementation of effective treatment methodology not only degrades the wastewater but can also produce energy through biogas production.

Wide ranges of eco-friendly and high-cost nanomaterials are tested by the research community in the treatment of wastewaters. These materials are developed with certain unique functional and surface characteristics for the purification of surface water and groundwater. In addition, these nanomaterials were also used in degradation of industrial effluents [2]. In recent decades, nanoparticles have been studied for their capacity as adsorbents. The size of the nanoparticles is considered as an important factor in deciding the chemical activities such as adsorption [3, 4].

The inorganic nanoparticle oxides produced from metals as well as nonmetals are considered as most promising nanoadsorbents. These oxide-based nanoadsorbents are employed for removing the hazardous pollutants present in wastewaters. Some of these nanoadsorbents reported in the past decade includes titanium oxides [5], titanium oxides and dendrimer composites [6, 7], manganese oxides [8], ferric oxides [9], zinc oxides [10], and magnesium oxides [11]. The successful use of nanoadsorbents on degradation of pollutants attributed to several reasons that include high surface area, less impact on environment, easy availability, and nongeneration of secondary pollutants [12] that requires further treatment, and thus these inorganic nanoadsorbents are considered as one among the best adsorbents.

Graphene is a type of carbon having layered structured with special features that tends to several environmental applications [13]. Graphene oxide (GO) which is an extension of carbon material that has two-dimensional structure is produced by oxidation of graphite layer by means of chemical method. Surprisingly, graphene is incredibly flexible even though its strength is more than 200 times higher than steel. In addition, it is ultralight in weight but highly tough in nature. It is possibly one of the extremely thinnest materials in the world with highly transparent nature. In the year 1962, graphene was observed through the electron microscope for the first time. Later in 2004, Andre Geim and Konstantin rediscovered and characterized the graphene nanoparticles for which they received Nobel prize for physics in the year 2010. Graphene is considered as one among the materials having wide surface area, i.e., it has a surface area about $2630\,m^2/g$ (theoretical) while the carbon nanotubes have a surface area of $1000\,m^2/g$.

Hummers' method was considered as one of the efficient as well as faster methods for the preparation of GO, in which pure carbon graphene combines to react with molecular oxygen. Another advantage behind this method is producing GO with relatively high carbon-oxygen ratio. GO has two main characteristic features when compared to other nanomaterials like carbon nanotubes (CNTs). In the first step of preparation, synthesis of single layer of GO which has maximum heavy metal ion adsorption is done. In the second step, chemical exfoliation of raw graphite without the addition of any metallic catalyst is carried out, which does not need the help of any complex instruments.

The contamination of heavy metal ions in water causes undesirable consequences [14]. To overcome the effect of contamination, various methods such as filtration, adsorption, precipitation, coagulation, ion exchange, oxidation processes, etc., [15] were carried out to remove the hazardous contaminants from wastewaters. Among the various methods, adsorption was sorted to be more efficient. It is familiarly employed in industries because of its less cost, simple design, less sensitivity, and easy operation towards the toxic pollutants. In this broad review, the structure, properties, and preparation methodologies of graphene oxide are elaborated. Subsequently, its applications on wastewater treatment as well as other major areas were reviewed along with the negative impacts of GO.

## 2. Structure of GO

Figure 1 describes the structure of graphene, graphene oxide, and reduced graphene oxide. The chemical and physical structure of GO has been the major subject of considerable discussion due to its complex nature characteristics and variability in sample to sample. Graphene oxide is nothing but the oxidative form of graphene as graphene is highly expensive and difficult to produce [16]. Rather, GO can be produced easily at less cost. Graphene oxide contains oxygen functionalization of about 20 to 30% in the basal plane. Several models were postulated to predict the structure of GO. Among these postulations, highly accepted model called Lerf-Klinowski model shows that basically, GO contains carbon basal plane with the epoxy and hydroxyl functional groups with the edges of the sheet terminated by carboxylic acid. The highly ordered $sp^2$ regions are present in long range interrupted by disordered $sp^3$ regions especially in carbon basal plane [17]. Furthermore, amorphous materials as well as defects present in small patches on the long range and presence of amorphous materials might be due to surface contamination.

## 3. Properties of GO

Since oxygen functional groups are present in its structure, graphene oxide dispersed rapidly in different solvents, which include organic solvents and water. The mechanical and electrical properties of graphene oxide composite are enhanced by combining the GO with matrices made of ceramic or polymers [18]. Graphene oxide, when there is a change in $sp^2$ bonding, can be widely used as an excellent insulator in relative terms of electrical flow. Furthermore, the tensile strength, elasticity, conductivity, and many more properties can be improvised by mixing GO with different polymers and other materials [19]. The reduced graphene oxide (referred as rGO) is produced due to the removal of the ionic oxygen groups present it. rGO has some properties differed from GO as it is highly difficult to disperse as it gets aggregated. The desired qualities of graphene oxide are obtained by modifying the functional groups involved in it. The fullerene-functionalized secondary amines as well as porphyrin-functionalized primary amines could be linked with platelets of GO in order to improvise the nonlinear optical behavior of GO. The fragments of GO can be attached with each other to produce stable and thin stable structures which can easily be stretched and folded. These structures are having wide range applications in storage of hydrogen, ion conductors, and in the production of membranes meant for nanofiltrations.

Graphene is a single layer of carbon atoms, tightly bound in a hexagonal honeycomb lattice. The speciality of graphene is its sp2 hybridization and very low atomic thickness, which allows it to dissolve in various solvents. Hence, it is performed through the structure of $\pi$-$\pi$ noncovalent conversion, which is carried out using surfactants, such as wrapping, for example, the interaction observed between 1-pyrenebutanoic acid succinimidyl ester (PyBS) and the potassium salt of coronene tetra-carboxylic acid. Graphene oxide (GO) and reduced graphene oxide (rGO) have been exploited for the fabrication of graphene-based nanocomposites. More interest is towards the development of a graphene adsorbent since it has a lot of novel graphene properties and a lot of applications [20]. This paper concise the properties of graphene namely electrical, optical, magnetic, chemical and mechanical characteristics.

## 4. Mechanical Properties

Van lier et al. [21], Reddy et al. [22], and Kudin et al. [23] described the mechanical properties of monolayer graphene including Young's modulus and fracture strength investigated by numerical simulations such as molecular dynamics. Ranjibartoreh in 2011 describes the defect-free graphene as the stiffest material, with 1.0 TPa Young's modulus which is usually described in nature and has high intrinsic strength of about 130 GPa. Terrones et al. [24] have described the high fracture strength and average young's modulus of 120 MPa and 22 GPa in graphene sheet functionalization. Park et al. [26] and Ruoff [27] have studied the strength and elastic properties of monolayer graphene through nanoindentation by using AFM where they showed that the GO paper mechanical properties can be improved by the introduction of cross-linking of individual platelets by divalent ions. The processed graphene papers have been investigated for its various mechanical properties such as tensile, indentation, bending, and superior hardness.

### *4.1. Tensile Test.*

The amount of stress and the stress-based dimensions can be explained by the following equation:

$$\begin{aligned} \varepsilon_x &= U_x, \\ \sigma_x &= \frac{F}{A}, \\ \varepsilon_x &= 1 * \frac{\left(\sigma_x - \nu\sigma_y\right)}{E}, \end{aligned} \tag{1}$$

where $E$ is Young's modulus, $F$ the tensile force, $A$ the cross section area, $\nu$ Poisson's ratio, $U_x$ and $\varepsilon_x$ the displacement

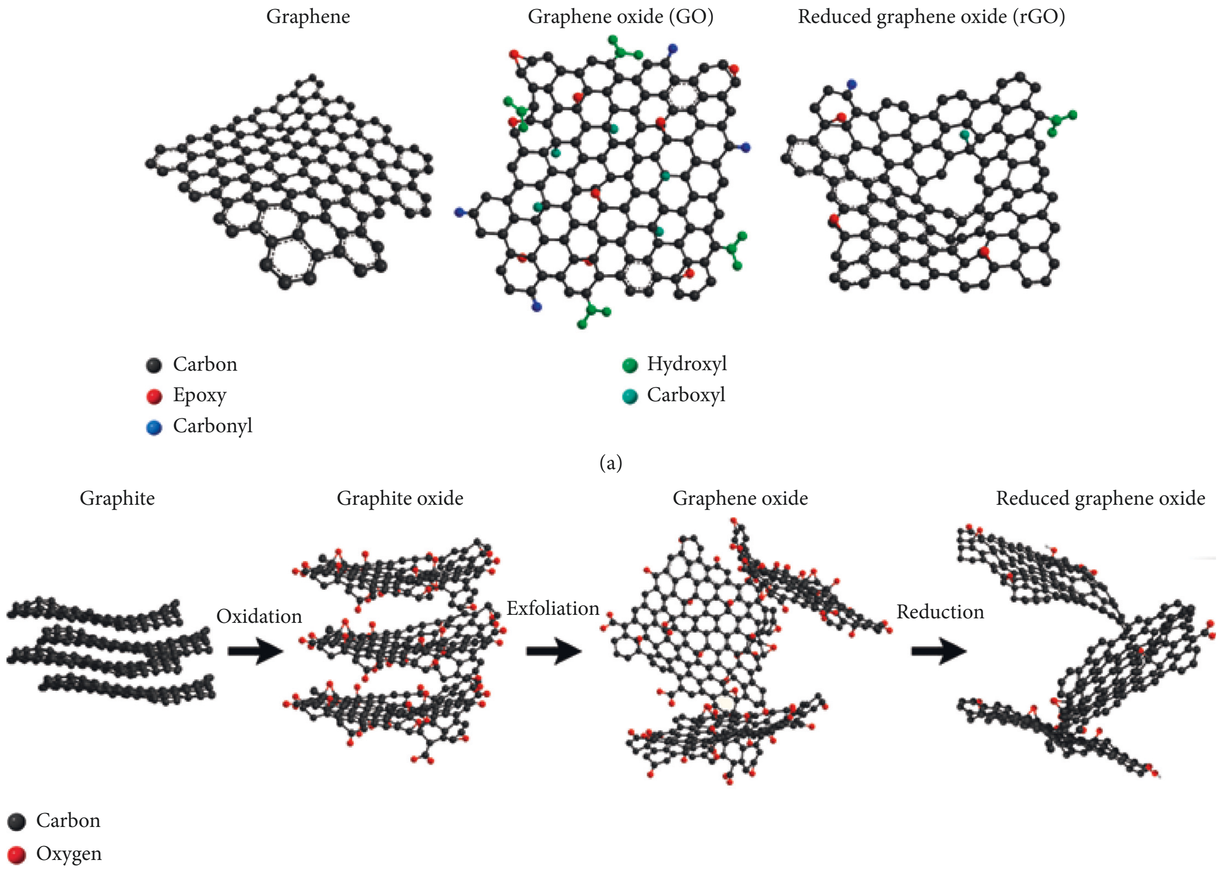


Figure 1: Graphene and graphene composite structures.

and the strain in $x$ direction, and $\sigma_x$ and $\sigma_y$ the stresses in $x$ and $y$ directions.

Dikin et al. [29] described the graphene paper's stress-strain curve and addition of graphene octadecylamine (G-ODA), as shown in Figure 2, which illustrates the direct behavior.

Stiffness ($S$) is the amount of an object that resists deformation ($A$) as response for an applied force ($F$).

$$S = \frac{F}{A}. \tag{2}$$

Relationship between Young's modulus and stiffness is determined as follows:

$$F = \frac{AE}{L}, \tag{3}$$

where $L$ is the length of strip.

Figure 3 shows that GP has greater Young's modulus and ultimate strength but G-ODA sheets exhibit higher stiffness.

Bucky papers can be prepared with consideration of different properties such as Young's modulus (0.8–24 GPa), ultimate tensile strength (10–74 MPa), and strain (1.5%–5.6%). Berhan et al. [30] states that the maximum Young's modulus and ultimate tensile strength in the samples of GP are 31.69 GPa and 78.294 MPa. Young's modulus of 20–40 GPa, ultimate tensile strength of 70–80 MPa, and ultimate tensile strain of 0.3%-0.4% were stated as mechanical properties of GP and graphene oxide papers.

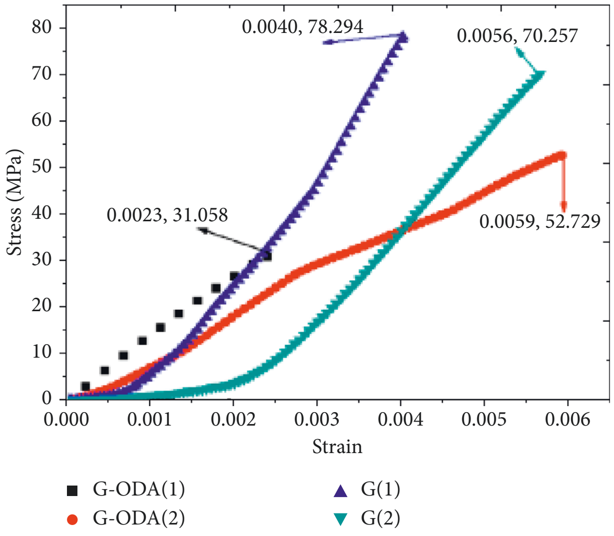


Figure 2: Stress-strain curves for the strip GP and G-ODA [28].

*4.2. Indentation Test.* The radius of a spherical indenter is 100 $\mu$m which is the most appropriate indenter for

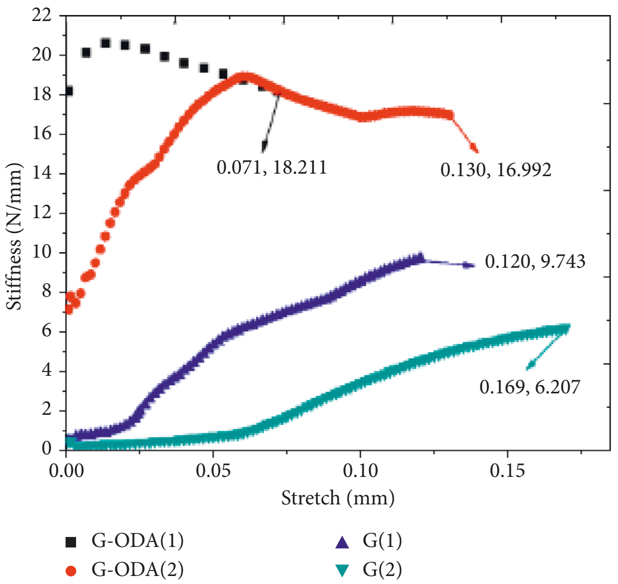


Figure 3: Stiffness vs stretch of GP and G-ODA strips [24].

measuring GP and G-ODA elastic modulus, hardness, yielding strength, and Poisson's ratio. The indentation tests are measured using Ultra Micro Indentation System (UMIS) and is repetitive for various GP points, whereas the heat treated one for GP and G-ODA varies with the thickness of 3 $\mu$m and 7 $\mu$m. Hence, the results of dimension test and tensile test for GP and G-ODA strips are illustrated in Tables 1 and 2 [24].

Then, follow the equation:

$$\left(\frac{1}{E}\right)^{*} = \frac{\left(1-\vartheta^{2}\right)}{E} + \frac{\left(1-\vartheta^{2}\right)}{E'},$$
$$E = \frac{P_h}{2a}. \qquad (4)$$

Hardness is calculated as

$$H_y = \frac{P}{\pi a^2}. \qquad (5)$$

Hardness and yielding strength of the materials have been appraised above.

*4.3. Bending Test.* The GP and G-ODA sheets' bending rigidity and modulus of elasticity have been determined through the bending test. The intensively loaded circular plate with deflection equation is given below:

$$W = \frac{F}{1 \propto D}\left[2r^{(2)} l \frac{r}{r_0} + \left(r_0{}^{2} - r^{2}\right)\right],$$
$$D = \frac{Eh^3}{1\left(1-\vartheta^2\right)}, \qquad (6)$$

where $R_0$ = ring inner radius, $r$ = radial distance of intensive loaded for the sheet center, $D$ = bending rigidity, $F$ = force concentrated, $E$ = modulus of elasticity, $h$ = sheet deflection, and $w$ = sheet deflection.

Table 1: Dimensions of GP and G-ODA strips.

| | Length (mm) | Width (mm) | Thickness ($\mu$m) |
|---|---|---|---|
| GP(1) | 30 | 5 | 3 |
| GP(2) | 30 | 5 | 3 |
| G-ODA(1) | 30 | 6 | 7 |
| G-ODA(2) | 30 | 6 | 7 |

The inner radius of two flat rings is 3 mm. Here, the sheet thickness of GP and G-ODA are 3 µm and 7 µm, respectively, which are rigidly fixed with the help of glue on the ring's flat surfaces. The modulus of elasticity for GP bending is 3.044 TPa and in the case of G-ODA is 0.7647 TPa.

## 5. Optical Properties

In graphene optical properties, the most familiar property is about the performance of sturdy quencher to several nanoparticles and luminescent dyes that are authorized as two probable competitive processes, namely, photo-induced electron transfer and intramolecular energy transfer that are expedited using a mechanism of through-bond because of luminophore covalent binding. The transparency of graphene is more firmly associated with the effect of quantum rather than properties of natural material [31].

The unit cell consists of carbon atoms represented by **A** and **B**, and **a1** and **a2** are the lattice vectors [32]. Graphene has a honeycomb crystal lattice network of carbon atoms with sp2 hybridization, whereas this lattice of honeycomb has been considered as saturation of triangular lattice along with two atoms per unit cell labeled as A and B. The view from point B is rotated by 180 degrees as compared to the view from point A. The Bravais lattice is a triangle that consists of two atoms per unit cell represented in Figure 4 and corresponding Brillouin zone, showing the high-symmetry points in Figure 5.

The graphene fine structure constant is utilized in the structure of zero gap Dirac band, and it is expressed in terms of the subsequent equation:

$$a = \frac{e^2}{\hbar}. \qquad (7)$$

Hence, the graphene dynamic conductivity ($G$) is constant as ($e^2/4\hbar$). The graphene reflectance ($R$) and transparency ($T$) can be estimated using the following equation:

$$T \approx 1 - \pi a,$$
$$R = \frac{\pi^2 a^2 T^2}{4}. \qquad (8)$$

The incident light of constant transmittance as $T \approx 97.7\%$ has been experimentally recognized in the range of visible infrared at 300–2500 nm, and linear transmittance has been reduced with the number of graphene layers.

The carriers with relativistic nature of graphene are a core of interpretation that the optical transmission provided using $\pi$ times of fine structure is constant. Significantly

Table 2: Tensile test results of GP and G-ODA strips.

| | Ultimate strain | Ultimate strength (MPa) | Young's modulus (GPa) | Stiffness (N/mm) | Maximum stretch (mm) |
|---|---|---|---|---|---|
| GP(1) | 0.0040 | 78.294 | 31.6969 | 15.8485 | 0.1205 |
| GP(2) | 0.0056 | 70.257 | 21.1987 | 10.5993 | 0.1697 |
| G-ODA(1) | 0.0023 | 31.058 | 15.4701 | 21.6582 | 0.0715 |
| G-ODA(2) | 0.0059 | 52.729 | 12.3094 | 23.4998 | 0.1302 |

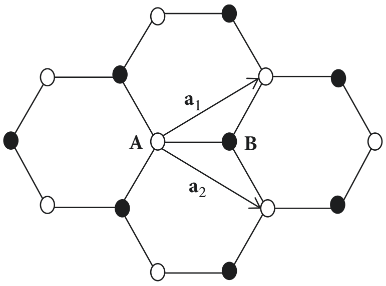


Figure 4: Honeycomb lattice structure of graphene.

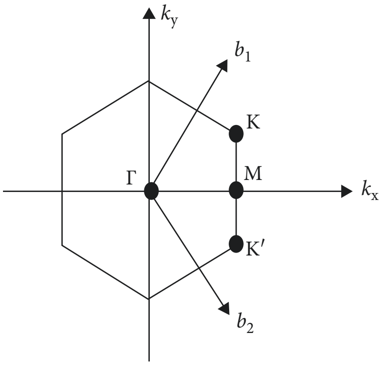


Figure 5: Brillouin zone showing high-symmetry points.

modulate the graphene electronic properties with lattice strain. The graphene optical response with polarization dependence consists of lattice strain induced in the graphene band structure, which can be monitored directly in the transmission experiment. Graphene and its bilayer are shown in Figure 6, and optical image of graphene is shown in Figure 7.

Figure 7 expresses graphene optical image flakes with the layer of 1, 2, 3, and 4 layers on a 285 nm thickness of $SiO_2$-on-Si substrate [33, 34].

In graphene, the magnetism has occurrence which is a topic of considerable interest, whereas the magnetism present in the graphene can be persuaded using the defect of vacancy or by hydrogen chemisorption. Bhowmick and Shenoy [35] and several researchers have proposed that an essential graphene magnetic property is zigzag edges. There are some convinced magnetic features involved in the graphene which are behavior of spin-glass, para magnetism, and phenomenon of magnetic switching like antiferromagnetic or ferromagnetic.

At room temperature, the graphene with ferromagnetic behaviour has limited saturation and magnetization value of about 0.004 to 0.020 emug$^{-1}$ after the diamagnetic background deduction. The graphene samples with magnetic properties created from EG, nanodiamond (DG) conversion, and graphite arc evaporation over hydrogen (HG) are represented. The magnetization with temperature dependence present in the HG and EG measured sample is shown in Figure 8 as 500 Oe, whereas the sample of graphene in room temperature with magnetic hysteresis is shown in Figure 9. Hence, the temperature increases as the MS value is increased but

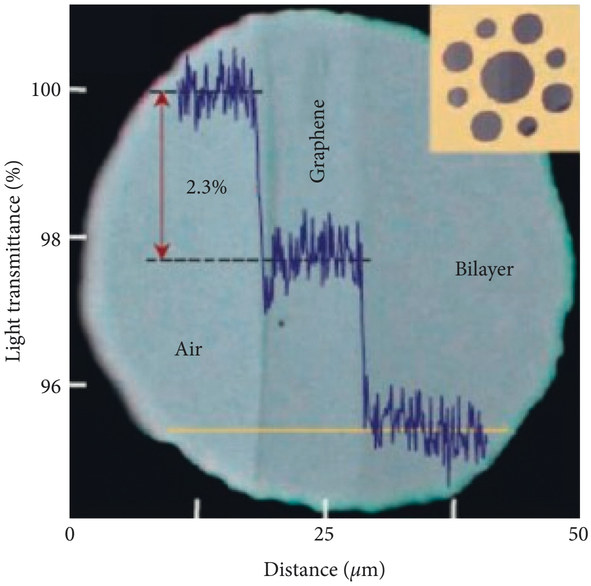


Figure 6: 50 μm aperture of photograph with partially covered using graphene and its bilayer.

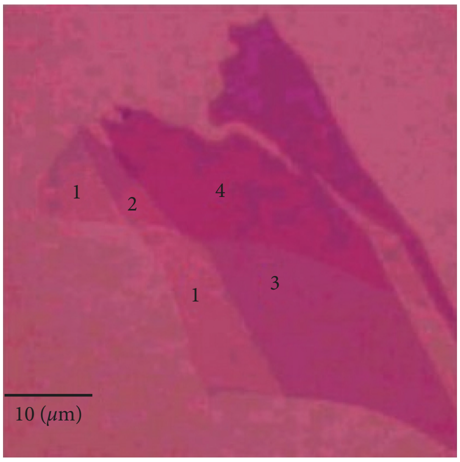


Figure 7: Multilayer graphene optical image flakes.

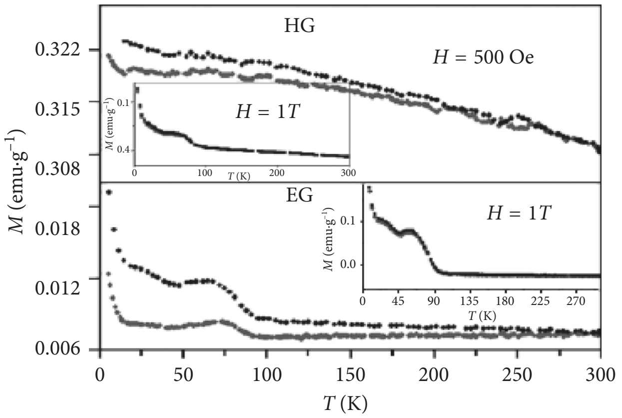


Figure 8: Temperature variation of magnetization of few-layer graphene.

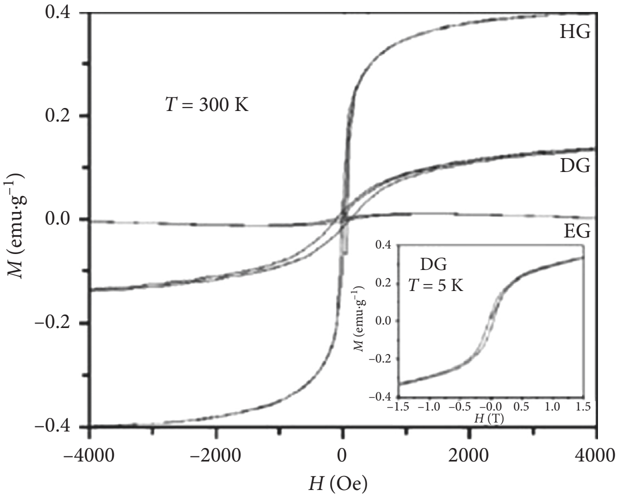


Figure 9: Magnetic hysteresis.

shown HG is the best feature of hysteretic in saturation. When the DG presented with saturation magnetization, MS is to low in comparison with HG.

The graphene modification with the magnetic nanoparticles is generally obtained using in situ reduction of iron, cobalt, or nickel salt precursors or assembly of the presynthesized magnetic nanoparticles on the surface of graphene-based frameworks.

## 6. Chemical Properties

Chemical doping is one of the most widely used techniques to tailor the surface and electronic structure of graphene. However, the relatively inert nature of graphene is the biggest challenge for chemical functionalization or doping of graphene to a high level. Recently, photochemical reactions been explored for addressing this issue [36]. A variety of photosources including sunlight, UV light, and exciter laser radiation have been applied to reduce the energy barriers of graphene reactions. It produces highly reactive chemical species under irradiation, mainly the free radicals. Photoinduced free radicals usually can overcome the high reaction barriers of graphene addition reactions. Under irradiation, the functional groups of CMG provide reactive sites for photochemical modifications, such as photo reduction and photo patterning [37].

*6.1. Free Radical-Based Photochemical Reactions.* Chlorine (Cl) radicals can be produced from $Cl_2$ by irradiation. Inspired by the addition reaction of chlorine and benzene to produce a well-known insecticide, hexa chloro cyclohexane ($C_6Cl_6$), Liu et al. [38] developed a photochemical approach to chlorinate graphene by covalently bonding chlorine radicals to the basal plane carbon atoms (Figure 10). In this case, graphene sheets with coverage of C–Cl bonds up to 8-atom percentage were formed.

Because the CQC bonds of graphene transformed from sp2 to sp3, the resistance of graphene increased over four orders of magnitude and a band was gap created [40]. Moreover, graphene sheets with desired chemical patterns can be prepared by localized photochlorination (Figure 11), offering a feasible approach to realize all graphene circuits. Theoretical calculations have been used to analyze the structural and energetic changes of chlorinated graphene in the photochemical process as shown in Figure 12. In the initial stage of photochemical reaction, photochemical molecules generated with chlorine atoms have been likely to adsorb in graphene for attaining a stable Cl-graphene charge [41]. The C orbital has retained sp2 hybridization, and the graphene was p-type doped. Further chlorination induced the formation of two adsorption states: one is covalent bonding of Cl pairs to the C atoms with a structure close to sp3 hybridization [42]. Successively, it changed into a more stable configuration: the neighboring Cl atoms bonded with carbon atoms arranged in a hexagonal ring. Another state is a nonbonding one. Two adjacent chlorine atoms combine with each other, forming chlorine molecules to desorb from the graphene surface [43], tuning the band gap of chlorinated graphene in the range of 0–1.3 eV by its chlorine coverage.

## 7. Electrical Properties

The graphene's electrical properties have been determined as the best while compared with several related materials, namely, carbon nanotubes due to its high electric conductivity and more surface area, whereas these properties provide a potential graphene for enhancing biosensors, electronics and probable battery cells.

Graphene is a two-dimensional array of sp2 carbon atoms with a hexagonal lattice structure, whereas the structure has more simple visualization as nanowire with the molecular scale. Hence, the graphene has more conductivity in a high surface area which creates its optimal use in the electrochemical cells. Graphene is comparatively low cost for producing since there are various methods for synthesizing it chemically. The rGO can obtained by reducing the GO either by quick thermal expansion or with hydrazine. The

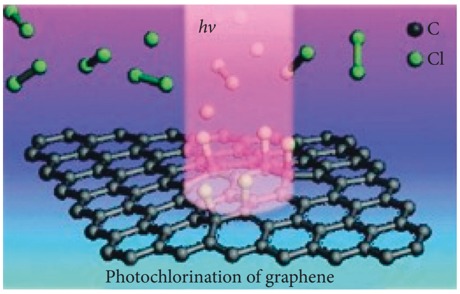


Figure 10: Schematic illustration of graphene photochlorination [39].

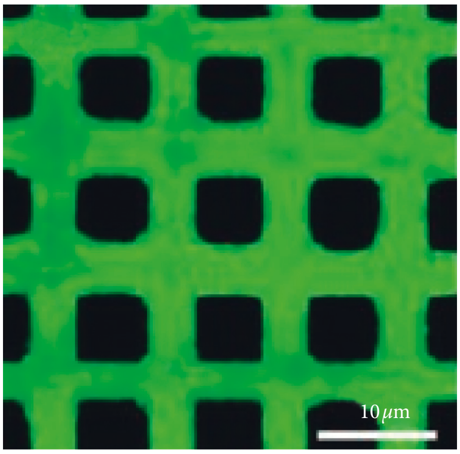


Figure 11: Raman *D* band mapping for a CVD-grown graphene film after a patterned photochlorination. [39].

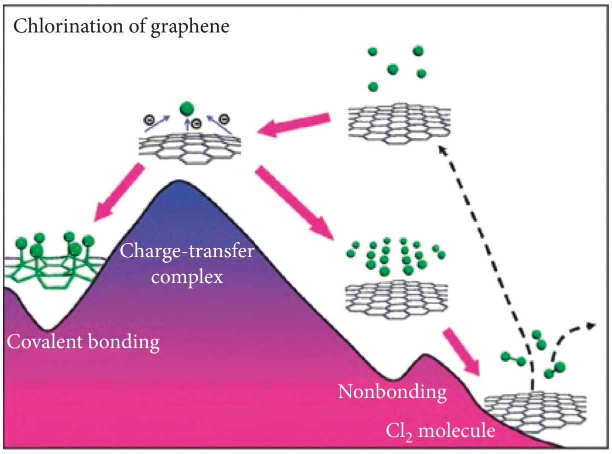


Figure 12: Schematic diagram for the evolution of various adsorptions [39].

structure of graphene and graphene oxide is illustrated in Figures 13 and 14, respectively.

In general, hydrazine is an organic reducing agent due to its reaction by products which are normally water and nitrogen gas, whereas hydrazine is utilized for reducing GO in order to produce chemically modified graphene.This modified chemical combination due to rGO with hydrazine does not eliminate all the impurities present in the material.

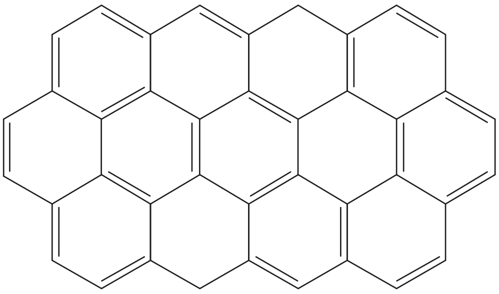


Figure 13: Chemical structure of graphene.

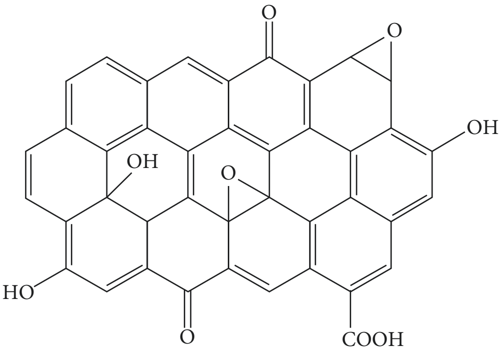


Figure 14: Chemical structure of graphene oxide.

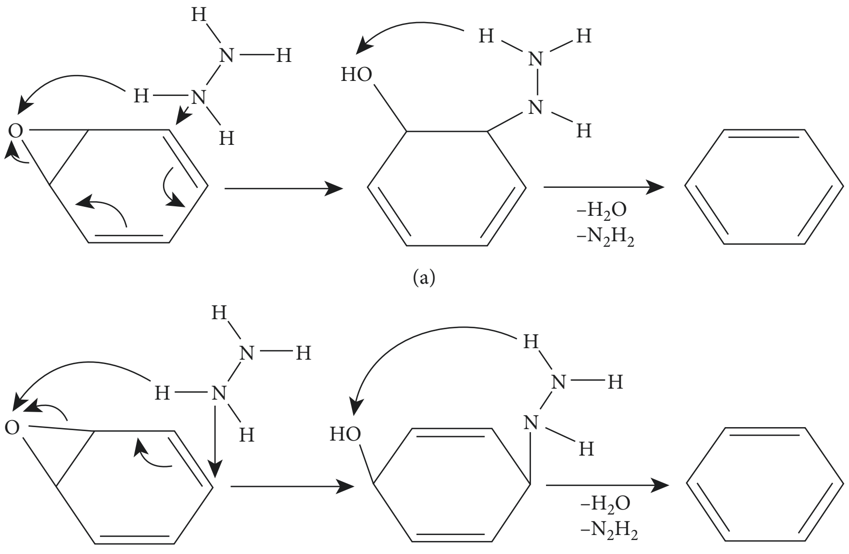
However, carbonyl, carboxyl, and hydroxyl groups are not extinguished from the surface of graphene completely using reduction of hydrazine. Therefore, Gao et al. have proposed a mechanism to reduce graphene using hydrazine as shown in Figure 15.

Most of the experimental research studies on graphene focus on the electronic properties. The most prominent property in the earlier research about graphene transistors is the capability for frequent tuning of carrier charges from holes and electrons. An example of the gate dependence in single layer graphene is shown in Figure 16. In this thinnest sample, this effect is most noticeable but the weakest gate dependence is shown in the sample of multiple layers because of electric field screening using the other layers.

Novoselov et al. [45] specified that at low temperatures and high magnetic fields, the exceptional mobility of graphene allows for the observation of the quantum Hall effect for both electrons and holes, as shown in Figure 17.

The quantum Hall effects of graphene shown above state the difference in unique bond structure compared with the traditional quantum Hall effects, whereas the plateaus occur at the half integers of $4e^2/h$ instead of typical $4e^2/h$. For more applications that are practical, one would like to utilize the strong gate dependence of graphene for either sensing or transistor applications, whereas no band gap is available in graphene and the respective resistant modifications are small. Hence, the less on/off ratio annoys the transistor of graphene using its nature. In addition, this limitation can be overcome by carving the graphene into narrow ribbons.

When the ribbon was made to shrink, the charge carrier momentum present in transverse direction evolved into quantized that made the results of band gap opening,



(a)

(b)

FIGURE 15: Reaction mechanisms for the chemical reduction of graphene oxide with hydrazine.

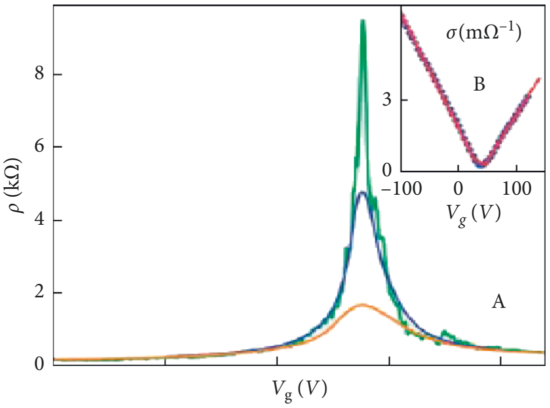


FIGURE 16: Resistivity of a single layer of graphene vs gate voltage [44].

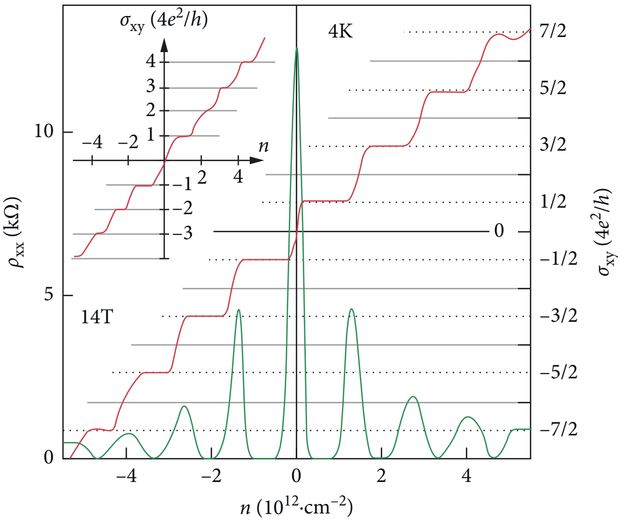


FIGURE 17: Single-layer graphene with quantum Hall effect [44].

whereas the width of ribbon is directly proportional to the band gap. This noticeable effect present in the carbon nanotube is based on the nanotube band gap which is directly proportional to its diameter. Li et al. [40] specify the band gap opening that is present in the graphene ribbon.

## 8. Preparation of GO

Micromechanical cleavage, epitaxial growth above SiC substrates, chemical vapor deposition, chemical reduction of GO through exfoliation, exfoliation of graphite in liquid phase, and unzipping the nanotubes made from carbon are some of the well-known most familiar techniques employed for graphene production [46]. These methods are effective in some terms with several merits as well as demerits with respect to its applications and operating conditions [47]. Among these abovementioned methods, liquid phase exfoliation technique has high potential for large-scale production of nanographene materials in cost effective manner.

In addition to the existing preparation methods, several other methods were also successfully tested. It includes exfoliation technique assisted by microwave, intercalation and exfoliation of graphite flakes by using gases, and mechanical exfoliation of graphite flakes using ball mill in liquid medium or continuous attraction of solid graphite blocks against rotating the glass substrates in a particular solvent along with simultaneous application of ultrasound [48]. The illustration of preparation is described in Figure 18.

Barahuie et al. [49] in 2017 had detailed about the preparation of miniature graphene sheets in mass production using four different types of methods, which helps to get sheets in economic cost suitable for introducing and using in various applications. Paredes et al. [50] in 2011 have

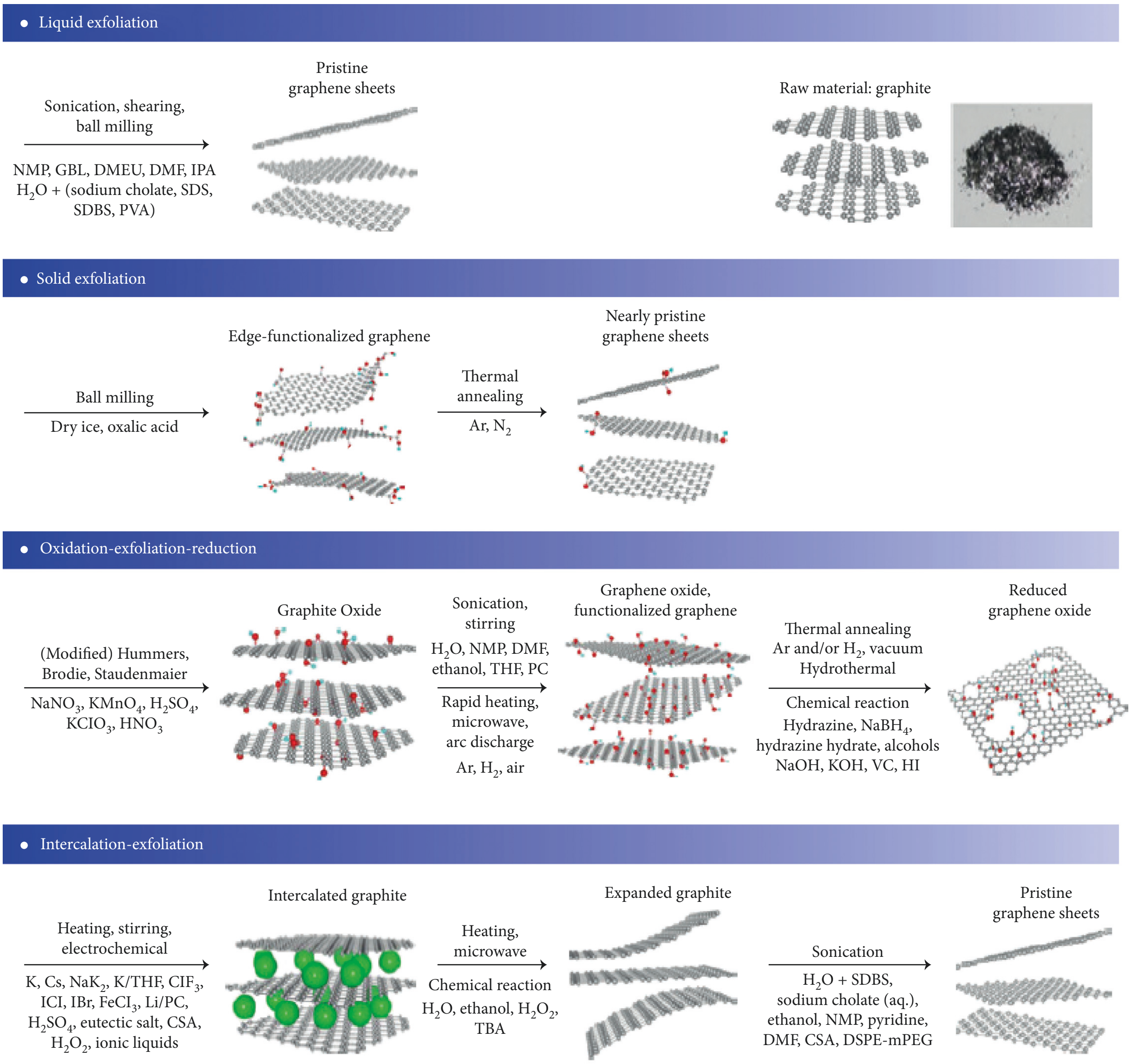


Figure 18: Four types of methods in the synthesis of small graphene sheets by exfoliation.

elaborately discussed about the preparation of graphene and its nanoparticles from various waste and bioprecursors like paper cups, hemp, glucose, rice husk, cookies, cockroach legs, and grass. Since there is a need for bulk graphene preparation, this is performed by using different precursors mentioned above [51]. In order to synthesis graphene and its nanoparticles, a detailed knowledge on the brief structure of GO is highly required which was elaborated in earlier section [52].

## 9. Graphene-Based Water Purification

There is a need for cleaning the waste generated during process in industries and factories, which pollutes air and water. Therefore, there is a search for a cost effective and highly efficient adsorbent. Due to its extremely wide surface area as well as abundance of functional groups, the graphene seems to be an ideal option to fit. The research community considered GO as an efficient and powerful choice for next generation filtration membrane. This is due to the fact that the next generation membrane should have certain potential advantages that include high selectivity and excellent permeability of desired molecules/ions. In addition to these merits, the membrane should be highly cost effective and should have good stability in terms of mechanical, chemical, and other aspects to manage wide range of applications. The chemical structure of graphene oxide itself enables it to act as membrane, and the GO has oxidative defects, which made it different from perfectly structured graphene.

Furthermore, the graphene oxide is not conductive since in graphene, the holes due to the defects made it viable to act as good membrane. The pores made through the channels present in the stack of two-dimensional GO layers, and the size of the pore is about 0.9 nm. GO membranes are chemically inert with numerous substances, which made it highly durable. In addition, GO is highly cost effective in comparison to pure graphene. Thus, less cost and higher durability with high selectivity and permeability made graphene oxide membrane as a good alternative for polymer membrane. Sreeprasad et al. [53] have shown the possibility of making large quantity of graphene nanomaterials in a cost effective manner in water purification.

Hu and Mi [54] demonstrated the efficacy of novel ion sieves made of graphene to separate the ions present in water. In previous years, several studies proposed membranes made of graphene that show exceptional molecular permeability; however, the permeable applications were restricted with the cutoff of around 9 A°. This restriction prevents these proposed membranes from separating the hydrated ions of common salts present in saline water. Another major constraint is swelling nature of membrane in the presence of water. The ion sieves proposed by Abraham et al. [55] were made of membrane with limited swelling in water, and the pore size ranged between 6.4 and 9.8 A°. This quality made the membrane more efficient on separating the hydrated ions from saline water, as in their work, about 97% of rejection of sodium chloride was achieved.

Recently, Mainak Majumder from Monash University developed a novel and revolutionary filter made of graphene, which might be the big solution for the water crisis across the world. The graphene-based filter was prepared by developing the viscous form of GO, which spread to produce a thin layer using a blade. The proposed methodology makes uniform arrangement in GO which attributes to produce the filter with special as well as highly impressive properties. The major advantage of this methodology includes the production of filters in a rapid manner with high effectiveness, and it can filter the particles larger than 1 nm. Figure 19 describes about the wastewater treatment.

## 10. Microorganism Removal by GO

Xue et al. [56] successfully prepared a series of GO composite hydrogels using redox-active crystalline ruthenium complexes as considerable noncovalent crosslinkers. The adsorbed bacteria due to the hydrogels then inactivated as the next stage. It was done by introducing a high voltage continuous electric pulse. Then, they were consequently removed completely from the hydrogels. Because of the effective bacteria removal rate, cost effective reusability, and low production cost, graphene oxide hydrogels are shown to be the promising choice for sterilization of the medical products or in the large-scale purification of drinking water.

## 11. GO Nanomaterials in Wastewater Treatment

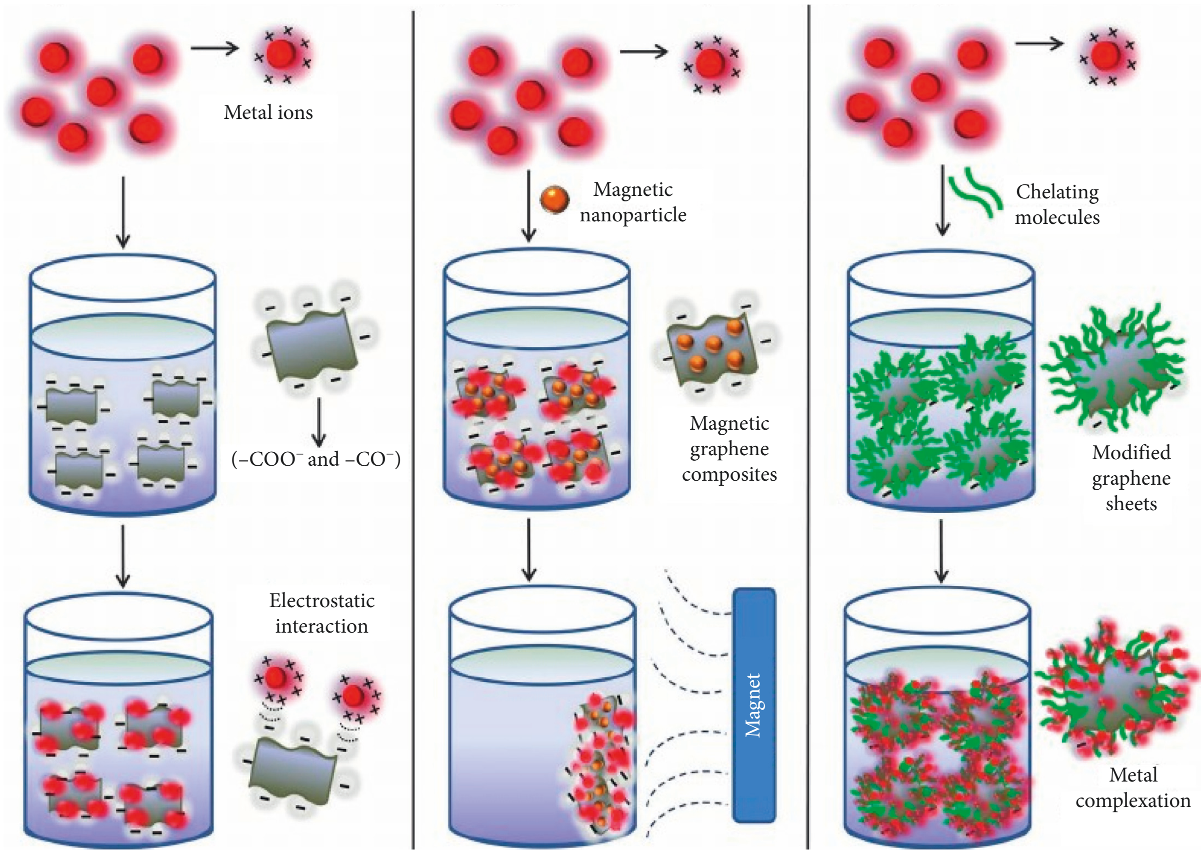
Graphene nanomaterials comprising graphene oxide (GO), reduced graphene oxide (rGO), pristine graphene (pGr), few layer graphene (FLG), and multilayer graphene (MLG) have a different role in wastewater treatment. Literatures clearly depicted that the last three materials mentioned here would be settled down consistently more easily than specific rGO in the foremost primary sediment, whereas GO remains in suspension, although it has been generally shown that the effective addition of a suitable coagulant can remove all the species from the liquid stream. There are no clear studies on the effect of nanomaterials in anaerobic digestive process in primary/secondary sludge [57].

The studies performed with aqueous solutions have depicted that wide range of minerals can adsorb in the top surface of graphene-family nanomaterials (GFNs) which leads to better primary sedimentation [58]. The sunlight, UV radiation in particular, as well as naturally occurring materials could easily reduce the GO into rGO. Different oxidative methodologies that include hydrogen peroxide, ozone, and Fenton's reaction can effectively oxidize the GFNs at rapid degradation rate. In addition to that, GO and RGO subject to the production of trihalomethanes, a byproduct, are used as a disinfectant. However, the specified list of tests have to be performed merely in wastewaters of primary, secondary, and the final tertiary effluents for a better understanding of the outcome of graphene nanomaterials. Most of the available nanomaterials in utilization have not been cost effective when compared to the conventional materials like activated carbon, and therefore future applications should be focusing on performance effective processes of nanomaterials [59].

Adsorption is one of the hopeful methods for the degradation of micropollutants due to several advantages such as simple design, less cost, better efficiency, etc. The graphene materials can also employed as photocatalyst, adsorbent, and disinfectants in wastewater treatment [60]. In this work, the various applications of graphene composite materials subjected to treating pharmaceutical industry wastewater were explained. Here, the effective mechanism of adsorption, used in removing the micropollutants [61] has reported a novel as well as inexpensive methodology to produce *Beta*-cyclodextrin integrated graphene oxide (GOCD) that has been fabricated to attain better adsorption of water-soluble organic dyes from aqueous solution. In this study, a simple sonolytic methodology was employed to produce GOCD. Another form of graphene oxide is well characterized for its adsorption properties by considering adsorption of the brilliant green (BG) dye by pseudo-second-order reaction kinetics. It also showed that the higher removal rate as well as better recyclability makes it a promising choice for the purification of wastewaters as well as recycling of water-soluble dyes in efficient manner.

## 12. Management of Organic Pollutants by Graphene

Of all the nanoparticle-based materials developed for the reduction of organic pollutants, graphene and its related materials seem to be efficient and are employed desirably to remove wide range of organic pollutants [62–65]. The combination of crystalline graphene with associated nanomaterials has shown to have various synergistic effects on the abatement of organic pollutants [66]. It has been rigorously shown that graphene and its nanomaterials remove organic pollutants by two approaches, namely, adsorption and photo



(a) (b) (c)

Figure 19: Wastewater treatment: electrical and magnetic approach. (a) Electrostatic interaction. (b) Magnetic nanocomposites. (c) Conjugation with molecules.

degradation [67]. For an eco-friendly atmosphere, the graphene material that is going to be used for adsorption during wastewater treatment should also be degraded at the earliest since the accumulation of graphene materials had been shown to cause toxic effect.

## 13. Heavy Metal Ion Adsorption by GO

The different heavy metal ions existing in water bodies are harmful to aquatic life, human beings, and surrounding environment [68], which has been a global concern for many years. GO is considered to be a peculiar adsorbent for the removal and reducing of metal ions such as zinc, copper, lead, cadmium, cobalt, etc. The adsorption affinity of GO to many metal ions seems to be strong and varies from the types of metal ions even though the adsorption selectivity of GO is poor. When the electronegativity of metal ions is higher, the attraction of the metal ions on the negatively electrified wide GO surface is stronger. Better adsorption of nano heavy metals on the surface of GO is attributed due to the presence of hydroxyl as well as carboxyl functional group in GO [69]. Presence of higher surface area, excellent mechanical strength, less weight, high flexibility, and chemical stability made GO more lucrative on removing heavy metals; the presence of multibonding functional group present on GO surface also improves the adsorption process. Figure 20 describes the adsorption of heavy metal ions by graphene composites [70].

## 14. Applications of Graphene Oxide

Graphene has been recently involved in the various research fields, which include biomedical, solar cells, batteries, super capacitors, supporting material for metal-based catalysts, low permeability components, biosensors, multi-functional materials for the purification of water, etc [71]. Due to widespread use of tetracycline antibiotics, tremendous amount of environmental pollution has been noticed, and removal of four such antibiotics (tetracycline, oxytetracycline, chlortetracycline, and doxycycline) from aqueous solution has been attempted using graphene nanoparticles [72]. Graphene has considerably high adsorption capacity than carbon nanotubes as well as granular activated carbon because of its reduced amount of compact bundle structure. The consequent impact of naturally available organic matter on the adsorption characteristics of synthetic organic compounds is said to be less on graphene. The consolidated results indicate that graphene can also serve as an effective alternative adsorbent for removing organic compounds from water [73].

A research group showed that the integration of a multilayered titanate nanosheet on the graphene enhances

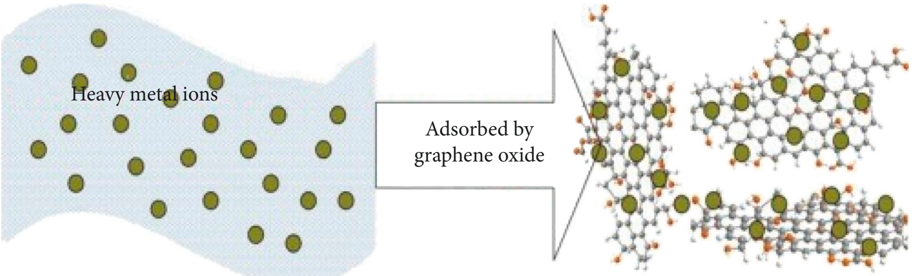


Figure 20: Metal ions adsorbed by graphene composite.

the algae-killing activity, highlighting the extreme beneficiary role of photo catalytic active titanate nanosheet [74]. Thus, the hybridization between nanographene and photo catalytically active inorganic nanosheets can help in removing harmful microorganisms like algal blooms in natural water. Heavy metal ions and ionic dyes often coexist which emphasizes an important as well as perilous source of environmental pollution [75].The multilevel magnetic graphene oxide (MGO) has been used as an efficient adsorbent for simultaneous removal of Cd(II)metal [76] and ionic coloring dyes like orange G(OG) and methylene blue (MB). Liu with his colleagues in 2012 synthesized a three-dimensional (3D) graphene oxide sponge (GO sponge) from a GO material suspension. It was then used to remove both the methylene blue (MB) and methyl violet (MV) dyes which are the main contaminants of the present dye manufacturing and most textile finishing factories.

Researchers produced reduced form of graphene oxides (RGOs) from GO, which was synthesized by modifying Hummers' method. This helps to develop a new nanocomposite comprising graphene oxide as a carrier as an active anticancer agent; this implies that GO could be very efficiently used for drug delivery for curing a dreadful disease like cancer. The substantial aggregation of pristine graphene nanosheet has been shown to decrease its extreme powerful adsorption capacity, thereby diminishing its various practical applications. To overcome this weakness, graphene-coated materials (GCMs) were synthesized by mixing graphene with silica nanoparticles ($SiO_2$). With the inherent support of large sum of $SiO_2$, the stacked interlaminated structures of graphene held open to express the adsorption sites in the interlayers. Here, the continuous adsorption of phenanthrene, which is an aromatic pollutant, loaded with graphene nanosheets, increased up to multifold compared with pristine graphene up to 100 times at the same absolute level. The adsorption of GCM increases with the combining amount of the graphene composite nanosheets and diminished with the introduction of complex oxygen-containing groups. GCM does not need a complex methodology for large-scale synthesis of graphene-coated materials. Graphene nanocoated materials using silica nanoparticles react to be a peculiar framework. It is found to be cost effective as well as highly efficient in removing aromatic pollutants from water. This can pave a way for enormous opportunities to use novel 2D nanomaterials (graphene) for environmental applications [77].

The modifiable electronic properties of GO nanomaterials make them interesting choice for photovoltaic energy conversion applications. Probably applications like photoluminescence, photovoltaic, and photo catalysis involve water splitting. GO is a p-doped semiconductor because electron-withdrawing oxygen functional groups reduce electron density on graphene [14]. Replacing the oxygen functionalities binding to the edge sites of GO results in the conversion of GO to an n-doped semiconductor. Alternate mode of doping with heteroatoms (e.g., nitrogen and boron) as replacements for carbon atoms in the hexagonal honeycomb lattice of graphene also generates *n*- or *p*-type conductivity. The effectiveness of this nanomaterial depends on the number of valence electrons associated with the dopant [15].

Photo catalytic reduction is a novel approach to GO reduction, which involves mechanisms that are different from those of photo thermal reduction. Under light irradiation, GO semiconductors do generate electron-hole pairs. The photo catalytic reduction of GO involves the transfer of photo generated electrons to other GO sheets and photo generated holes reacting with water, which results in the formation of peroxide. Sun et al. [63] adopted this approach and added isopropanol as photo generated hole trapping into the GO quantum dots suspension under UV light irradiation. Yeh et al. [78] presented a hydrothermal strategy using ammonia solution for fabricating the amino-functionalized GOQDs from GO sheets. Li et al. [69] were able to produce nitrogen-doped GO quantum dots (NGOQDs) by a simple hydrothermal route, using nitrogen-doped graphene as the starting material. This was obtained by annealing GO in an ammonia influenced atmosphere. Han et al. [79] reported an electrochemical approach for synthesizing boron-doped GOQDs. Here, the development of three types of GOQDs was carried out at low temperatures, with diameters in the ranges of 1–4, 4–8, and 7–11 nm, via acidic oxidation without any reduction routes. This indicates that large GOQDs have low oxidation levels [80] and these nanomaterials can be used in many applications.

Several earlier studies have motivated the development of alternative energy sources. In that, solar energy is considered as the most valuable energy source due to its abundance, clean, and eco-friendly. There are photovoltaic devices, based on the concept of electrified charge separation at the interface between two substances with different conduction mechanisms. This field is dominated by the solid-state junction device produced using silicon. On the other hand, high-energy requirements, high temperature, and high vacuum processes are needed to construct these conventional devices. One strategy for the development of chemical-based solar energy conversion is by using semiconductor-liquid junction solar cells. Graphene-based nanomaterials have been used as a medium for electron transfer and transportation to enhance solar energy conversion efficiency. Different from disk-like GOQDs, carbon quantum dots (CQDs) are spherical nanoparticles consisting of graphene nanosheets with less than 10 nm in size [78]. These CQDs are considered as core structures ending with hydrogen atoms, in which the graphitic core exhibits size-dependent absorption and large absorption coefficient.

Analogous to the sensitive surface of graphene, CQDs are typically surface functionalized with oxygen-containing functional groups (i.e., carboxyl and hydroxyl) during synthesis, rendering them highly dispersible molecules and stable in polar solvents. Briscoe et al. [81] prepared three different types of CQDs by simple hydrothermal carbonization of glucose, chitin, and chitosan, where the CQDs are named as G-CQDs, CT-CQDs, and CS-GQDs, respectively. GO quantum dots shown to possess accessible triplet states due to their edge effect have longer lifetime and diffusion lengths. In addition to a high extinction coefficient, modifiable band gap, and homogeneous size distribution, GOQDs synthesized by stepwise solution processes seem to be more suitable for solar energy conversion compared to that of some metal-based quantum dot sensitized solar cells. Algothmi et al. [82] have reported on the performance of active graphene oxide composite (Ca-$Alg_2$/GO) gel in removal of $Cu^{2+}$ ions from aqueous solution. Here, it shown that the encapsulated GO had more adsorbing property than the calcium alginate alone. Resin loaded with magnetic $\beta$-cyclodextrin and GO sheet (MCD-GO-R) was synthesized successfully [83] and suggested to be an excellent adsorbent for Hg(II) removal.

Fakhri [84] investigated the use of GO as a mere alternative adsorbent for removing aniline from aqueous solution. Cao and Li [13] have extensively highlighted the adsorption of carbon-based graphene in the removal of inorganic pollutants in wastewater purification. Oil in wastewater can be stabilized by GO. It flocculated by either an increase or a decrease in pH conditions. Graphene and its corresponding derivatives have been examined for pollution management. Poornima Parvathi et al. [85] have shown that the electrical characteristics such as photo catalytic and chemical characteristics such as antibacterial properties of graphene are obtained when synthesized from sugar and combined with sand particles.

Gupta et al. [86] have established the synthesis of sugar-derived graphene material supported on sand. This work describes an eco-friendly green approach for the synthesis of nanographene material from sugar cane, which is a common disaccharide. Here, a suitable methodology was introduced to immobilize the material along with sand without any need of binder, ending with the synthesis of composite material, referred to as GSC (graphene sand composite). Complete conversion of sugar to graphene carbon suggests a green methodology for the materialization of an active adsorbent material. Materials of this kind are expected to contribute to purification of drinking water. Recently, researchers found that the GO can be used as barrier and protective coating in the packaging industry. It can be achieved by modifying the structure of GO by removing the oxygen atoms present in the GO sheets so that a collapse in channels present inside the GO can be induced.

## 15. Toxic Effects of GO

Recent studies investigating the potential release of carbon-based nanomaterials and other nanoparticles by various industries have indicated that release will happen due to production, consumption, and reuse of these nanomaterials. Since the release of graphene into the environment is going to increase in coming years for wastewater treatment, we should also look upon its toxic effect in the environment. Nguyena et al. [87] aimed to determine the acuteness of destroying microbial community by graphene through biological treatment process.

## 16. Conclusion and Recommendations

This work clearly illustrates the efficacy of GO on widespread range of pollutants generated from different industries. Due to its ideal properties, the synthesis and preparation of GO membrane offer tremendous opportunities to change its physicochemical properties. The necessity for making the GO is due to its most cost-effective sustainable alternate behavior to the longtime existing thin-film composite membranes for water separation applications. In order to improve its full potential for its practical applications, we have to resolve the most challenging problems by producing high quality of graphene via environmentally friendly processes. The present and the latest graphene-based water purification systems are improved further by considering the following aspects: (1) improvement of water treatment efficiency on a widespread range of pollutants, (2) extension of the applicability towards different pollutant species, (3) upgrading the recovery rate from the tested system, and (4) enhancement and improving the effectiveness of the material reusability. With all the above features mentioned, it is very much clear that graphene can substitute most of the nanomaterials used for wastewater treatment and can be opted as one of the leading nanomaterials for many applications.

## Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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