



Assessment of Different Technologies using Graphene-Based Materials for the Adsorption of Atrazine in Polluted Water



Ahmed Hellal^a, Hazem Abdelsalam^b, Walid Tawfik^{a,*}, Medhat A. Ibrahim^d and Souad A. Elfeky^a

^a Department of Laser in Meteorology, Photochemistry & Agriculture (LAMPA), National Institute of Laser Enhanced Sciences, Cairo University, Giza, 122613, Egypt

^b Department of theoretical physics, National Research Centre Giza, 12266, Egypt

^c Department of Laser in Meteorology, Photochemistry & Agriculture (LAMPA), National Institute of Laser Enhanced Sciences, Cairo University, Giza, 12613, Egypt ^d Spectroscopy Department, National Research Centre Giza, 122613, Egypt

Abstract

Triazine herbicides like atrazine are common because of their effective weed control and affordable price. (70,000–90,000 tons of estimated annual worldwide use). It is crucial to conduct study on atrazine elimination from the environment because of the substance's stable structure, difficulty in the breakdown, prolonged environmental residence duration, and toxicity to both organisms and people. In surface and groundwater, atrazine was detected over the maximum allowable levels (3 μg L⁻¹ in the US, 0.1 μg L⁻¹ in Europe, and 3.0 μg L⁻¹ by the WHO for drinking water) As a result, many processing technologies, including adsorption, photochemical catalysis, biodegradation, and others, have been developed and are frequently used for atrazine degradation and removal. Recently, attention has been focused on carbon-based nanomaterials, particularly carbon nanotubes and Graphene, as cutting-edge materials for environmental applications. In particular, functionalized derivatives of carbon nanotubes and Graphene remove atrazine from contaminated Water. This critical review evaluates the development of different functionalized carbon nanotubes and graphene employed to remove pesticides and atrazine from polluted water, including the production and characterization processes of functionalized graphene, their applications for atrazine adsorption, and the effects of functionalization science on the adsorption efficiency. Further enhancing their adsorption and better modeling adsorption mechanisms are also indicated.

Keywords: Atrazine, Graphene, Raman, Functionalization, Doping, adsorption, and treatment.

1. Introduction:

Any poisonous agent intended to eradicate organisms that harm crops or environmental plants economically is a pesticide. All pesticides disrupt the pest organism's regular metabolic functions, and they are frequently categorized according to the kind of organisms they are meant to control, Like Phytocides, fungicides, insecticides, and fumigants.[1] Weeds compete with plants for water, nutrients, and light, reducing the quantity and/or

quality of the output.[2]. For instance, a decrease in corn production if uncontrolled, might rise to 30 to 90%. As a result, farmers use weed control techniques.

[3-4]. The most common water-soluble herbicide used worldwide is atrazine, [5]. It chemically consists of chlorotriazine and contains a ring structure called the triazine ring, along with five nitrogen atoms and a chlorine atom with molecular formula C₈H₁₄ClN₅. Atrazine is a colorless, odorless powder that isn't very combustible, reactive, or volatile. It comes in granular, wettable powder,

*Corresponding author e-mail: walid_tawfik@niles.edu.eg (W. Tawfik)

Receive Date: 26 May 2023, Revise Date: 14 July 2023, Accept Date: 31 July 2023

DOI: <https://doi.org/10.21608/ejchem.2023.213587.8025>

©2024 National Information and Documentation Center (NIDOC)

emulsifiable concentration, and ready-to-use forms. [6]. It has a melting point between 173 and 175 degrees Celsius, is 33 parts per million soluble in water at 20 degrees Celsius and is readily soluble in organic solvents [7]. There are more than 300 products that contain atrazine [8]. Many of them are only appropriate for use by experts.

Some can be used for domestic purposes. Atrazine-containing products may be labeled for use on soil, roadsides, sports fields, and lawns. After harvest, certain items can be applied to maize, sorghum, sugarcane, macadamia nuts, guava, or wheat stubble. [9]. Recently, more than 30 thousand tonnes have been applied annually, treating nearly 75 percent of the maize acreage. Although atrazine is loosely linked to the soil and has a low water solubility, it can seep into groundwater and surface waters. Atrazine is one of the herbicides that are most frequently found in surface and ground waterways in areas where it is applied. [10]. In the north of Egypt, atrazine residues detected in surface irrigation water ranged from 3.125 ± 0.0894 (at Kafer El- Dawwar) to 109.181 ± 15.778 $\mu\text{g/L}$ (at Hosh Essa) [11]. The World Health Organization (WHO) states that the permitted limit is limited to $2 \mu\text{g l}^{-1}$ [12]. The Environmental Protection Agency (EPA) approved the Maximum Contaminant Level (MCL) for atrazine as $3 \mu\text{g l}^{-1}$ under the Safe Drinking Water Act, which went into force in 1992 [13]. The legal guidelines of the European Economic Council (EEC) limit the concentration of each pesticide in drinking water to 0.1 g l^{-1} . [14]. Water should not include any pesticides, according to Indian Specifications [15]. As a result, there are currently no regulations regarding the permitted limit of atrazine content in effluent released into aquatic bodies. It is advised that atrazine be banned in the U.S. due to its endocrine-disrupting effects, potential carcinogenic effect, and epidemiological and sperm level reduction in men. Atrazine exposure can be dangerous and, in some situations, lead to health problems [16]. Water is one of the basic essential life needs for all living organisms. Approximately 75% of our planet is covered by water unfortunately 98 % of them are seawater which is unsuitable to use as drinking water, the remaining 2% consists of 1.6 % freshwater but is kept as ice water in the planet's poles, 0.36 % as groundwater and only 0.036% is valid drinking

water found in rivers and lakes [17]. The globe's population is expanding at a tremendous rate, and both industrialization and agriculture are developing quickly, which increases the demand for pure water, making it more valuable and essential as a resource in some regions of the world. Recently, a report published innature revealed that over 80% of the world's population is affected by serious threats to water security. [18]. Water treatment is increasingly necessary due to water shortages and the growing needs of the global population. Because of the intricate chemical combinations found in wastewater, conventional wastewater treatment is sometimes insufficient to eliminate the pollutant load. [19]. Adsorption is one of the most efficient procedures in modern wastewater treatment technologies, and it is widely used by industry and academic researchers to remove various contaminants [20]. Excellent adsorption performance toward organic compounds is exhibited by graphene nanosheets. [21]. It has an exceptional electrical, optical, chemical, thermal, and mechanical structure with an atom-thick two-dimensional layer. 1,2 It is a desirable material for many applications [22-23]. To satisfy the requirements in the practical extended scope of applications, Graphene frequently has to be chemically modified [24-25].

2. Graphene and functionalized graphene quantum dot:

2.1 Graphene

A single layer of graphite is called graphene that contains sp^2 hybridized and partially filled orbitals above and below the sheet's plane carbon atoms organized in a hexagonal lattice. Contrary to what may be expected, "graphene" is frequently preceded by "monolayer," "bilayer," or "few-layer." As shown in figure 1.

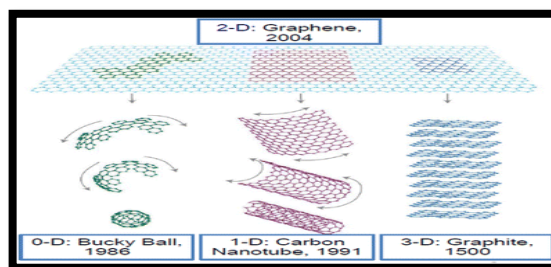


Figure 1: Structure of graphene and its dimensions with copyright permission [26]

The optimized graphene sheet has been demonstrated to be well-ordered and to exhibit a number of peculiar behaviors, such as non-corrosive qualities, tunable surface chemistry, high surface areas (2630 m²g⁻¹), a high Young's modulus (1.0 TPa), a high thermal conductivity of roughly 5000 W m⁻¹ K⁻¹, and a high electron mobility of 2.5 10⁵ cm² V⁻¹ s⁻¹ [27–29]. Its extended surface area appears to offer a strong affinity for the target analyte, making it a potent sorbent in the adsorption process. So graphene Materials have been selected as the building blocks for novel adsorbents with improved or added functionalities. [30–31]. Although those remarkable properties of Graphene need to be chemically modified to meet specific functions in wide applications of use [32–33]. Chemical functionalization is a successful method for modifying the structure and characteristics of Graphene [34–35].

2.2 Synthesis of Graphene and Graphene quantum dot

Any procedure for producing or extracting Graphene, based on the required size, purity, and efflorescence of the particular result, is referred to as synthesizing Graphene. From the graphite source available at a low cost, graphene-based material can be manufactured or created utilizing various mechanical or chemical processes [36]. There are two basic issues, though. How to manufacture graphene sheets at a large enough scale is one, because it is not easy to exfoliate graphite to produce graphene monolayer sheets and the other is its homogeneity of produced Graphene [37]. Graphene flakes were first created by micromechanical cleavage from bulk graphite; however, this approach has a very poor yield and is difficult to regulate. [38] There have been more recent reports of attempts to extract graphene sheets using silicon carbide heat treatment, chemical oxidation, or exfoliation of graphite. [39–45]. Traditionally, methods for creating nanomaterials have been categorized as "top-down" or "bottom-up." as demonstrated in figure 2. [46]. Graphene oxide (G.O.) [47], single-walled carbon nanotubes (SWCNTs) [48], multi-walled carbon nanotubes (MWCNTs) [49],

Graphene [50], and, more recently, porous carbon derived from metal-organic frameworks (MOFs) are the primary starting materials for top-down synthesis of GQDs. Typically, the precursors are treated using acid, hydrothermal, solvothermal, electrochemical, laser ablation, or exfoliation. Bottom-up approaches of synthesis for GQDs assemble fundamental building pieces with relevant qualities, including elemental precursors, such as atoms, molecules, or nanoclusters, by manipulating their interactions to enable the environmentally friendly large-scale manufacture of these nanomaterials. [51–52]. In this approach, one of the ways to create GQDs is the continuous injection of ethylene gas into an argon plasma to produce a beam of carbon atoms that was then dispersed in a chamber to produce GQDs that could be controlled in size [53]. For laser-induced photochemical stitching, haloaromatic substances like dichlorobenzene and chlorobenzene have been employed as carbon sources [54]. GQDs are thus created by solution chemistry's oxidation of polyphenylene dendritic precursors [50]. These nanomaterials can also be created by charring polycyclic aromatic hydrocarbons (PAHs) in a strong acid, such as H₂SO₄, before hydrothermal treatment.

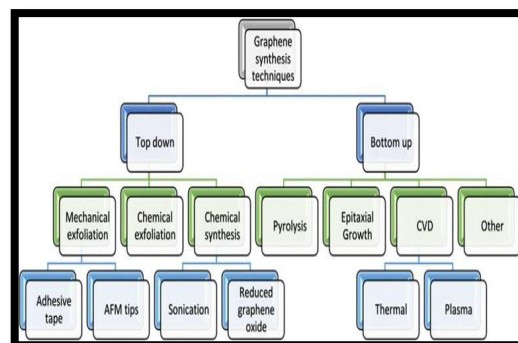


Figure 2 Different methods of graphene synthesis copyright with Permission of [55].

2.3 Synthesis of Functionalized and doped graphene

Carboxylate graphene was produced by treating the G.O. with an aqueous suspension of potassium hydroxide (KOH) and hydrogen peroxide solution (H_2O_2). All chemicals possessed analytical purity. More specifically, after 40 ml of the G.O. suspension with a concentration of 0.3 wt% was poured into polypropylene capsules, portions of the 60% KOH and 35% H_2O_2 aqueous solutions were added. The mixture was then cooked for 24 hours at 80 °C while being stirred. After cooling to room temperature, the resultant suspension of carboxylate graphene was centrifuged for 12 minutes at 18200 g while washing the precipitation with 30 cc of pure water. To completely remove the impurities from the manufactured C-XY Graphene, the aforementioned technique was carried out four times. During the synthesis, a pH meter was used to monitor the suspensions' pH levels. [56]. Modifying the electronic properties of graphene by doping and/or surface passivation is successful. [57]. One of the crucial methods for functionalizing or creating novel carbon compounds is a hydrothermal reaction [58] Graphene oxide served as the raw material for the hydrothermal approach of producing Nitrogen-doped G.O and urea served as the reducing-doping agent [59].

3- Structure and electronic properties

Graphene is classified as a zero-band gap material due to the energy dispersion of its charge carriers. This feature results in an infinite exciton Bohr radius in pure Graphene. tiny size graphene quantum dots exhibit remarkable characteristics because of quantum confinement and edge effects, which surpass those of nanosheets. [60]. They both affect the physical properties. Quantum confinement positively affects the electronic bandgap structures of GQDs [61]. The zigzag and armchair graphene edges as demonstrated in figure 3 exhibit unique quantum confinement features. The electrical structure of graphene is significantly impacted by these edges. It has been proved that graphene nanoribbons (GNRs) possessing predominant zigzag edges have a smaller band gap (0.14 eV) due to localized states on zigzag edges. Compared to similarly-sized graphene nanoribbons with distinct chair edges, there is a difference in the energy gap of 0.38 eV. [62]. As a result, with a graphene sheet of finite size, quantum confinement develops and becomes dominant in GQDs. [63]. It has been found

that when the amount of conjugated carbon atoms in GQDs increases the energy gap narrows. [64].

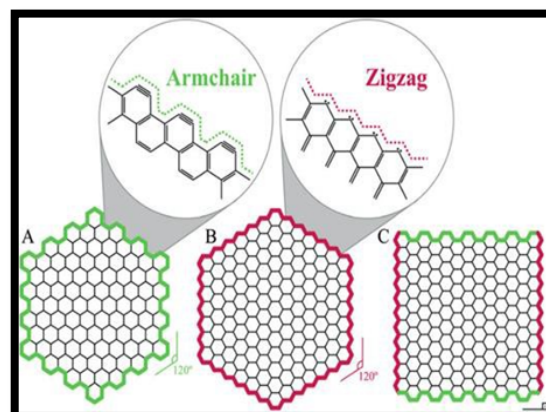


Figure 3. Graphene structure types of Zigzag and armchair with Copyright Royal Society of Chemistry @ (2014) permission [65]

4- Effect of functionalization and doping.

Functionalization causes the bandgap to slight reduction; The outcome emerges due to the transfer of charge from the functional groups to QGD [66]. To achieve bandgap narrowing, GQDs are conjugated with polyaromatic compounds to increase the size of the -conjugated sp^2 -carbon network. This is done because the bandgap of pristine QGD (Distance between π and π^* orbitals) is in inverse relation to the amount of the sp^2 domain. So that as the polyaromatic molecules become larger, the resulting QGD bandgap becomes narrower. [67] On the other side, the functionalization increases the total dipole moment strongly depending on the effect of the attached functional group [68] covalent or noncovalent methods for chemically modifying Graphene can be used. Through the covalent functionalization of the graphene basal plane see Figure 4, the " π - π " conjugation system undergoes deformation, where chemically unsaturated SP^2 covalent bonds change to SP^3 hybridization. This process leads to the transformation of planar aromatic carbons to a tetrahedral geometry with longer bonds. In contrast, Graphene's atomic and electronic structures are preserved by noncovalent functionalization, dangling bonds can form covalent bonds. A graphene sheet with dangling bonds will behave differently at its edge sites than it will at its basal plane which is more reactive on the edge side. [69-70].

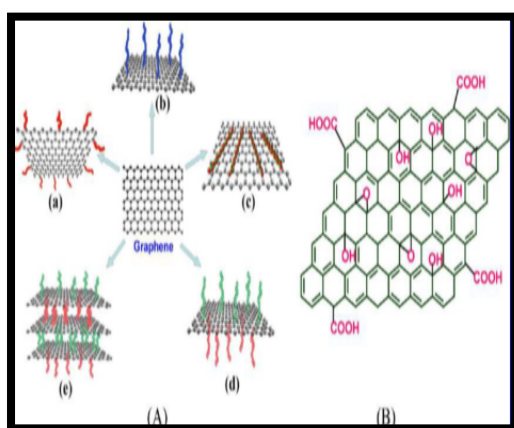


Figure 4 (A) Functionalization possibilities for graphene: (a) edge-functionalization, (b) basal-plane-functionalization, (c) noncovalent adsorption on the basal plane, (d) asymmetrical functionalization of the basal plane, and (e) self-assembling of functionalized graphene sheets. (B) Chemical structure of graphene oxide Copyright © 2013, American Chemical Society with permission [70].

4.1. Hydrogenation of pristine Graphene

Hydrogenation is the most common and uncomplicated chemical alteration that can be made to Graphene. Because carbon-carbon bonds are not broken, just one hydrogen can attach to each lattice carbon [71] A hydrogen atom is chemisorbed onto a flat monolayer graphene sheet to begin ideal hydrogenation. A relatively strong C-H bond formation requires an adsorption barrier of around 0.2 eV, which is high enough to prevent graphene hydrogenation in ambient conditions. Fortunately, the abundant tiny corrugations that appear as hills and valleys on a realistic graphene

layer significantly lowers the energy barrier for hydrogen adsorption [72-74]. If Graphene undergoes a full Hydrogenation process where all carbon atoms are saturated covalently with hydrogen the Graphene is called graphane as shown in figure 5 [75]. It seems that hydrogenation effect on electronic state of Graphene. With more hydrogen present, the band gap of hydrogenated Graphene widens and decreases electron mobility [76]. Many studies calculate hydrogenated graphene band gap. Son et al. verified this observation using ultraviolet photoelectron spectroscopy to quantify the band gap directly. The highest band gap they

discovered was 3.9 eV [77]. Approximation of the green function and screened Coulomb–interaction W (G.W. approximation) has given a bandgap of 5.4 eV [78]. Hydrogenation can acquire magnetic properties of graphene by adding the hydrogen atoms to the deformed planar graphene lattice, which increases spin-orbit interaction, creates local magnetic moments, and causes ferromagnetism [79-85]. Additionally, graphane exhibits antiferromagnetism, which is removed by decreasing the hydrogenation degree [86].

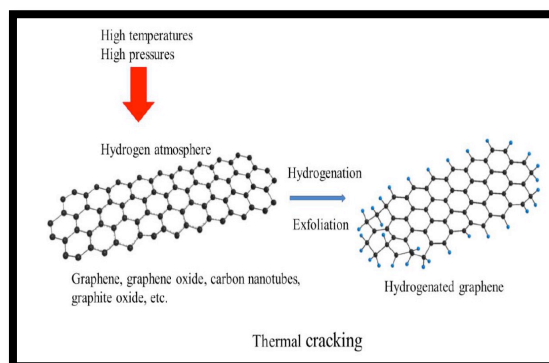


Figure 5. Production of hydrogenated graphene by thermal cracking of graphene-based material with Elsevier and Copyright Clearance Center Chemical Engineering Journal @ 2020 permission [87].

3. Graphene oxidation

Due to its essential relevance and future uses, graphene oxidation has recently been the subject of significant study [88-90]. In the standard state of a carbon atom in a graphene structure, the electron configuration consists of 1s², 2s², and 2p², with the p orbital electrons being distributed due to the single-layer structure of graphite. When we oxidized the graphite powder, the 2s electron jumped to the 2p_z state, whereas the hybridization in graphene is sp², which results in the generation of a free π electron in an excited state and the attachment of oxygen atoms to the free π electron (p_z electron) during the oxidation of graphite powder, forming C-O bonds in the graphite layers, causing the conversion of sp² to sp³ hybridization and several orders of magnitude reduction in electrical conductivity [91-92]. More significantly, graphene oxidation provides a model for the chemical functionalization of Graphene, which is crucial for adjusting its electrical, mechanical, and

optoelectronic properties [93-95]. Graphene oxide (GO), a one-layer form of graphite oxide, can be synthesized chemically using different methods. Graphene oxide can have a wide range of compositions depending on the production procedures and conditions see figures 6.a and 6.b.[96].

By adjusting the degree of oxidation using proper chemical processes, the sp^2 / sp^3 ratios in GO can be controlled which gives novel materials with new properties in each hybridization ratio [97]. Furthermore, GO possesses an oxygen atom that can create two covalent connections instead of just one, which makes adding oxygen to Graphene a more complicated process. For the oxidation of Graphene, three different chemical processes have been developed. The first involves oxidizing Graphene directly with potent oxidizing agents including concentrated sulfuric acid, concentrated nitric acid, and potassium permanganate are examples of substances that can cause oxidation [98]. The other approach involves exfoliating graphite after it has been oxidized by electrochemical, Hummers' Brodies Staudenmaier's, or other procedures [99-101]. Carbon nanotubes are lengthwise sliced and unravelled in the third oxidation process (CNTs).

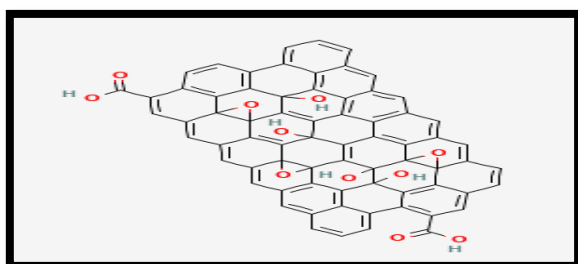


Figure 6.a. diagram depicting the functional groups of GO is presented, with A representing epoxy bridges, B representing hydroxyl groups, and C representing pairwise carboxyl groups. This diagram aims to inform knowledgeable readers in a neutral and general domain copyright permission [102].

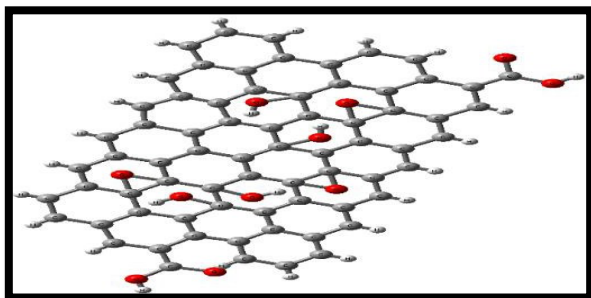


Figure 6.b. 3D GO diagram with functional groupings. A stand for epoxy bridges, B stands for hydroxyl groups, and C stands for pairwise carboxyl groups C copyright permission [102].

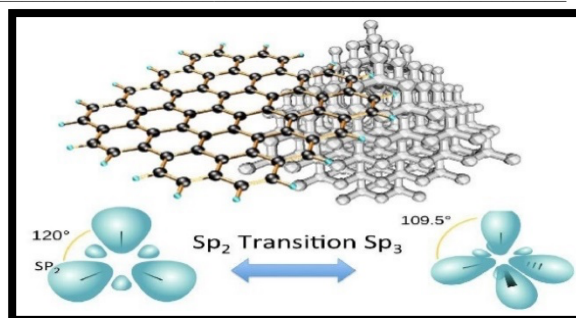


Figure 6.C. Graphene hybridization SP^2/SP^3 with copyright Permission [103]

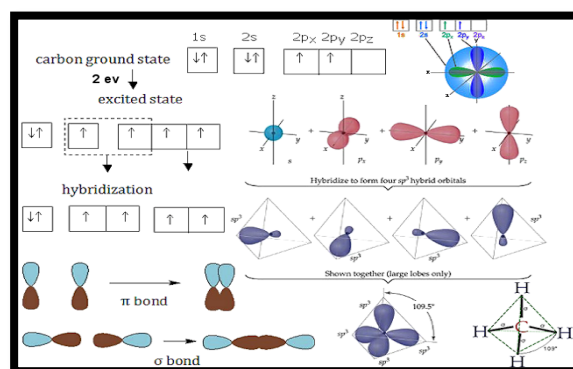


Figure 6.d. Hybridization depicts how the infusion of 2 eV of energy transformed electron probability distributions into a tetrahedral structure known as sp^3 Scaffolds with copyright permission [104]

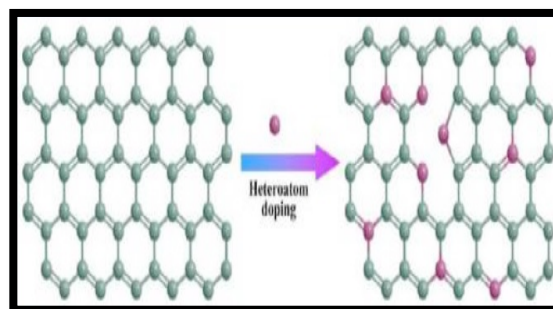


Figure 7 Doping graphene with heteroatoms (such as N) with Copyright © 2013, American Chemical Society permission [70]

The band gap of graphene oxide is proportional to the number of oxygen atoms. The band gap expands to several electron volts as the degree of oxidation rises. [105]. While the band gap in virgin graphene is zero, the band gap widens due to oxygen functionalization. The band gap expands to several electron volts as the degree of oxidation grows (oxygen coverage), which determines the electronic characteristics of the produced material [106-108].

4. Graphene Doping

Doping is the method of introducing heteroatoms into the carbon sp^2 lattice during the chemical functionalization of graphene see figure 7. Doping is a reliable method of modifying the electrical structures and electronic characteristics of graphene-based materials. [109-112]. Graphene is an atomically thin electrically active surface, any interaction with unrelated matter might cause its Fermi level to change [113-114]. Doping graphene with electron-withdrawing (p-type) species such as Boron or electron-donating (n-type) species such as phosphorus and nitrogen can increase electron density and electrochemical properties [115]. For example, because the boron atom is less electronegative than the carbon atom, when it is doped in graphene, it provides p-type conductivity. [116].

5. Adsorption mechanism

Adsorption is the process by which a molecule or ion existing in a gaseous or liquid bulk clings to the surface of a solid, or very rarely a liquid., q ($mg\ g^{-1}$) is the amount of adsorbed per mass unit of adsorbent q_m ($mg\ g^{-1}$) is the maximum amount of adsorbate in the adsorbent C (ml^{-1}) is the concentration of adsorbate in the environment b (mg^{-1}) is the equilibrium constant related to the enthalpy of the process. The enthalpy of adsorption is a measure of the heat released during adsorption, At a fixed temperature, the differential enthalpy of adsorption Δh^- is defined as the change in the total enthalpy of the system (gas phase, host, and guest molecules) when a molecule is transported from the gas phase to the adsorbed phase. [128-129].

The adsorbent's surface is engaged, and that adsorbate does not penetrate into the structure [117]. Two types of adsorptions can be distinguished: physical adsorption (also known as physisorption), in which the adsorbate sticks to the surface due to physical forces, and chemical adsorption if the adsorbate is chemically bound to the adsorbent's surface. Physisorption Vander Waals adsorption is another name for this adsorption, which occurs when atoms, particles, or ions that adsorb on surfaces naturally attract one another. Because the atom or molecule that experiences physical adsorption is not chemically reactive, physical adsorption is not specific [118-120]. Chemical adsorption, also known as chemisorption, is the second kind. This sort of hydrogen bond is created between the surface and the atoms, molecules, or ions that adsorb on the surface. Chemical adsorption is distinguished by privacy (specific) since it occurs under particular conditions, and adsorption may not occur on another surface under the same conditions or on the surface itself when the surrounding conditions change. As the

adsorption process achieves equilibrium, adsorption isotherms may be used to investigate the relationship and interaction between the absorbent and adsorbate [121-123]. When a molecule is absorbed onto a specific volume of adsorption surface, heat is emitted, which is proportionally related to this released heat [124]. Many factors affect on adsorption process Like pH [125], Temperature Effect, Nature of Adsorbate, and surface area [126-127] There are many types of isotherms. The isotherms of Langmuir and Freundlich are the most commonly utilized. Many models describe the adsorption, one of them is the following equation describes the Langmuir isotherm.

$$q = \frac{bq_m C}{1 + bC}$$

b (mg^{-1}) is the equilibrium constant related to the enthalpy of the process. The enthalpy of adsorption is a measure of the heat released during adsorption, At a fixed temperature, the differential enthalpy of adsorption Δh^- is defined as the change in the total enthalpy of the system (gas phase, host, and guest molecules) when a molecule is transported from the gas phase to the adsorbed phase. [128-129].

H : is equal to the total enthalpy, H_{sys} : relates to the system enthalpy (host and guest molecules) H_g : to

$$\Delta h \left(\frac{-\partial \Delta H}{\partial n} \right)_{v,T} = \left(\frac{-\partial \Delta H_{sys}}{\partial n} \right)_{v,T} - \left(\frac{-\partial \Delta H_g}{\partial n} \right)_{v,T}$$

the enthalpy of a reference gas stage, n : is the quantity adsorbed or "loading", V : Is system volume T : Temperature.

When typically, the change in enthalpy is less than $20\ kJ\ mol^{-1}$ ($0.2\ eV$), that means adsorption is physical, with no newly formed bonds and adsorption system (adsorbate and adsorbent), with no change to their both chemical and energetic state. Moreover, the opposite situation will happen when the change in enthalpy is more than $40\ kJ\ mol^{-1}$ ($0.4\ eV$) to $400\ kJ\ mol^{-1}$ [129].

6. Graphene-based Materials for the removal of pollutants from water

Nano-based adsorbents for atrazine removal are receiving a lot of attention from researchers. Various adsorbents, such as nanoparticles, nanometals, MgO particles, and carbon-based materials, were used for atrazine removal [130]. Because of their greater surface area and adsorption capability, materials based on Graphene have been discovered as suitable adsorbents in decontaminating water [131]. In 2004 Faur et al got successfully adsorption of pesticides onto activated carbons in the form of fibers, of high

specific surface area ($1,460 \text{ m}^2 \text{ g}^{-1}$), the pesticides (atrazine, methylatropine, des isopropyl atrazine, simazine) showed the influence of the adsorbate's solubility ranged from 370 mg g^{-1} for simazine, 238.1 mg g^{-1} Atrazine DIA and DEA 119 and 303 mg g^{-1} respectively [132]. Valentina f. Domingues et al. in 2007 as shown in Table 1 used a granulated activated carbon (GAC) to adsorb α -cypermethrin and the maximum adsorption was $186 \pm 12 \text{ (}\mu\text{g/g)}$ [133]. In Chen et al 2010 and Wang et al the groups were able to adsorb and extract pesticides at a low level, were 6 pyrethroid pesticides (Bifenthrin, Permethrin, Cypermethrin, Fenvalerate, Deltamethrin, and Cyhalothrin in $10\mu\text{g/L}$ –1level with recovery of more than 88% using Graphene-coated fiber was adsorbed efficaciously, In the second group in 2012 was able to absorb

Neonicotinoids pesticides in the range $0.5\text{--}5 \mu\text{g/L}$ level with the recovery of more than 94%, by magnetic graphene nanoparticles respectively [134–135]. In their publication (Yan et al 2008) studied the adsorption of atrazine on carbon Nanotubes using Two kinds of carbon nanotubes with different structures, namely SMWNT20 and r-MWNT, The maximal adsorption capacities of SMWNT20 and r-MWNT were determined using the Langmuir model at 298 K, and they are 31.37 mg/g and 100.43 mg/g , respectively [136]. In a recent study in 2021, a graphene Nano sheet positively adsorbs atrazine. The optimal conditions for atrazine removal using G.O. Nano sheets had a maximum atrazine removal effectiveness of 97.01% when dosed at 121.45 mg/L , $27.69 \text{ }^\circ\text{C}$, and pH 5.37, according to statistical calculations. [137]

Table 1. Carbon-based nanomaterials and their capacity in to adsorb pesticides and atrazine in the aqueous medium Copyright © 2013, American Chemical Society permission [70]

Nano-adsorbent	Surface area $\text{m}^2 \text{ g}^{-1}$	Target pollutants	Maximum capacity of adsorption		STSD-2
			Theoretical	Experimental	Reference
Granulated activated carbon	972	α -cypermethrin	-	$186 \pm 12 \mu\text{g/g}$	DOMINGUES et al (2007) [133]
Graphene-coated silica	328.2	organophosphorus pesticides	-	$170 \text{ mg}/150 \text{ mg}$	Xiaotong Liu et al (2013) [138]
carbon nanotubes(r-MWNT)	299.63	(6 Pesticides) Atrazine	Positive adsorption	110.8	X.M.Yan (2008) [136]
Reduced graphene oxide	-	Chlorpyrifos		Reduced graphene oxide	
Graphene oxide-supported nanoscale zero-valent iron	82.55–183.20	Atrazine	-	25 mg/l dose	Rong Xing et al (2020) [139]
graphene derivatives, h-BN, and BNC heterostructures	-	Atrazine	Strong physical interaction (DFT)	-	Arezoo Goli et al 2020 [140]
SWNTs single-walled carbon nanotubes (SWNTs)	405.95		-	53.77 mg/g	Shi et al. (2010) [141]
MWCNTs multi-walled carbon nanotubes	174	Atrazine	-	51.5 mg/g	Ellerie et al. (2013) [142]
Graphene quantum dots nanomaterials GQD	1221	Oxamyl carbamat e insecticide		130.10 mg/g	Shilpi Agarwala et al 2016 [143]

7- Spectral identification of graphene-based material

Raman spectroscopy can be used to swiftly, nondestructively, and with high resolution identify the lattice structure and the electrical, optical, and phonon properties of carbon materials, such as three-dimensional (3D) diamond and graphite, 2D graphene, 1D carbon nanotubes, and 0D fullerenes.

[144-150]. Raman spectroscopy is the study of the inelastic scattering of light by materials, including crystals and molecules [151]. To comprehend why the Raman spectroscopy has been crucial in the advancement of the science relating to sp² Nanocarbons, it is necessary to take into account a number of factors necessary to take into account several factors: The Raman polarizability tensor is strongly modulated by vibrations in carbon nanostructures, and the scattering processes are resonant due to the electrons, ensuring a strong response.

The Raman spectra shows high peaks because of strong C-C bonds. Even a small change in frequency (less than 1%) can be easily seen using common spectrometers. [152-153]. The principal Raman signature for all sp² carbons is the G band, which is connected to the stretching of the C-C bond and appears as a peak (or multipeak feature) at about 1585 cm⁻¹ (see Figure 8). The primary sp² Raman signal of disorder is the D band (or defects). It is seen as a peak that measures between 1250 and 1400 cm⁻¹. The quantifying disorder can be done using the D band intensity.

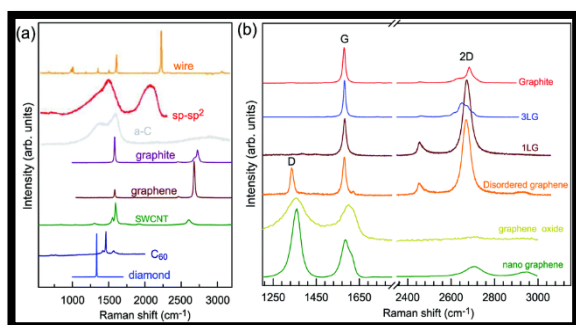


Figure 7.a. Raman spectra of carbon solids and nanostructures, such as amorphous carbon (a-C), (a) Raman spectra of carbon solids and nanostructures such as carbon wires, sp-sp² carbon, amorphous carbon (a-C), graphite, graphene, single-walled

carbon nanotubes (SWNT), C60, and diamond. Raman spectra of carbon wire, sp-sp² carbon, a-C. (b) Raman spectra of graphene-derived materials such as graphite, 1LG, 3LG, disordered graphene, graphene oxide, and nanographene with copyright permission [154]

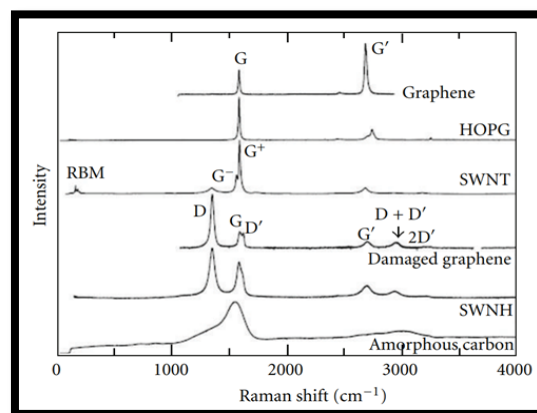


Figure 8. Raman spectra of numerous sp² nanocarbon. The G band, which is connected to C-C bond stretching (see eigenvector is the major Raman signature for all sp² carbons and appears as a peak (or multipeak feature) at roughly 1585 cm⁻¹ Copyright @2012 with permission of [155]

Conclusion

This review addressed the utilization of Graphene- and carbon nanotube-based nanomaterials for the adsorption of specific pesticides, particularly the most prevalent and harmful Atrazine pesticide. Various modified carbon-based nanomaterials have been used to adsorb pesticides and atrazine and following functionalization, the adsorption performance and adsorptive capacity improve. In recent years, carbon-based nanomaterials have been utilized to adsorb herbicides. This article summarizes the preparations, characterizations, and applications of these materials. The impacts of Doping oxidation, hydrogenation of pristine Graphene in adsorption, coexisting ions, adsorption isotherms, kinetics, thermodynamics, and other pertinent mechanisms, on the adsorption of atrazine by functionalized carbon-based nanomaterials, were examined. However, additional study is still required to concentrate on the preparation of more refined carbon-based nanomaterials for wastewater with combined pollutants.

References

- 1) Mohamed A. Hassaan and Ahmed, (2020), Pesticides pollution Classifications, human health impact, extraction and treatment techniques, The Egyptian J. of Aquatic Research., Vol. 46 ,Pg 207-220.
- 2) E. El-Sobky E.A and N.Z.A. El-Naggar. 2016. Effect of weed control treatments and planting density in maize (*Zea mays* L.). Egypt. J. Agron. 38: 55-77.
- 3) Abouzinea, H.F., M.A.M. Ahmed, A.T. Eldabaa and M.S.A. Abd El-Wahed. 2013. A comparative study on the productivity of two yellow maize cultivars grown under various weed control management. Middle-East J. Agric. Res. 2: 56-67.
- 4) Khaliq, T., T. Mohmood and A. Masood. 2004. Effectiveness of farmyard manure, poultry manure and nitrogen for corn (*Zea mays*) productivity. Int. J. Agric. Biol. 2: 260-263. Köck-Schulmeyer, M., A. Ginebreda, C. Postigo, T. Garrido, J. Fraile, M. López de Alda and D. Barceló. 2014. Four Year Advanced Monitoring Program of Polar Pesticides in Groundwater of Catalonia (NE-Spain), Sci. Total Environ. 470–471: 1087-98.
- 5) Thurman, M.D., Goolsby, M.T., Meyer, M.S., Mills, M.S., Pomes, M.L., and Kolpin, D.W., 1992, A reconnaissance study of herbicides and their metabolites in surface water of the Midwestern U.S. using immunoassay and GC-MS, Environmental Science and Technology, 26, 2440-2447
- 6) INCHEM (2011) Atrazine Fact Sheet.
Available: <http://www.inchem.org/documents/icsc/icsc/eics0099.htm>
- 7) NPIC Product Research Online (NPRO): Atrazine; National Pesticide Information Center: Corvallis, OR, 2019.
- 8) Martins, E.C.; de Freitas Melo, V.; Boone, J.B.; Abate, G. Sorption and desorption of atrazine on soils: The effect of different soil fractions. Geoderma 2018, 322, 131–139. [CrossRef]
- 9) Roberts, T. Atrazine. Metabolic Pathways of Agrochemicals; Part One: Herbicides and Plant Growth Regulators; The Royal Society of Chemistry: Cambridge, UK, 1998
- 10) U.S. Geological Survey Science in the Decade 2007–2017 (USGS, 2007)
- 11) Mohamed A.F. Abuzeid; Atef M.K. Nassar; Alaa M. H. Khozimy “Atrazine Residues in Surface Water from Various Agricultural Areas of ElBehera Governorate, Egypt” 2022.
- 12) WHO (1993) Guidelines for drinking- water quality. Vol. 1. Recommendations, 2nd ed., World Health Organization, Geneva.
- 13) U. S. National Library of Medicine (1995) Hazardous substances databank. Bethesda, MD.
- 14) Council of European Communities (1980) Council directive of 15 July, 1980 relating to the quality of water intended for human consumption (80/778/EEC), Official Journal of the European Communities, L229.
- 15) Environmental (Protection) Rule of India (1986), Gazette of India, S.O. 844(E), 19.11.1986.
- 16) Rohr, J.R., and Crumrine, P.W., 2005, Effects of an herbicide and an insecticide on pond community structure and process, Eco Apps, 15(4), 1135-1147
- 17) WHO/UNICEF Joint Monitoring Programme (JMP) for Water Supply and Sanitation (2010) Progress on Sanitation and Drinking Water.
- 18) Vörösmarty CJ, McIntyre PB, Gessner MO, Dudgeon D, Prusevich A, et al. (2010) Global threats to human water security and river biodiversity. Nature 467: 555-561.
- 19) Escher B, Leusch F, Chapman H (2011) Bioanalytical tools in Water Quality Assessment. IWA Publishing.
- 20) Rao MM, Reddy DH, Venkateswarlu P, Seshaiha K (2009) Removal of mercury from aqueous solutions using activated carbon prepared from agricultural byproduct/waste. J Environ Manage 90: 634-643.
- 21) SaraKhalihaa , AntonioBianchia , AlessandroKovtun (2022) , Graphene oxide nanosheets for drinking water purification by tandem adsorption and microfiltration , Italy
- 22) K. Rana, J. Singh and J.–H. Ahn, J. Mater. Chem. C, 2014, 2, 2646–2656. 4 D. Wei, B. Wu, Y
- 23) Guo, G. Yu and Y. Liu, Acc. Chem. Res., 2013, 46, 106–115
- 24) S. Eigler and A. Hirsch, Angew. Chem. Int. Ed., 2014, 53, 7720–7738. 14 Y. X. Xu, H. Bai, G

- 25) W. Lu, C. Li and G. Q. Shi, *J. Am. Chem. Soc.*, 2008, 130, 5856–5857.
- 26) Bhuyan, M.S.A., Uddin, M.N., Islam, M.M. et al. Synthesis of graphene. *Int Nano Lett* 6, 65–83 (2016). <https://doi.org/10.1007/s40089-015-0176-1>
- 27) C. Lee, X. D. Wei, J. W. Kysar and J. Hone, *Science*, 2008, 321, 385–388
- 28) A. A. Balandin, S. Ghosh, W. Z. Bao, I. Calizo, D. Teweldebrhan, F. Miao and C. N. Lau, *Nano Lett.*, 2008, 8, 902–907
- 29) R. R. Nair, P. Blake, A. N. Grigorenko, K. S. Novoselov, T. J. Booth, T. Stauber, N.M. R. Peres and A. K. Geim, *Science*, 2008, 320, 1308
- 30) Q. Liu, J.B. Shi, G.B. Jiang, Application of Graphene in analytical sample 619 preparation, *TrAC-Trends Anal. Chem.* 37 (2012) 1-11
- 31) L. Wang, X.H. Zang, C. Wang, Z. Wang, Research developments for 621 applications of Graphene in sample preparation, *Chinese J. Anal. Chem.* 42 622 (2014) 136-144.
- 32) Perreault, F., Fonseca de Faria, A., Elimelech, M., 2015. Environmental applications of graphene-based nanomaterials. *Chem. Soc. Rev.* 44, 5861e5896
- 33) S. Eigler and A. Hirsch, *Angew. Chem. Int. Ed.*, 2014, 53, 7720–7738.
- 34) Y. X. Xu, H. Bai, G. W. Lu, C. Li and G. Q. Shi, *J. Am. Chem. Soc.*, 2008, 130
- 35) M. Quintana, E. Vazquez and M. Prato, *Acc. Chem. Res.*, 2013, 46, 138–148
- 36) B. Yuan, Ch. Bao, L. Song, N. Hong, K. M. Liew and Y. Hu, *Chemical Engineering Journal*, 2014, 237, 411–420
- 37) Jianchang Li 1,2, Xiangqiong Zeng The Preparation of Graphene Oxide and Its Derivatives and Their Application in Bio-Tribological Systems *Lubricants* 2014, 2, 137-161; doi:10.3390/lubricants2030137.
- 38) K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, *Science* 2004, 306, 666
- 39) D. Li, M. B. Muller, S. Gilje, R. B. Kaner, G.G. Wallace, *Nat. Nanotechnol.* 2008, 3, 101.
- 40) X. Fan, W. Peng, Y. Li, X. Li, S. Wang, G. Zhang, F. Zhang, *Adv. Mater.* 2008, 20, 1
- 41) Y. Hernandez, V. Nicolosi, M. Lotya, F. M. Blighe, Z. Sun, I. T
- 42) McGovern, B. Holland, M. Byrne, Y. K. Gun'ko, J. J. Boland, P. Niraj, G. Duseberg, S. Krishnamurthy, R. Goodhue, J. Hutchison, V. Scardaci, A. C. Ferrari, J. N. Coleman, *Nat. Nanotechnol.* 2008, 3, 563
- 43) Y. Si, E. T. Samulski, *Nano Lett.* 2008, 8, 1679.
- 44) G. Wang, J. Yang, J. Park, X. Gou, B. Wang, H. Liu, J. Yao, *J. Phys. Chem. C* 2008, 112, 8192
- 45) J. T. Robinson, F. K. Perkins, E. S. Snow, Z. Wei, P. E. Sheehan, *Nano Lett.* 2008, 8, 3137
- 46) J. Shen, Y. Zhu, X. Yang, J. Zong, J. Zhang and C. Li, One-pot hydrothermal synthesis of graphene quantum dots surface-passivated by polyethylene glycol and their photoelectric conversion under near-infrared light, *New J. Chem.* 36 (2012) 97-101.
- 47) Y. Zhang, H. Gao, J. Niu, B. Liu, Facile synthesis and photoluminescence of graphene oxide quantum dots and their reduction products, *New J. Chem.* 38 (2014) 4970-4974
- 48) Y. Dong, H. Pang, S. Ren, C. Chen, Y. Chi, T. Yu, Etching single-wall carbon nanotubes into green and yellow single-layer graphene quantum dots, *Carbon* 64(2013) 245-251
- 49) L. Minati, S. Torrenzo, D. Maniglio, C. Migliaresi, G. Speranza, Luminescent graphene quantum dots from oxidized multi-walled carbon nanotubes, *Mater. Chem. Phys.* 137 (2012) 12-16.
- 50) A. Ananthanarayanan, X. Wang, P. Routh, B. Sana, S. Lim, D. Kim, K. Lim, J. Li, P. Chen, Facile synthesis of graphene quantum dots from 3D Graphene and their application for Fe³⁺ sensing. *Adv. Funct. Mater.* 24 (2014) 3021-3026.
- 51) X. Yan, X. Cui, Large, solution-processable graphene quantum dots as light absorbers for photovoltaics, *Nano Lett.* 10 (2010) 1869-1973
- 52) R. Liu, D. Wu, X. Feng, K. Mullen, Bottom-up fabrication of photoluminescent graphene quantum dots with uniform morphology, *J. Am. Chem. Soc.*

- 133 (2011) 15221-15223
- 53) J. Kim, J.S. Suh, Size-Controllable and Low-Cost Fabrication of Graphene Quantum Dots Using Thermal Plasma Jet, *ACS Nano* 8 (2014) 4190-4196.
- 54) R. Gokhale, P. Singh, Blue luminescent graphene quantum dots by photochemical stitching of small aromatic molecules: fluorescent nanoprobes in cellular imaging, *Part. Part. Syst. Charact.* 31 (2014) 433-438.
- 55) Vestince B. Mbayachi, Euphrem Ndayiragije, Thirasara Sammani, Sunaina Taj, Elice R. Mbuta, Atta ullah khan, Graphene synthesis, characterization and its applications: A review, *Results in Chemistry*, Volume 3, 2021, 100163, ISSN 2211-7156
- 56) S A Ryzhkov et al 2020 *J. Phys.: Conf. Ser.* 1695 012008 On the synthesis of the carboxylated Graphene via graphene oxide liquid-phase modification with alkaline solutions *Journal of Physics: Conference Series*
- 57) Shen, J., Zhu, Y., Yang, X. & Li, C. Graphene Quantum Dots: Emergent Nanolights for Bioimaging, Sensors, Catalysis and Photovoltaic Devices. *Chem. Commun.* 48,3686–3699 (2012)
- 58) Zhou Y, Bao QL, Tang LAL, Zhong YL, Loh KP (2009) Hydrothermal dehydration for the “green” reduction of exfoliated graphene oxide to Graphene and demonstration of tunable optical limiting properties. *Chem Mater* 21(13):2950–2956
- 59) Hui-Lin Guo, a Peng Su, a Xiaofeng Kanga and Sheng-Ke Ning Synthesis and characterization of nitrogen-doped graphene hydrogels by hydrothermal route with urea as reducing-doping agents *Journal of Materials Chemistry A*
- 60) Y. Sun, Y. Zheng, H. Pan, J. Chen, W. Zhang, L. Fu, K. Zhang, N. Tang and Y. Du, *npj Quantum Materials*, 2017, 2, 5
- 61) M. A. Sk, A. Ananthanarayanan, L. Huang, K. H. Lim, P. Chen, *J. Mater. Chem. C* 2014, 2, 6954.
- 62) K. Nakada, M. Fujita, G. Dresselhaus and M. S. Dresselhaus, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1996, 54, 17954–17961
- 63) K. A. Ritter and J. Lyding, *Nat. Mater.*, 2009, 8, 235–242.
- 64) A. K. Geim and K. S. Novoselov, *Nat. Mater.*, 2007, 6, 183–191.
- 65) Facure, Murilo & Schneider, Rodrigo & Mercante, Luiza & Correa, Daniel. (2020). A review on graphene quantum dots and their nanocomposites: From laboratory synthesis towards agricultural and environmental applications. *Environmental Science Nano.* 7. 10.1039/d0en00787k
- 66) Bikash Mandal , Sunandan Sarkar , Pranab Sarkar Exploring the electronic structure of graphene quantum dots *J Nanopart Res* (2012) 14:1317 DOI 10.1007/s11051-012-1317-3
- 67) X. Hai, J. Feng, X. Chen, J. Wang, *J. Mater. Chem. B* 2018, 6, 3219.
- 68) Yibo Yan, Jun Gong, Jie Chen, Zhiping Zeng, Wei Huang, Kanyi Pu, Jiyang Liu, and Peng Chen Recent Advances on Graphene Quantum Dots: From Chemistry and Physics to Applications
- 69) Hazem Abdelsalam, Hanan Elhaes b, Medhat A. Ibrahim Tuning electronic properties in graphene quantum dots by chemical functionalization: Density functional theory calculations *Chemical Physics Letters* 695 (2018) 138–148
- 70) *Acc. Chem. Res.* 2013, 46, 1, 31–42 Publication Date: October 3, 2012 <https://doi.org/10.1021/ar300122m>
- 71) G. Shi and X. Wang, *Phys. Chem. Chem. Phys.*, 2015, DOI: 10.1039/C5CP05212B
- 72) 4J. O. Sofu, A. S. Chaudhari, and G. D. Barber, *Phys. Rev. B* 75,4 (2007).
- 73) Cortes-Arriagada, S. Gutierrez-Oliva, B. Herrera, K. Soto, A. Toro-Labbe, The mechanism of chemisorption of hydrogen atom on Graphene: Insights from the 11 reaction force and reaction electronic flux, *J. Chem. Phys.* 141 (2014)
- 74) Y. Miura, H. Kasai, W.A. Dino, H. Nakanishi, T. Sugimoto, Effective pathway for hydrogen atom adsorption on Graphene, *J. Phys. Soc. Jpn.* 72 (2003) 995-997.14
- 75) J.C. Meyer, A.K. Geim, M.I. Katsnelson, K.S. Novoselov, T.J. Booth, S. Roth, 15 The structure of suspended graphene sheets, *Nature* 446 (2007) 60-63
- 76) D. C. Elias, R. R. Nair, T. M. G. Mohiuddin, S. V. Morozov, P. Blake, M. P. Halsall, A.C. Ferrari, D. W. Boukhvalov, M. I. Katsnelson, A. K. Geim and K. S. Novoselov, *Science*, 2009, 323, 610–613
- 77) T.O. Wehling, M.I. Katsnelson, A.I. Lichtenstein, Adsorbates on Graphene: 2 3 4 5 6 7 8 9 10 11 12 13

14 15 16 17 18

- 78) Son, J., Lee, S., Kim, S. et al. Hydrogenated monolayer graphene with reversible and tunable wide band gap and its field-effect transistor. *Nat Commun* 7, 13261 (2016). <https://doi.org/10.1038/ncomms13261> 5J. Son, S. Lee,
- 79) S. Lebegue, M. Klintonberg, O. Eriksson and M. I. Katsnelson, *Phys. Rev. B*, 2009, 79, 245117.
- 80) Sahin, R.T. Senger, S. Ciraci, Spintronic properties of zigzag-edged triangular graphene flakes, *J. Appl. Phys.* 108 (2010).
- 81) J.H. Lee, J.C. Grossman, Magnetic properties in graphene-graphane superlattices, *Appl. Phys. Lett.* 97 (2010)
- 82) M.J. Schmidt, D. Loss, Edge states and enhanced spin-orbit interaction at graphene/graphane interfaces, *Phys. Rev. B* 81 (2010)
- 83) H. Sahin, C. Ataca, S. Ciraci, Magnetization of graphane by dehydrogenation, *Appl. Phys. Lett.* 95 (2009)
- 84) J. Berashevich, T. Chakraborty, Sustained ferromagnetism induced by H- vacancies in graphane, *Nanotechnology* 21 (2010)
- 85) Whitener, Review Article: Hydrogenated Graphene: A user's guide, *J. Vac. Sci. Technol.*, A 36 (2018)
- 86) H. Sahin, C. Ataca, S. Ciraci, Electronic and magnetic properties of graphane 39 1 nanoribbons, *Phys. Rev. B* 81 (2010).
- 87) Yuhuan Fei, Siyuan Fang, Yun Hang Hu, Synthesis, properties and potential applications of hydrogenated graphene ,*Chemical Engineering Journal*, Volume 397, 2020, 125408, ISSN 1385-8947, <https://doi.org/10.1016/j.cej.2020.125408>
- 88) Li JL, Kudin KN, McAllister MJ, Prud'homme RK, Aksay IA, Car R. Oxygen-driven unzipping of graphitic materials. *Phys Rev Lett.* 2006 May 5;96(17):176101. doi: 10.1103/PhysRevLett.96.176101. Epub 2006 May 2. PMID: 16712313.
- 89) Dikin, Dmitriy A, Stankovich, Sasha , Piner, Richard D , "Preparation and characterization of graphene oxide paper" *Nature*, 448, 457 DO - 10.1038/nature06016 (2007).
- 90) Eda, G., Fanchini, G. and Chhowalla, M. Large-Area Ultrathin Films of Reduced Graphene Oxide as a Transparent and Flexible Electronic Material. *Nature Nanotechnology*, 3, 270-274. (2008) <http://dx.doi.org/10.1038/nnano.2008.83>
- 91) Geim, A.K. and Novoselov, K.S. The Rise of Graphene. *Nature Materials* (2007), 6, 183-191. <https://doi.org/10.1038/nmat1849>
- 92) Jergel, Matej , Susi, Toma , Mittelberger, Andreas, Meyer, Jannik C, Kotakoski, Jani 'Chemical Oxidation of Graphite: Evolution of the Structure and Properties' *J. Phys. Chem. C* (2017) , 929 , 935 122 <https://doi.org/10.1021/acs.jpcc.7b10912>
- 93) Wu, Xiaosong and Sprinkle, Mike and Li, Xuebin and Ming, Fan and Berger, Claire and de Heer, Walt A "Epitaxial-Graphene/Graphene-Oxide Junction: An Essential Step towards Epitaxial Graphene Electronics" *Phys. Rev. Lett.*(2008), 101 , 2 , 026801. Doi = 10.1103/PhysRevLett.101.026801
- 94) Jung, I and Dikin, D. A. and Piner, R. D. and Ruoff, R.S "Tunable electrical conductivity of individual graphene oxide sheets reduced at "low" temperatures, *Nano letters* (2008), 12 ,8 DOI = {10.1021/nl8019938}
- 95) Mattevi C, Eda G, Agnoli S, Miller S, Mkhoyan K, A. Celik O, Mastrogianni D, Granozzi G, Garfunkel E, Chhowalla M., *Adv. Funct. Mater.*, 2009, vol. 19 pg. 2577
- 96) Tsuyoshi Nakajima and Akihiro Mabuchi and Rika Hagiwara 'A new structure model of graphite oxide; *journal of Carbon* 1988 ,V. 26 ,pg. 357-361
- 97) Brodie Benjamin Collins 1859XIII. On the atomic weight of graphite *Phil. Trans. R. Soc.* 149249–259 01 January 1859 <http://doi.org/10.1098/rstl.1859.0013>
- 98) K. S. Subrahmanyam, S. R. C. Vivekchand, Govindaraj and C. N. R. Rao, *J. Mater. Chem.*, 2008, 18, 1517–1523.
- 99) Hummers, W.S. and Offeman, R.E. (1958) Preparation of Graphitic Oxide. *Journal of the American Chemical Society*, 80, 1339-1339. <http://dx.doi.org/10.1021/ja01539a017>
- 100) Park, S., Ruoff, R. Chemical methods for the production of graphene's. *Nature Nanotech* 4, 217–224 (2009). <https://doi.org/10.1038/nnano.2009.58>
- 101) Vaishali Gupta, Neeraj Sharma, Uday Singh, Mohd. Arif, Arun Singh, Higher oxidation

- level in graphene oxide, *Optik*, Volume 143, 2017, Pg. 115-124, ISSN 0030-026, <https://doi.org/10.1016/j.ijleo.2017.05.100>.
- 102) Kim S, Chen J, Cheng T, et al. PubChem 2023 update. *Nucleic Acids Res.* 2023;51(D1):D1373–D1380. doi:10.1093/nar/gkac956
- 103) Aversa, R., Petrescu, R.V.V., Petrescu, F.I.T. and Apicella, A. (2018) Nanodiamond for Structural Biomimetic Scaffolds. *Journal of Materials Science and Chemical Engineering*, 6, 6-17. <https://doi.org/10.4236/msce.2018.64002>
- 104) <https://universe-review.ca/R13-16-graphene.htm>
- 105) Velasco, Miguel, Perez, Alfonso Alvarez-Quintana, J.Cao, Yu Nyborg, L.Licea, Liliana Selective band gap manipulation of graphene oxide by its reduction. *Carbon*, (2015), volume 93 DO - 10.1016/j.carbon.2015.06.013
- 106) Shen, Y. et al. Evolution of the bandgap and optical properties of graphene oxide with controllable reduction level. *Carbon N. Y.* 62, 157–164 (2013)
- 107) Wahab, H. S., Ali, S. H. & Abdul, H.M. Synthesis and Characterization of Graphene by Exfoliation of Graphite Flakes. 1, 130–135 (2015)
- 108) Yan, J. A., Xian, L. & Chou, M. Y. Structural and electronic properties of oxidized graphene. *Phys. Rev. Lett.* 103, 1–4 (2009)
- 109) Dacheng Wei, Yunqi Liu, Yu Wang, Hongliang Zhang, Liping Huang, and Gui Yu “Synthesis of N-Doped Graphene by Chemical Vapor Deposition and Its Electrical Properties” *Nano Letters* 2009 9 (5), 1752-1758 DOI: 10.1021/nl803279t
- 110) Wang X, Li X, Zhang L, et al. N-doping of graphene through electrothermal reactions with ammonia. *Science* (New York, N.Y.). 2009 May;324(5928):768-771. DOI: 10.1126/science.1170335. PMID: 19423822.
- 111) Zhao L, He R, Rim KT, Schiros T, Kim KS, Zhou H, Gutiérrez C, Chockalingam SP, Arguello CJ, Pálová L, Nordlund D, Hybertsen MS, Reichman DR, Heinz TF, Kim P, Pinczuk A, Flynn GW, Pasupathy AN. Visualizing individual nitrogen dopants in monolayer graphene. *Science*. 2011 Aug 19;333(6045):999-1003. doi: 10.1126/science.1208759. PMID: 21852495.b
- 112) M. Riede, C. Urich, J. Widmer, R. Timmreck, D. Wynands, G. Schwartz, W.-M. Gnehr, D. Hildebrandt, A. Weiss, J. Hwang, S. Sundarraj, P. Erk, M. Pfeiffer, and K. Leo, “Efficient Organic Tandem Solar Cells based on Small Molecules,” *Adv. Funct. Mater.* 21(16), 3019–3028 (2011)
- 113) Drechsel, B. Männig, F. Kozłowski, M. Pfeiffer, K. Leo, H. Hoppe, Efficient organic solar cells based on a double P-I-N architecture using doped wide-gap transport layers, *Appl. Phys. Lett.* 86 (2005) 244102
- 114) M.-L. Yang, N. Zhang, K.-Q. Lu and Y.-J. Xu, *Langmuir*, 2017, 33, 3161-3169.6. A. Omidvar, *Mater. Chem. Phys.*, 2017, 202, 258-265. *New Journal of Chemistry*.
- 115) Agnoli, Stefano. Favaro, Marco. "Doping graphene with boron: a review of synthesis methods, physicochemical characterization, and emerging applications" *Journal of Materials Chemistry*, (2016), 4DO- 10.1039/C5TA10599D
- 116) Junaid M, Khir MHM, Witjaksono G, Tansu N, Saheed MSM, Kumar P, Ullah Z, Yar A, Usman F. “Boron-Doped Reduced Graphene Oxide with Tunable Bandgap and Enhanced Surface Plasmon Resonance”. *Molecules*. 2020 Aug 1;25(16):3646. doi: 10.3390/molecules25163646. PMID: 32796504; PMCID: PMC7465222.
- 117) Y Artioli, . Introduction The Chemistry of Adsorption Equations for Adsorption University of Padua, Padua, Italy
- 118) Moore, W.J. (1972) “Partial Molar Entropy and Partial Molar Heat Capacity of Electrons in Metals and Superconductors” *Physical Chemistry*. 4th Edition, Prentice-Hall, Englewood Cliffs, New Jersey, 538-539.
- 119) Mhemeed, Amal” A General Overview on the Adsorption” 2018, vol 9 pg.16127-16131
- 120) Hayward, D. O. and Tranpell, B. M. W., “Chemisorption”. Butter Worths, 2nd ed., (1964).
- 121) Tompkins, F. C., “Chemisorption of gasses on metals”. Academic Press, (1978).
- 122) Szabo, Z. G. and Kallo, D., “Contact Catalysis”. (1976) Vol. 1, Elsevier Scientific publishing comp., Copenhagen, p.134
- 123) Al-Grawi, E.D.C., and G.R.L. Al-Awsi. 2018. “Expression of CDKN2A (P16/Ink4a) among Colorectal Cancer Patients: A Cohort Study.” *Journal of Pharmaceutical Sciences and Research* 10

- 124) Saleh, Jalal Mohammed, "Surface Chemistry and Assistive Factors". College of Science Press - University of Baghdad (1980). 2010.08.008
- 125) Awad, K. M., "The principle of soil chemistry". Basrah University Press, Basrah (1986). 135) Wang W, Li Y, Wu Q, Wang C, Zang X, Wang Z (2012) Extraction of neonicotinoid insecticides from environmental water samples with magnetic graphene nanoparticles as adsorbent followed by determination with HPLC. *Anal Methods* 4:766–772. <https://doi.org/10.1039/c2ay05734d>
- 126) Haj Ali, A. and El – Bishtawi , R. , "Removal of Lead and Nickel ions using zeolite tuff". *J. chem.* (1997). *Tech.Biotechnol.* , 69, 27 – 34 136) X.M. Yan , B.Y. Shi, J.J. Lu, C.H. Feng, D.S. Wang, H.X. Tang Adsorption and desorption of atrazine on carbon nanotubes , *Journal of Colloid and Interface Science* 321 (2008) 30–38.
- 127) Myers, A. L.; Monson, P. Adsorption in Porous Materials at High Pressure: Theory and Experiment. *Langmuir* (2002), 18, 10261–10273 137) S.Muthusarayanan a,b, K. Balasubramani c, Rahul Suresh d, R. Sankar Ganesh E,N. Sivarajasekar a, , H. Arul f, K. Rambabu g, , G. Bharath g, V.E. Sathishkumar h, A.P. Murthy i,Fawzi Banat g Adsorptive removal of noxious atrazine using graphene oxide nanosheets:Insights to process optimization, equilibrium, kinetics, and density functional theory calculationsv (2021) <https://doi.org/10.1016/j.envres.2021.111428>
- 128) Myers, A. L. Thermodynamics of adsorption in porous materials. *AIChE J.* (2002), 48, 145–160. 138) Liu, Xiaotong and Zhang, Hongyan and Ma, Yongqiang and Wu, Xiaoli and Meng, Lixuan and Guo, Yunlong and Yu, Gui and Liu, Yunqi", ="Graphene-coated silica as a highly efficient sorbent for residual organophosphorus pesticides in water", *J. Mater. Chem. A*,"2013",Vol.15, Pg.1875-1884
- 129) Do DD, Nicholson D, Fan C. Development of equations for differential and integral enthalpy change of adsorption for simulation studies. *Langmuir.* 2011 Dec 6;27(23):14290-9. doi: 10.1021/la203531j. Epub 2011 Nov 7. PMID: 22013949 139) Rong Xinga , Jingjing Hea , Pulin Haoa , Wenjun Zhoua,b, (2020). Graphene oxide-supported nanoscale zero-valent iron composites for the removal of atrazine from aqueous solution *Colloids and Surfaces A: Physicochemical and Engineering Aspects* Vol. 589, 20 ,DOI: <https://doi.org/10.1016/j.colsurfa.2020.124466>
- 130) Ahmad Munir, Riaz Umair, Iqbal Shazia, Ahmad Jahangir, Rasheed Hina, Al-Farraj Abdullah S. F., Al-Wabel Mohammad IAdsorptive Removal of Atrazine From Contaminated Water Using Low-Cost Carbonaceous Materials*Frontiers in Materials* . Vol9(2022) DOI=10.3389/fmats.2022.909534 140) Arezoo Goli and Heshmatollah Alinezhad and Masoud Darvish Ganji , ,(2020) ."Theoretical insights into the performance of graphene derivatives, h-BN and BNC heterostructures in the adsorption and elimination of atrazine: An all-electron DFT study: *Diamond and Related Materials* vol.108, Pg. 107967
- 131) Liu Q, Shi J, Zeng L, Wang T, Cai Y, Jiang G (2011) Evaluation of Graphene as an advantageous adsorbent for solid- phase extraction with chlorophenols as model analytes. *J Chromatogr A* 1218:197–204. <https://doi.org/10.1016/j.chroma.2010.11.022> *MaterialsFrontiers in Materials* . Vol 9(2022) DOI=10.3389/fmats.2022.909534 141) Shi, B., Zhuang, X., Yan, X., Lu, J., and Tang, H. (2010). Adsorption of Atrazine by Natural Organic Matter and Surfactant Dispersed Carbon Nanotubes. *J. Environ. Sci.* 22 (8),1195–1202.doi:10.1016/s1001-42(09)60238-2
- 132) Faur C, Métivier-Pignon H, Le Cloirec P (2005) Multi component adsorption of pesticides onto activated carbon fibers. *Adsorption* 11:479–490
- 133) Dominguez VF, Priolo G, Alves AC, Cabral MF, Delerue-matos C (2007) Adsorption behavior of a-cypermethrin on cork and activated carbon. *J Environ Sci.HealPart.B*42:649 <https://doi.org/10.1080/03601230701465635>
- 134) Chen J, Zou J, Zeng J, Song X et al (2010) Preparation and evaluation of graphene-coated solid-phase micro- extraction fiber. *Anal Chim Acta* 678:44–49. <https://doi.org/10.1016/j.aca>

- 142) Ellerie JR, Apul OG, Karanfil T, Ladner DA. Comparing graphene, carbon nanotubes, and superfine powdered activated carbon as adsorptive coating materials for microfiltration membranes. *J Hazard Mater.* 2013 Oct 15;261:91-8. doi: 0.1016/j.jhazmat.2013.07.009. Epub 2013 Jul 13. PMID: 23911830.
- 143) Shilpi Agarwala , Inderjeet Tyagib , Vinod Kumar Guptaa,b, Ali Fakhric, , Nima Sadegh (2016). Adsorption of toxic carbamate pesticide oxamyl from liquid phase by newly synthesized and characterized graphene quantum dots nanomaterials *Journal of Colloid and Interface Science* Vol. 478, 15 Pg.430-438 <https://doi.org/10.1016/j.jcis.2016.06.029>
- 144) Milani A, Tommasini M, Russo V, Li Bassi A, Lucotti A, Cataldo F, Casari CS. Raman(2015) spectroscopy as a tool to investigate the structure and electronic properties of carbon-atom wires. *Beilstein J Nanotechnol.* 17;6:480-91. doi: 10.3762/bjnano.6.49. PMID: 25821689; PMCID: PMC4362090.
- 145) A. Ferrari, J. Meyer, V. Scardaci, C. Casiraghi, M. Lazzeri, F. Mauri, S. Piscanec, D. Jiang, K. Novoselov and S. Roth, et al., *Phys. Rev. Lett.*, 2006, 97, 187401.
- 146) F. Tuinstra and J. L. Koenig, "Raman Spectra of Graphite," *The Journal of Chemical Physics*, Vol. 53, No. 3, 1970, pg. 1126-1130. doi:10.1063/1.1674108
- 147) V. Raman, *The Molecular Scattering of Light*, Nobel Lecture, 1930
- 148) A. Jorio, M. S. Dresselhaus, R. Saito, and G. Dresselhaus, *Raman Spectroscopy in Graphene Related Systems*, WileyVCH, Weinheim, Germany, 2011
- 149) F. Tuinstra and J. L. Koenig, "Raman spectrum of graphite," *Journal of Chemical Physics*, vol. 53, no. 3, pp. 1126–1130, 1970
- 150) Wu, Jiangbin & Lin, Miao-Ling & Xin, Cong & Liu, He-Nan & Tan, Ping-Heng. (2018). Raman spectroscopy of graphene-based materials and its applications in related devices. *Chemical Society Reviews*. 47. 10.1039/C6CS00915H.
- 151) V. Raman, *The Molecular Scattering of Light*, Nobel Lecture, 1930.
- 152) A. Jorio, M. S. Dresselhaus, R. Saito, and G. Dresselhaus, (2011) *Raman Spectroscopy in Graphene Related Systems*, WileyVCH, Weinheim, Germany,
- 153) F. Tuinstra and J. L. Koenig, (1970) "Raman spectrum of graphite," *Journal of Chemical Physics*, vol. 53, no. 3, pp. 1126–1130,
- 154) Wu, Jiangbin & Lin, Miao-Ling & Xin, Cong & Liu, He-Nan & Tan, Ping-Heng. (2018). Raman spectroscopy of graphene-based materials and its applications in related devices. *Chemical Society Reviews*. 47. 10.1039/C6CS00915H.
- 155) Jorio, A. (2012). *Raman Spectroscopy in Graphene-Based Systems: Prototypes for Nanoscience and Nanometrology*. ISRN Nanotechnology. 2012. 10.5402/2012/234216