

**CHEMICAL SURFACE MODIFICATION OF
GRAPHENE NANOPATELETS BY
CARBOXYLATION PROCESS FOR ENHANCED
SORPTION CAPACITIES**

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by

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LIST OF ABBREVIATIONS

BET	Brunauer–Emmett–Teller
CNT	Carbon nanotube
DLG	Double layers graphene
FLG	Few layers graphene
FTIR	Fourier-transform infrared spectroscopy
fGNPs	Functionalize graphene nanoplatelets
GNPs	Graphene nanoplatelets
GO	Graphene oxide
H ₂ SO ₄	Sulphuric acid
HCl	Hydrochloric acid
HNO ₃	Nitric acid
HRTEM	High-resolution transmission electron microscopy
KMnO ₄	Potassium permanganate
MB	Methylene blue
MG	Malachite green
MLG	Multilayers graphite
RAMAN	Raman spectroscopy
RBBR	Remazol blue R
RB	Remazol black
RBV	Remazol brilliant violet 5R
rGO	Reduce graphene oxide
SEM	Scanning Electron Microscope
SLG	Single layer graphene
SWCNT	single- walled carbon nanotubes

TGA	Thermogravimetric Analysis
UV Vis	Ultraviolet–visible spectroscopy
2D	two- dimensional
1D	one-dimensional

LIST OF SYMBOLS

A_T	Temkin constant related to equilibrium binding energy
b	Langmuir constant
b_T	Temkin constant related to the heat of adsorption
C_0	Initial dye concentration
C_t	Final dye concentration at time t
ΔG	Gibbs free energy
ΔH	Enthalpy change
K_1	Pseudo first-order constant rate
K_2	Pseudo second-order constant rate
K_F	Freundlich constant
K_L	Standard thermodynamic equilibrium constant
n	Adsorption intensity related to Freundlich isotherm
q_e	Adsorption capacity at equilibrium
q_m	Monolayer adsorption capacity related to Langmuir constant
q_{cal}	Calculated adsorption capacity
q_{exp}	Experimental adsorption capacity
R	Universal gas constant
R^2	Correlation coefficient
R_L	The dimensionless separation factor
ΔS	Entropy change
T	Absolute temperature
X^2	Chi-square
ξ	Removal efficiency

**PENGUBAHSUAIAN PERMUKAAN KIMIA GRAPHENE
NANOPLATELETS MELALUI PROSES KARBOKSILASI UNTUK
MENINGKATKAN KAPASITI PENJERAPAN**

ABSTRAK

Tujuan tesis ini adalah untuk mengkaji pengubahsuaian permukaan karbon melalui pengikatan kimia atau fizikal melalui proses karboksilasi untuk aplikasi pemulihan alam sekitar seperti penyingkiran pewarna dari air kumbahan. Pemfungsian graphene nanoplatelet (fGNP) diperlukan dalam banyak aplikasi alam sekitar dan fungsian yang tepat adalah merupakan pendekatan yang efisien untuk meningkatkan keupayaan penjerapan graphene. fGNP adalah antara bahan yang menjanjikan untuk penyingkiran pewarna kerana semua karbon nanomaterial ini mempunyai luas permukaan spesifik yang tinggi dan mempunyai keupayaan untuk mewujudkan interaksi elektrostatik yang kuat dengan pelbagai kumpulan fungsi yang mengandungi oksigen dan sistem π -elektron. Kesan fGNP belum dikaji secara meluas, dan banyak kumpulan penyelidikan di seluruh dunia hanya memberi tumpuan kepada permukaan CNT, graphene, GO dan rGO. Dalam tesis ini, pendekatan mudah untuk pengubahsuaian permukaan dan perfungsian nanoplatelet graphene dikaji. Pendekatan ini melibatkan fungsian penyebaran serpihan grafena dengan jenis asid dan isipadu nisbah volumetrik untuk membuktikan keadaan terbaik untuk penyebaran yang lebih besar. Dua jenis asid yang digunakan dalam pendekatan ini iaitu asid sulfurik dan asid nitrik. Pengubahsuaian kimia yang mudah dengan pengoksidaan asid mendorong penyebaran mudah dalam air dan kapasiti penyerapan tinggi metilena biru. Ciri-ciri morfologi, struktur dan bahan kimia fGNP dikaji oleh satu set teknik pencirian pelengkap seperti Fourier

transformed infrared spectroscopy (FTIR), mikroskop elektron scanning (SEM), mikroskop elektron penghantaran resolusi tinggi (HRTEM), analisis thermogravimetric (TGA), Spectroscopy Raman dan pengukuran potensi Zeta . Kawasan permukaan BET nanoplatelet graphene (GNP) dan fGNP adalah dalam lingkungan $115-150 \text{ m}^2 / \text{g}$. Kesan suhu ($30-60 \text{ }^\circ \text{C}$), masa hubungan (5 hingga 55 minit), dan kepekatan pewarna awal ($25-200 \text{ mg} / \text{L}$) terhadap prestasi penjerapan penyerap telah disiasat. Kapasiti penjerapan maksimum fGNP meningkat daripada $112 \text{ mg} / \text{g}$ kepada $151 \text{ mg} / \text{g}$ pada pH 4 dan $60 \text{ }^\circ \text{C}$. Ini boleh dikaitkan secara langsung dengan peningkatan kumpulan berfungsi seperti hidroksil dan karboksil pada permukaan adsorben diubah suai yang menghasilkan prestasi penjerapan yang lebih tinggi daripada GNP yang diubahsuai. Data keseimbangan yang diperolehi dinilai menggunakan isotem, model penjerapan kinetik dan kajian termodinamik. Untuk penyerap fGNP1, data isotherm dijelaskan dengan ketara oleh model Langmuir. Kajian kinetik mendedahkan bahawa model kadar pseudo-first order adalah yang lebih baik dengan data eksperimen. Nilai parameter termodinamik, termasuk ΔG^0 ($9.39, 9.21$ dan 9.45 untuk suhu $30 \text{ }^\circ \text{C}$, $45 \text{ }^\circ \text{C}$, dan $60 \text{ }^\circ \text{C}$), ΔH^0 ($8.85 \text{ kJ} / \text{mol}$) dan ΔS^0 ($-1.57 \text{ kJ} / \text{mol}$) . Dari keputusan experiment, fGNP menunjukkan bahawa penjerapan MB adalah proses spontan dan endotemik.

CHEMICAL SURFACE MODIFICATION OF GRAPHENE NANOPLATELETS BY CARBOXYLATION PROCESS FOR ENHANCED THE SORPTION CAPACITIES

ABSTRACT

The aim of this thesis is to investigate the surface modification of carbon through chemical or physical attachment via carboxylation process for environmental remediation applications such as dye removal from wastewater. Chemical functionalization of graphene is required in many environmental applications and proper functionalization is an efficient approach to improve the adsorption capacity of graphene. Functionalized graphene nanoplatelet (fGNP) is a promising material for dye removal as this all-carbon nanomaterial possesses high specific surface area and has the ability to create a strong electrostatic interaction with a variety of oxygen-containing functional groups and π -electron systems. The effect of fGNP has not been widely explored, and many research groups worldwide have been focusing only on CNT, graphene, GO and rGO surfaces. In this thesis, a facile approach for the surface modification and fGNP were investigated. The approach involves fGNP with different type of acid and volumetric ratio acid to prove the best condition for greater dispersibility. Two type of acid used in this approach which are sulphuric acid and nitric acid. Their facile chemically modification by acid oxidation induces both facile dispersion in water and high adsorption capacity of methylene blue. Morphological, structural and chemical properties of the fGNP are deeply investigated by a set of complementary characterization techniques such as Fourier transformed infrared spectroscopy (FTIR), Scanning electron microscopy (SEM), High-resolution transmission

electron microscopy (HRTEM), Thermogravimetric analysis (TGA) , Raman Spectroscopy and Zeta potential measurement. The BET surface areas raw GNP and functionalize GNP were in the range of 115-150 m²/g. Effects of temperature (30-60 °C), contact time (5 to 55 min), and initial dye concentration (25-200 mg/L) on adsorption performance of adsorbents were investigated. The maximum adsorption capacity of fGNPs increased from 112 mg/g to 151 mg/g at pH 4 and 60 °C. This can be directly linked to the increased of functional groups such as hydroxyl and carboxyl on the surface of modified adsorbents resulting in higher adsorption performance of fGNP. The equilibrium data gained were evaluated using isotherms, kinetic adsorption models and thermodynamic studies. For fGNP1 adsorbents, the isotherm data were significantly described by Langmuir model. The kinetic study revealed that the pseudo-first-order rate model was in better agreement with the experimental data. The values of the thermodynamic parameters, including ΔG^0 (9.39, 9.21 and 9.45 for temperature 30°C., 45°C, and 60 °C respectively), ΔH^0 (8.85 kJ/mol) and ΔS^0 (-1.57 kJ/mol). From the results, fGNP showed that MB adsorption is a spontaneous and endothermic process.

CHAPTER 1

INTRODUCTION

This chapter presents the background of the current research works which covers topics such as graphene, graphene nanoplate (GNPs) and modification of GNP via functionalization and application for dye removal. Separate sections are assigned for each of these topics. Then, the impulses of the current work are expressed after recognizing the issues faced. A set of objectives are outlined, and the contributions of the existing study is described. Finally, the organization of chapters in this thesis is given.

1.1 Graphene and Graphene Nanoplates (GNPs)

In 2009, Geim and Novoselov, physicists from Manchester University, won the Nobel Prize in Physics for pioneering new scientific experiments in the discovery of the two dimensional material called graphene (Geim, 2009). Then, many studies have been carried out on this almost completely transparent material and researchers have tried to understand its unique properties. Graphene is known as a carbon family member consisting of sp^2 -bonded carbon atoms arranged in a two-dimensional honeycomb grid (Spyrou and Rudolf, 2014) (Figure 1.1), which is stronger than steel and can be a better conductor than any other material. Graphene, with its atomic thickness, is the lightest material in the world (Fuchs and Goerbig, 2008). Graphene has excellent mechanical and electrical properties with Young's modulus of 1.0 TPa and a stiffness of 130 GPa (Lee et al., 2008), optical transmittance of 97.7% (absorbing 2.3% of white light) (Nair et al., 2008), superior thermal conductivity about 3000 - 5000 $W.m^{-1}.K^{-1}$ (Chhowalla et al., 2013) and good flexibility. Besides, it also has an extreme specific surface area of 2600 $m^2.g^{-1}$ (Stoller et al., 2008) and

high porosity, making them ideal for adsorption. Besides, the famous forms of graphene-based material are graphene layer, turbostratic carbon, bilayer graphene, trilayer graphene, multi-layer graphene (MLG), few-layer graphene (FLG), exfoliated graphite (EG), graphene oxide (GO), reduced GO (rGO), and GNPs. This combination of excellence features has made graphene-based material as a promising material for a broad range of applications including biological engineering (Edirisinghe, 2018), drug delivery (Liu et al., 2018b), biosensor(Afsahi et al., 2018), biological agents (Nayak et al., 2018), tissue engineering (Bai et al., 2018), contaminant sensing (Ullah et al., 2018), energy production (Zhou et al., 2018), and composite materials (Chan et al., 2018).

GNPs in one of the graphene derivatives consisted of single to few layers of sp^2 -bonded carbon atoms that interface to form two-dimensional particles with nanometer scale . Today, GNPs are among the outstanding materials as they can be produced at low cost and meet the necessity of a large specific surface area due to the direct exfoliation of inexpensive graphite flakes, e.g. by ultrasonics in acid baths, followed by chemical oxidation and reduction of graphite oxide nanoplatelets (Geng et al., 2009). GNPs has also recently gained strong attention as a new and ideal materials for the detection of environmental pollution involving water treatment (Anshuman et al., 2018; Kumar et al., 2019; Kumar et al., 2017), heavy metal ion detection (Zhang et al., 2018) and green technology (Li et al., 2018).

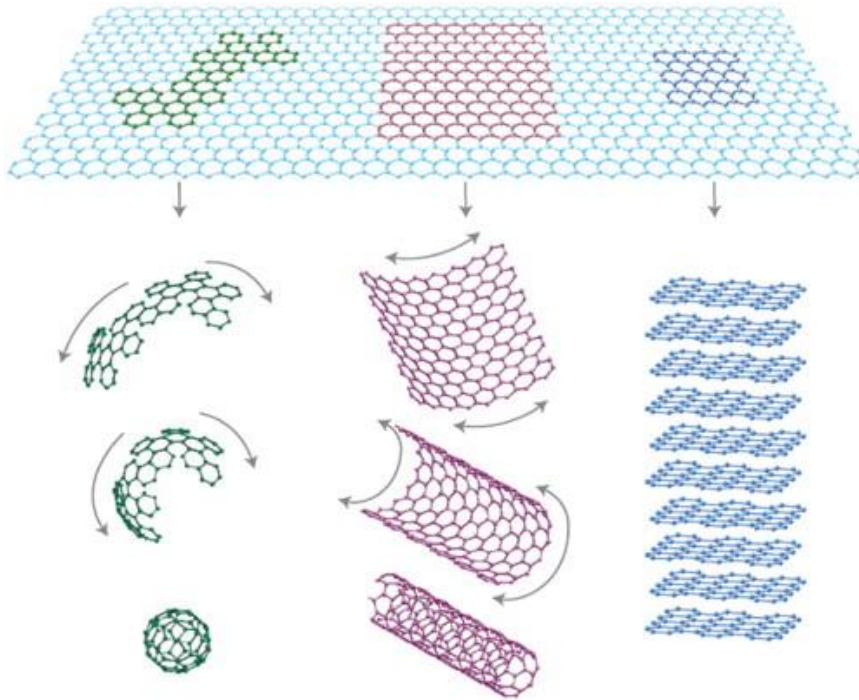


Figure 1.1 Mother of graphene (Geim and Novoselov, 2010)

1.2 Modification of graphene

Graphene exists in various forms (different number of layers, different structural groups, functional group and etc.) and graphenic material is employed as a general term to design a material within this family of carbon-based 2D materials. Graphene or carbon nanotubes (CNTs) can be described as nanoscale and stable carbon materials with no functional groups on their surface (Fu and Yang, 2013). This gives to both its high hydrophobic character and its inert nature which is unfavourable to facile graphene processing required for some applications. Many studies on CNTs for environmental applications have been reported during the past years. Ibrahim and the co-worker reported that functionalized multi walled CNTs (MWCNTs) showed good dispersibility in water and were efficient for adsorption of organic pollutants (Ibrahim et al., 2014). Arami and co-workers revealed that the adsorption capacity of modified CNTs with cationic surfactants was more significant

compared to pristine CNTs. (Arami et al., 2014). In comparison with CNTs, the graphene and GNPs have an appropriate high-specific surface area and more accessible surface that could facilitate wide environmental remediation opportunities. However, it is difficult to integrate graphene or GNPs into materials because usually they must be dispersed at a certain stage during the material designing. This is the reason why chemical modification of graphene based material is an intensive research field. Moreover, according to De Sanctis and the co-workers, graphene itself has a weak absorption of light, making it deficient for collecting solar light efficiently. Thus, they modified the charge carrier dynamics of graphene by functionalizing it as in return it could lead to enhanced photo response and the hybridization with nanoparticles; increasing that way, efficiency of photodetection (De Sanctis et al., 2018). Graphene has zero band gap and its inertness weakens graphene's competitive strength in semiconductor and sensor fields. It is useful for functional nanoelectronic devices to open graphene through doping, intercalation and striping (Namvari and Namazi, 2015; Zhong et al., 2018; Tománek, 2018). Besides, the graphene based material is intensively studied as efficient adsorbent for metal ions and dyes, as it has high surface area, high stability and electron rich structure. However, they cannot be directly used in environmental medium as it is hydrophobic and impermeable to water. Thus, vital steps are acquired to change and enhance the sorption ability. To improve the interaction of graphene-based material with foreign molecules, it is necessary to modify its surface either by covalent or non-covalent functionalization methods (Dong et al., 2013; Boretti et al., 2018; Homaeigohar and Elbahri, 2017; Ussia et al., 2018). Covalent functionalization is a process for adding new functional groups to the carbon surface, which can usually be divided into two main categories. First, carboxyl, hydroxyl and epoxy reactions

that spread on graphene, preferentially at its defected edges. Secondly, the covalent attachment of organic function groups directly to sp^2 carbon atoms of pristine graphene (Wang, 2016). Chemical functionalization allows the chemical and physical properties of the resulting materials to be tuned, which can give rise to new properties (Chua and Pumera, 2013; Georgakilas et al., 2012). Moreover, chemical functionality added to graphene-based material can promote uniform dispersion and enhance its compatibility especially with polymer matrices (Zainal Abidin et al., 2018) and aqueous media. Development of highly precise and selective chemical functionalization methods for modification of graphene-based material which fulfil the requirements of a targeted application is currently a challenge.

1.3 Application of graphene for dye removal

Textile industries consume huge amounts of water and chemicals, particularly in the dyeing and finishing processes. Besides, textile industries focus primarily on colored cloth production and approximately 700,000 tons of dyes are produced per year that about 20 percent of which are discharged in the effluents (Holkar et al., 2016; Chequer et al., 2013). Discharge of highly colored synthetic dye wastes could be extremely harmful to marine organisms; they may even be resistant to natural biological degradation (Holkar et al., 2016; Tahir et al., 2016; Khan and Malik, 2014). These substances are highly visible and unneeded as they can change the natural appearance of water ecosystem which affects marine life, including water plants and plankton, interfering in sunlight activation; limiting the process of photosynthesis and oxygenation of water aquifers (Bennett, 2014).

Basically, there are two types of common dyes used in the textile industry which are basic and reactive dye. Basic dye is a cationic stain from positively charged

nitrogen or sulfur atoms that reacts on the surface of the substrate with anionic sites (Alatalo et al., 2015) The examples of basic dyes are methylene blue (MB) and malachite green (MG) which are made up of amino groups or alkylamino groups and usually it is used for cotton, paper, wool, silk, nylon, and modified acrylic fibers (Purwar, 2016). Whereas, Remazol blue R (RBBR), Remazol black (RB) and Remazol brilliant violet 5R (RBV) are reactive dyes which are usually used as the starting material for polymeric dye production. Both dyes appear to be comparably economical, broad shade range and have good brightness. However, compared to basic dyes, reactive dyes are not easily biodegradable, even after extensive treatment, color can continue to remain in the effluent (Gürses et al., 2016; Anjaneyulu et al., 2005). Research and innovation in processes related to dye adsorption and removal are therefore crucially needed to reduce the environmental impact from textile industry.

1.4 Problem statement

The textile industry and its effluents are considered as one of the major contributors to environmental pollution problems worldwide. In South East Asia, particularly in Malaysia, the growth of the batik sector has become a sustainable local industry from its early start in the 1930s until now. However, the batik industries generate huge amount of extremely polluted wastewater which could risk the environmental footprint and human health. Besides, several findings have reported that the standard wastewater treatment processes for the textile industry could not degrade many of dyes found in the effluents, resulting in a substantial effort to find an effective and comprehensive way for dye removal.

Different approaches including physical and chemical methods can be considered for dye removal. These include sedimentation (Chen, 2004), biological treatment (Lokesh and Sivakiran, 2014), nanofiltration (Cheah et al., 2018), coagulation (Liang et al., 2014), advanced oxidation (Dehghani et al., 2016), electrochemical treatment (Chen et al., 2018) and adsorption process (Aslam Malana et al., 2016; Elsagh et al., 2017). Among those potential technology, adsorption is considered as one of the most efficient and simple methods for removing dye from wastewater.

Carbon-based nanomaterials such as graphenic materials have recently been reported as effective sorbents for waste water treatment because of their larger surface area and specificity (Perreault et al., 2015). Although most of the graphenic materials possess excellent properties, but there are also boundaries for some applications. Single layer graphene (SLG) and double layer graphene (DLG), for example, have a high structural quality but not available in high quantities while for graphene oxide (GO) and reduced graphene oxide (rGo), they are highly functionalized and exhibit too much of defects on the surfaces. Thus, this limitation makes the sorption process difficult to control. GNPs can be one of the promising materials which have high structural quality and commercial value. However, oxygen-containing surface groups have to be introduced by post-synthesis treatment in e.g. acid oxidation for example to make graphene hydrophilic and improve the interactions between the graphenic material and water (Tang et al., 2018; Mahmoodi et al., 2017; Ren et al., 2018).

This study proposes a facile and simple approach for the surface modification of graphene nanoplatelets (GNPs) using combination of sulfuric and nitric acids. Graphene dispersibility and adsorption capacity were investigated for degradation of

MB. Kinetic study on the adsorption of MB on fGNP was conducted after the completion of the reaction.

1.5 Research objectives

The aim of this research is to chemically modify the surface of graphene to enhance its adsorption capability for application of dye removal. The specific objectives of this research are:

1. To study the control surface properties of high-quality GNPs by covalent functionalization using acid treatment.
2. To evaluate the effect of experimental parameters (effect of contact time, temperature, initial concentration and pH) on adsorption of dye.
3. To determine the isotherms, kinetics and thermodynamics of the adsorption process using the prepared adsorbents.

1.6 Scope of study

The purpose of this study is to modify the surface of high-quality GNPs by carboxylation to induce the hydrophilic character to the graphene to be used as adsorbent. The chosen approach for the chemical treatment is oxidation by acids because of its ease of use. Graphenic materials present under various types depending on the used synthesis method. They have different characteristics which induce different chemical reactivities. This is the reason why the experimental conditions used have to be optimized for each graphenic materials. The used graphene was rather thick GNPs of high structural quality. For the functionalization, the effect of different acid concentrations, acid treatment time, and acid ratio on the functionalization level have been investigated. MB is chosen as the model pollutant

in this study because it is a pollutant widely found in various dye industries. The characterization of the GNPs was performed by a set of complementary techniques: Zeta Potential, Scanning Electron Microscope (SEM), Fourier-transform infrared spectroscopy (FTIR), High-resolution transmission electron microscopy (HR-TEM), Thermogravimetric Analysis (TGA), Raman spectroscopy, Brunauer–Emmett–Teller (BET), and Ultraviolet–visible spectroscopy (UV-Vis). The performance of the modified GNPs for MB removal was tested by varying several parameters. The study was conducted at different initial MB concentrations, contact times, and different solution temperatures. Subsequently, thermodynamic, kinetics and equilibrium studies were performed to evaluate the adsorption process.

1.7 Thesis organization

This thesis consists of five chapters. Chapter 1 (Introduction) gives a brief description regarding graphene and chemical modification methods towards the application of dye removal. It also consists of the problem statement that gives out an idea regarding the research direction in the field. The objectives and the scope of the present study are then explained.

Chapter 2 (Literature review) describes the background information regarding the nanomaterials and their applications. This chapter gives a background information regarding the alternative novel material which is graphene that leads to this research. This chapter begins with the properties of graphene, surface modification, graphene dispersion, comparison of several graphene functionalization methods, and application in dye removal. This chapter also includes process variables and kinetic study.

Chapter 3 (Materials and Methods) describes the materials and chemicals used and their characteristics. Detailed methodology, experimental set up and catalyst preparation are explained and shown in this chapter. This continues by giving the experimental procedures which include characterization of the raw and the functionalized GNPs, investigation parameters and kinetic study.

Chapter 4 (Results and Discussion) provides the findings obtained from the present research work. This chapter is the main component of this work and consists of eight sections which include the functionalization of graphene nanoplatelets, effect of parameter study towards dye removal, structural, surface and chemical characterization, adsorption performance for both GNPs and the fGNPs towards the MB removal, adsorption isotherm, kinetic and thermodynamic study. Last part will be the proposed mechanism of MB adsorption on fGNPs.

Chapter 5 (Conclusions and Recommendations) summarizes the conclusions from the findings in this work, the future recommendations also have been presented in this section.

CHAPTER 2

LITERATURE REVIEW

This chapter gives a background overview regarding the used nanomaterial, i.e. graphene. This chapter begins with the types, properties and chemical modifications of graphene. This chapter also discusses the adsorption process, which includes the involved mechanisms and influencing factors. In addition, the properties of dye, dye removal methods and types of isothermal, kinetic and thermodynamic studies for dye adsorption are addressed in this section.

2.1 Graphene

Despite the recent interests associated with graphene, the material itself is not a recent innovation. In fact, graphene occurs naturally as distinct layers in the lamellar structure of mineral graphite and has been the subject of academic studies for nearly 70 years. Nevertheless, the 2D carbon allotrope and theoretical structure were not identified until 2004, when Novoselov and co-workers documented the first successful isolation of single layer graphene using the mechanical exfoliation method (Novoselov et al., 2004). Since then, graphene has gained tremendous interest throughout a variety of fields, both in research and industry. As a result, the literature pertaining to graphene has grown immensely, with close to 12,000 peer-reviewed articles published in 2015 alone.

This chapter begins with a general discussion regarding the unique, two-dimensional structure of graphene and its implications on reactivity and material properties. Next, properties of graphene including adsorption, electronic, mechanical and optical properties are described. Then, surface modification via functionalization

process and dispersion of graphene is reviewed. Lastly, a comparison of the functionalization methods of graphene for environmental remediation is presented.

2.1.1 Single-layer graphene and other types of graphene

Graphene, as a two-dimensional (2D) material, consists of sp^2 -bonded carbon atoms (C) with a honeycomb structure of only one layer. A carbon atom has four valence electrons, three of them (σ -bonding and π -bonding) are connected to its closest neighbours and create a honeycomb structure (Lemme, 2010). These four valence electrons occupy an orbital vertically to the one-dimensional (1D) sheet creating delocalized π -bonds making it possible to create a two-dimensional electron gas with high mobility inside the sheets as shown in Figure 2.1 (Lemme, 2010; Hwang, 2012). Figure 2.1 shows the geometry of graphene and its bonds. The delocalization of the π electrons allows high mobility of the graphene sheets up to $15,000\text{--}200,000\text{ cm}^2/(\text{V}\cdot\text{s})$, limited by interactions during bilayer growth with the substrate, or any contaminant particles (Kwon et al., 2009; Mattevi et al., 2011). Thus, the cleanliness, grain size and interference with the substrates are very important factors for the growth and use of graphene for high mobility and ultra-fast application. Besides, Bianco and co-workers, have discussed well about the nomenclature of graphene including graphene, graphene layer, turbostratic carbon, multi-layer graphene, few-layer graphene, graphite nanoplates; graphite nanosheets; graphite nanoflakes, etc (Bianco et al., 2013)

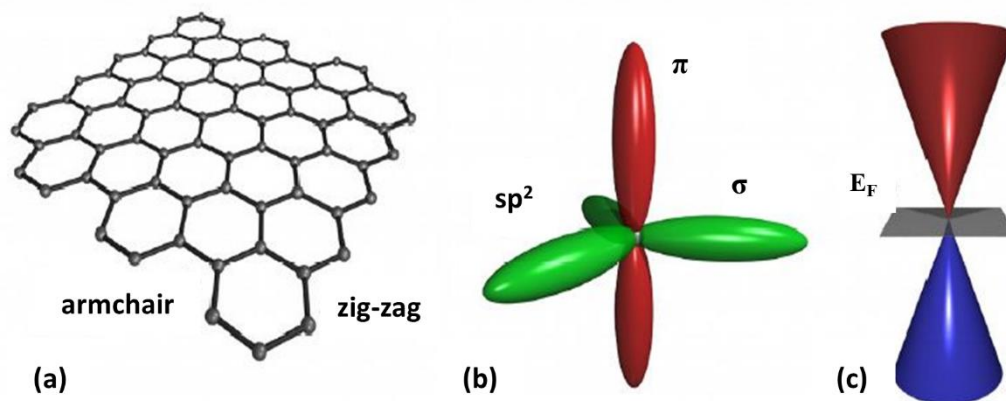


Figure 2.1 Geometry of graphene and the bonding (Sood et al., 2015)

Single- and double-layer graphene (SLG and DLG, respectively) have one single and two sheet(s) of graphene, respectively. Their synthesis is now well controlled by CVD and they are produced at the wafer scale (Xue et al., 2017). But, for few-layer (FLG, 3-5 layers) and multi-layer (MLG, 6-10 layers) graphene, it can be produced in large quantities at a reasonable cost; however, purity is not the main issue in this case. Recently, Lin and co-workers have developed an eco-friendly and easy method known as jet cavitation (JC) to prepare few layer graphene (FLG) derived from artificial graphite without adding any strong acids and oxidants. They detected few amount of functional groups and structural defects, but these FLGs demonstrated excellent performance in some applications (Lin et al., 2018). Similarly Shamsudin and co-workers, they developed an eco- and cost-effective way to synthesize FLG using a table-top CVD system method. In this study, they found that the addition of forming gas during the deposition process could enhance the quality of graphene (Shamsudin et al., 2016). Many studies have been conducted but an economically feasible process must be developed for mass production. Exfoliation techniques have the potential for the large-scale production of low-cost graphene. Yuan and colleagues developed a simple method named mechanical

exfoliation to synthesize well-dispersed MLG, which was the ozone-assisted sonication of the natural graphite. In this study, they used no chemical reagents or organic solvents for the process and found that the dispersion of graphene was stable after a period without significant damage to the overall structure (Yuan et al., 2016). Besides an easily scalable and widely accessible approach has been reported by Yi and co-workers to produce high-quality FLG with average thickness of ~ 1.5 nm ($\sim 20\% \leq 1$ nm). They suggested that use of kitchen blender can attribute to the exfoliation mechanism where the normal force and lateral force exfoliate graphite into graphene flakes. As a result, they found that FLG was free of basal-plane defects and oxidation (Yi and Shen, 2014). In addition to SLG, DLG, FLG and MLG, graphene oxide (GO) and reduced graphene oxide are (rGO) also categorized as type of graphene (Figure 2.2).

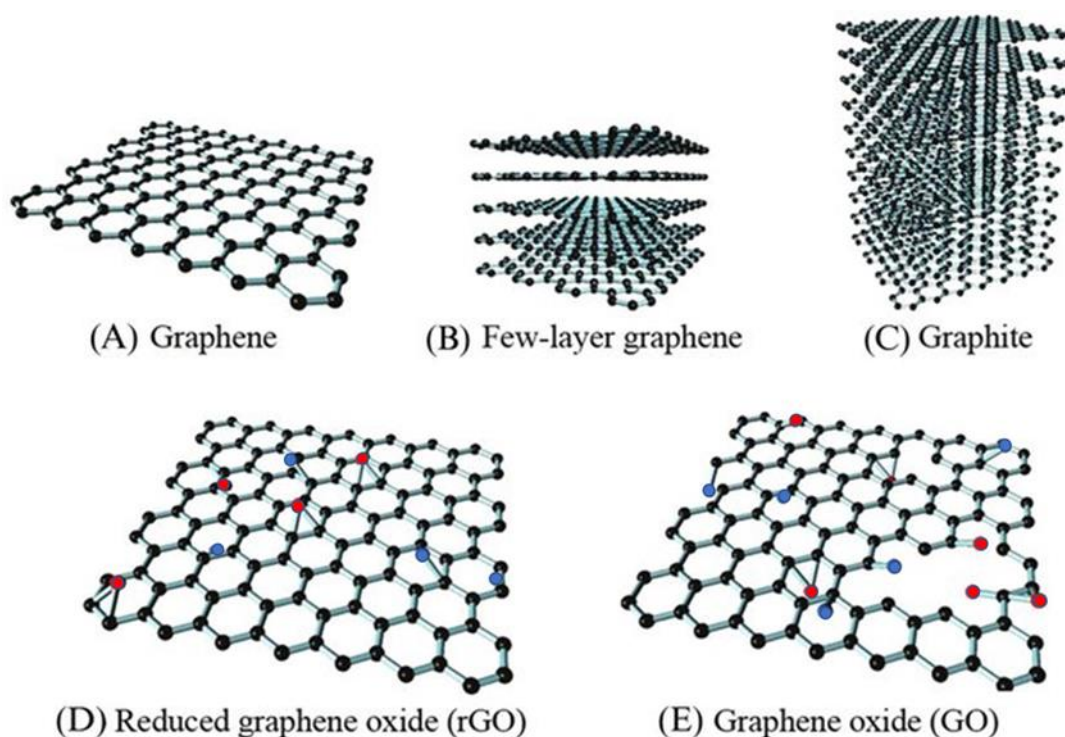


Figure 2.2 Main types of graphene nanomaterials (Kiew et al., 2016); carbon atoms in black, oxygen in red and hydrogen in blue.

Similar to graphene, GO and rGO also have a 2D structure, but GO consists of a sp^2 and sp^3 carbon system including oxygen (and hydrogen) belonging to covalent functional groups and defects in the honeycomb structure. rGO, usually formed by reduction of GO, consists mainly of a honeycomb network of sp^2 carbon containing a non-negligible number of defects (Messina et al., 2017) since the reduction process is normally only partial. There are few Hummer's methods developed for GO synthesis by many researchers since several decades ago and are still in use today with minor modifications (Brodie, 1859). Yuan and co-workers have showed a preparation method of GO using oxidation process where it was described through inducing the ultrasonic in the rate-determining step. As a result, they found that the addition of potassium permanganate ($KMnO_4$) really marked the beginning of the reaction from the border of the pristine graphene flakes to the centre and a higher degree of oxidized products, with more carboxylic acid groups on its edges were produced (Yuan et al., 2017). Although it has been developed for over a century, the specific chemical structure of GO is still not quite clear. Besides, strongly modified GO sheets consist partly of tetrahedrally bonded sp^3 carbon atoms, which are slightly above or below the graphene plane (Schniepp et al., 2006). GO appears to be atomically rough due to structural distortion and the presence of covalently bonded functional groups (Paredes et al., 2008; Mkhoyan et al., 2009). Several groups have also reported that highly defective regions can be observed on the surface of GO using scanning tunnel microscopy (STM), which is probably due to the presence of oxygen and other groups (Paredes et al., 2009; Gómez-Navarro et al., 2010). Graphene nanoplatelets (GNPs) or flakes consist of several graphene layers with a mean thickness of 5 – 10 nm in different sizes up to 50 μm (Kairi et al., 2018). GNPs have been chosen to be used in this work instead of GO or rGO

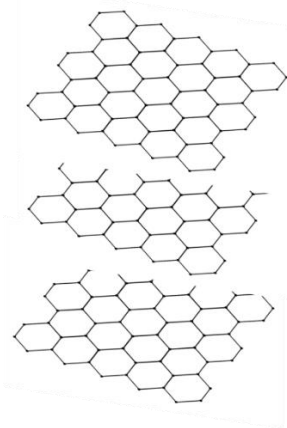
graphene types. GNPs are close to MLG but their number of layers can be also higher than 10. They are easily commercially available at low cost. They are interesting nanoparticles consisting of short stacks of platelet-shaped graphene sheets like those discovered in carbon nanotube walls, but in a planar shape. Their good structural quality and their availability make GNPs the ideal graphenic material for their controlled chemical modifications contrary to the highly functionalized GO.

2.1.2 Properties of graphene nanoplatelets

The remarkable properties of graphene such as large surface area, good chemical stability, and graphitized basal plane structure, allow it to have strong π - π interactions with the aromatic moieties present in many dyes (Konicki et al., 2017; Gupta and Khatri, 2017). The conjugated structure along with the basal plane of the graphene tends to lead to a system of delocalized π -electrons that can create dispersion forces. Compared to the pristine graphene, GNPs have also excellent electric and thermal conductivity (Moosa et al., 2016). Besides, due to their unique size and morphology, GNPs can achieve improved barrier properties such as permeability characteristics and mechanical properties such as stiffness, strength, and surface hardness. In many composite applications, GNPs may substitute carbon fibres, carbon nanotubes, nano-clays or other compounds. For the modification of GNPs, hydrogen or covalent bonding capability can be added at the platelet borders by functionalization process useful for applications that require multiple property improvements (Han et al., 2012; Yadav and Cho, 2013; Qin et al., 2015; Poon et al., 2015). Besides, GNPs with a larger surface area and more active edges are more likely to form defects with easy modification compared to CNTs. However, together with the outstanding property of GNPs, still, there is lack in some aspects that might

limit its functionality in certain applications. Low GNP hydrophilicity is one of the greatest barriers in the environmental applications. Therefore, tailoring the adsorption properties using chemical methods such as the insertion of new functional groups (Wang et al., 2013; Awad et al., 2018), cross-linking (Zhang et al., 2017) and polymer grafting (Kochameshki et al., 2017) can significantly improve the adsorption capacity.

Table 2.1 Basic physical and chemical properties of GNPs (Papageorgiou et al., 2017; Moosa et al., 2016; Giglio, 2017).

Structural formula	
Lateral size	< 0.1-2 μm
Thickness	10-15 nm
Specific surface area	280-1550 m^2/g
Young's modulus	1.05 TPa
Thermal conductivity	2000 – 5000 W/m.K

2.2 Adsorption

Adsorption is one of the famous methods of treatment for the removal of dissolved organic pollutants such as dyes from industrial wastewater. This is due to the advantages of the adsorption process, which can be regenerated at low cost, sludge-free operation and possible for recovery of the adsorbent. Generally, an adsorption process can be defined as the attraction phenomenon of any atom, molecule, ion or particle on the surface of a solid. The adsorption phenomenon is an occurrence in which the molecules are attracted and retained on the solid surface. Normally, this technique depends on the strength of the interactions involving ionic, covalent or metallic bonds between the adsorbent and the adsorbed molecules. There are two basic terms used in the adsorption process which are adsorbent and adsorbate (Figure 2.3). Adsorbent can be defined as the solid substance that adsorbs solute molecules from a liquid or gas while adsorbate is the material undergoing surface adsorption. There are three classes of adsorbents that are commonly used in the industrial sector, which are oxygen-containing, carbon-based and polymer-based compounds. Among these adsorbents, carbon-based compounds such as activated carbons and carbonaceous nanomaterials such as carbon nanotubes (Ma et al., 2012) and graphene have become commonly used as adsorbents for the treatment of aqueous effluents. This is due to their large surface area, micro-pore structure, high adsorption capacity and high degree of surface reactivity (Qu et al., 2013). Akhbar and his colleagues have identified the alternative adsorbents such as single-walled carbon nanotubes (SWCNTs), functionalized SWCNTs (SWCNT-COOH), graphene and GO for cationic dye removal. Few parameter conditions were considered before evaluating the dye removal efficiency, such as pH, contact time

and initial dye concentration, and they found that all adsorbents worked effectively for dye removal (Elsagh et al., 2017).

Adsorption is apparently considered to be one of the most effective technologies for removing various pollutants from water. Interestingly, different types of materials are used as adsorbents including graphenic materials. Functionalized graphene and GO were found to be highly adsorptive and had a high capacity to many pollutants, such as dyes and heavy metals (Fan et al., 2012; Xu et al., 2012). The adsorption capacity of the modified graphenic materials can be mainly attributed to two aspects which is first, the oxygen-containing functional groups and second the aromatic matrix. The first ones favor adsorption of hydrophilic species due to electrostatic interactions or hydrogen bonds, and the second one has affinity with hydrophobic organics by π - π stacking or hydrophobic interactions (Gómez-Navarro et al., 2010; Yang and Xing, 2010; Şinoforoğlu et al., 2013). However, the comparative ratio of the two functional regions in functionalized graphene is adaptable and varies greatly with oxidation conditions, making the modified graphene a material of structural heterogeneity with a different adsorption selectivity (Compton and Nguyen, 2010). In addition, it is obviously mentioned in previous works that the structural features greatly influence the adsorption performance of modified graphenic material. Thus, a comprehensive study on the effects of structural features, such as oxidation degree of modified graphene, towards its adsorption behaviour is very useful for understanding the adsorption mechanisms especially for interactions between functionalized graphene and the contaminants. Generally, the mechanisms of adsorption can be classified into three classes which are physisorption, chemisorption and electrostatic adsorption. Physisorption occurs due to the driving forces of weak molecular forces such as van der Waals.

Chemisorption takes place when a chemical reaction forms chemical bonds between the adsorbate and the adsorbent. For electrostatic adsorption, it involves the adsorption of ions by Coulombic forces, and is normally referred to as ion exchange.

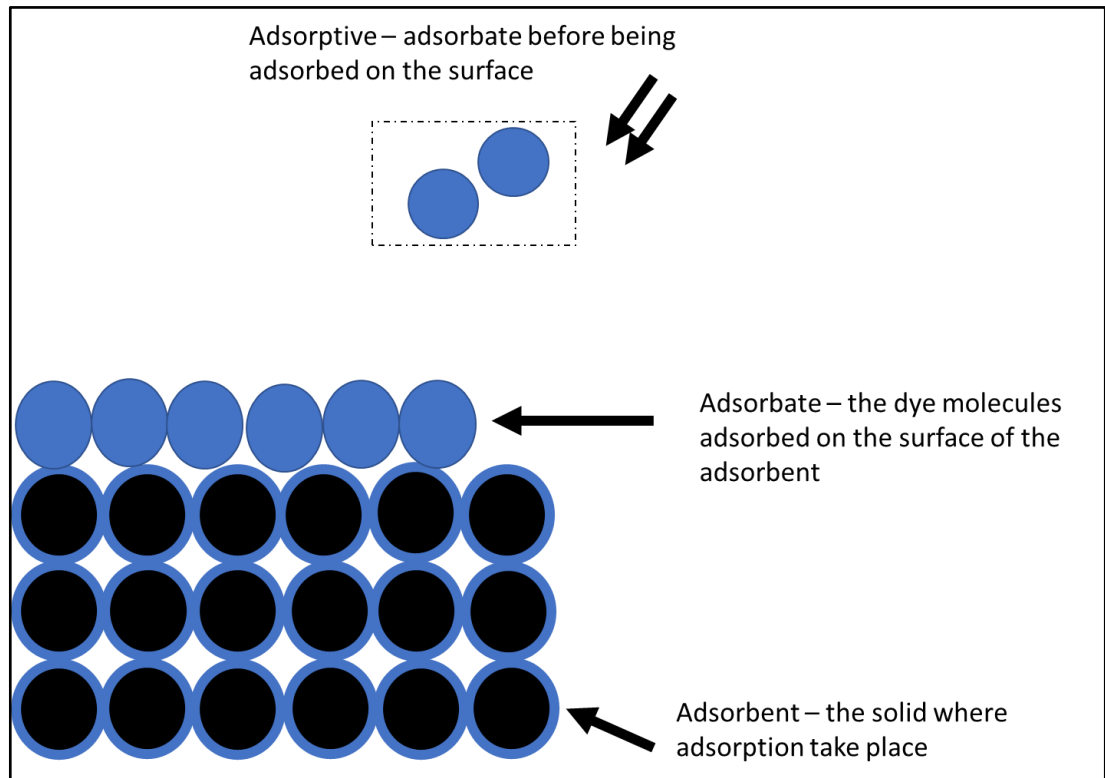


Figure 2.3 Schematic diagram of the interactions between adsorbents and adsorbate

2.2.1 Physisorption and chemisorption

Physisorption or chemisorption depends on the type of attractions between the adsorbate and the adsorbent. Table 2.2 shows a comparison of the physisorption and chemisorption characteristics.

Table 2.2 Comparison of the physisorption and chemisorption characteristics (Jaafar, 2006)

Characteristics	Physisorption	Chemisorption
Energetics and kinetics	Required low enthalpy values (20 – 40 kJ mol ⁻¹)	Required high enthalpy values (40-500 kJ mol ⁻¹)
Interaction	Van der Waals force acts as an attracting force between the adsorbent and adsorbate	Chemical bond acts as an attracting force between the adsorbent and adsorbate
Type of reaction	Reversible process	Irreversible
Temperature	Low	High
Type of adsorption	Multi-layer	Monolayer
Activation energy	Very low	High

2.2.2 Factors influencing adsorption

There are few factors that could affect the adsorption process: surface area and porosity of the adsorbent, the nature of the adsorbate, hydrogen ion concentration (pH) of the solution and temperature. Adsorption is a surface phenomenon where the degree of adsorption is proportional to the portion of the total available and accessible surface area. Based on most researches, the adsorption of a solid adsorbent is higher when the solid particles are finer and more porous (Pathania et al., 2017; Han et al., 2017). In addition, the nature of the adsorbate could also affect the adsorption process, in which the adsorption process increases by increasing the solubility of the adsorbate in the solvent. Higher solubility gives stronger interactions between the solute and the solvent. The adsorption process can also be affected by the pH of the solution and adsorbent where hydrogen and hydroxide ions are adsorbed quite strongly. At acidic pH conditions, the hydroxyl and carboxyl groups on the surface of the adsorbents are protonated and they inhibit the binding of the

dye ions. An excess of H^+ ions compete with dye ions for the adsorption sites. With an increasing pH of the dye solution, the surface groups will be deprotonated resulting in an increase of negatively charged sites which favours adsorption of the cationic dyes due to electrostatic attraction (Ong et al., 2007). Temperature also influences the adsorption phenomenon. However, usually for small temperature variation, the variation in adsorption is not significant. The physicochemical nature of the adsorbent/adsorbate interactions can influence both the rate and the adsorption capacity by considering few parameters. Firstly, the surface functional groups and secondly, the structural details such as molecular structure, dimension and the configuration. High adsorption capacity of carbon-based adsorbents can be attributed to the significant amounts of carbonyl and carboxyl groups which present on the adsorbent surface. Besides, increasing the concentration of the appropriate functional groups might change the involved interaction (Yu et al., 2018; Almarri et al., 2009). In summary, because of the numerous involved factors the adsorption mechanisms are complex, the adsorption capacity of each adsorbate/adsorbent will be difficult to predict and a parametric study remains of great interest for investigation of dye removal.

2.3 Chemical modification of graphene

Several methods of chemical and physical functionalization have been explored to induce chemical modifications of graphene. Initial studies have shown that the chemical functionality of the surface of GNPs would play a crucial role in adapting their properties and applications. Generally, each carbon atom is joined to three neighbours, which make the bonding is essentially sp^2 . However, there might be a small amount of sp^3 , such as pentagons and heptagons on the basal plane and at

the edges of graphene sheets (Zhang et al., 2003). Early research on the production of graphene mainly focused on graphite or graphite oxide. Basically, GO, rGO and GNPs are among the most essential graphene derivatives for such applications which require a relatively high amount of material. GO bears a lot of defects which dramatically lower its physical properties. For rGO, the reduction of GO will remove most of the oxygen-containing functionalities, including hydroxyl, carboxylic acid and epoxy groups, causing graphene surface hydrophobicity to decrease. GNPs has a high-quality structure with greater properties, but it needs to be functionalized by an effective method in order to increase its dispersion ability in water and dye molecules. Protection of the graphene structure is therefore a priority during any modification. Generally, chemical modification can be achieved through non-covalent and covalent functionalization. Non-covalent functionalization employs additives such as surfactants that will adsorb on the graphene surface usually by van der Waals forces or π - π stacking interactions. However, these surface agents create a layer that can compromise any further adsorption of dyes. For covalent functionalization, introduction of functional groups increases the amounts of defects in the graphene structure. According to Gupta and the co-workers, the optimization of oxygen functionality in graphenic materials is an important aspect for preserving the chemical stability of the structure (Gupta et al., 2017).

2.3.1 Covalent functionalization of graphene

Approaches for covalent functionalization of GNPs are discussed in this section. Basically, two general routes are used coming from fullerene and carbon nanotube chemistry (Varghese et al., 2015).

1. The formation of covalent bonds between free radicals or dienophiles and pristine GNP C=C bonds at its basal plane.
2. Chemical attack which is expected to mainly occurs at the GNP edges where there are a lot of defects of greater reactivity than the sp² carbons of the basal plane.

The GO and modified GNPs can form “colloidal” aqueous dispersions which normally have high stability that gives high negative surface charge value (Kashyap et al., 2014). Surface charge, which consists of inherent and variable charges, is determined by the material structure. Li and the co-workers found that the zeta potential value of GO is more negative than that of rGO at the same pH and this could occur because of the surface negative charge mainly due to the ionization of oxygen-containing functional groups. Huang and co-worker also discussed that the GO dispersion stability is attributed to the repulsion of electrostatic forces of negatively charged GO, where the charge can be changed by altering the pH (Huang et al., 2013). Moreover, realizing that altering the surface of graphene is crucial to enhance the properties of graphene, this modification became the starting step to synthesize composites of graphene, GO or functionalized GNPs with metal and metal oxide nanoparticles (Sahraei and Ghaemy, 2017) (Pan et al., 2017). Commonly, the functional groups such as azomethine ylide, aryne, nitrene, carbenes (Park and Yan, 2012) have been found to form incredible complexes consistent with graphene and produce flexible varieties that are excellent starting point for further graphene nano-material revolution and functionality. Figure 2.4 shows the schematic diagram from Feng and the co-workers works where they prepared reduced graphene oxide-azobenzene (rGO-AZO) hybrids via covalent functionalization using free radical diazotization for long-term solar thermal storage