CHEMICAL SURFACE MODIFICATION OF GRAPHENE NANOPLATELETS 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_2SO_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 brillant 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
Ct	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 merupakam 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 m^2 / g. Kesan suhu (30-60 ° C), masa hubungan (5 hingga 55 minit), dan kepekatan pewarna awal (25-200 mg / L) terhadap prestasi penjerapan penyerap telah disiasat. Kapasiti penjerapan maksimum fGNP meningkat daripada 112 mg / g kepada 151 mg / g pada pH 4 dan 60 ° 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 ° C, 45 ° C, dan 60 ° C), ΔH^0 (8.85 kJ / mol) dan ΔS^0 (-1.57 kJ / 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 m^2/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).

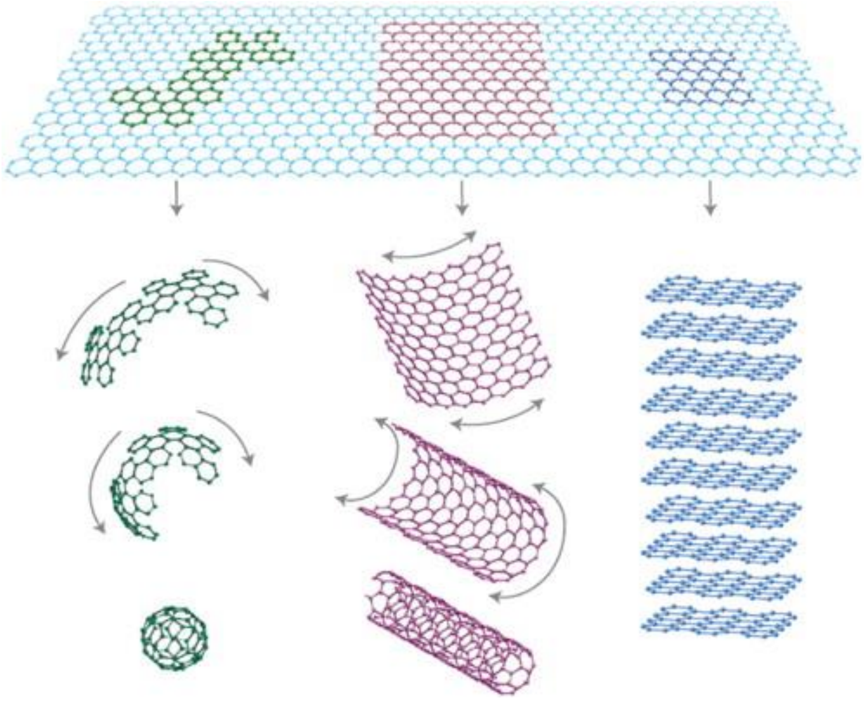

Figure 1.1 Mother of graphene (Geim and Novoselov, 2010)

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