

**SYNTHESIS AND CHARACTERIZATION OF CARBON-
BASED NANOCOMPOSITES FOR EFFICIENT REMOVAL
OF HYDROCARBONS FROM WATER**

BY

ABDULLAHI BIODUN OLABINTAN

A Thesis Presented to the
DEANSHIP OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

In

CHEMISTRY

APRIL, 2020

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN- 31261, SAUDI ARABIA

DEANSHIP OF GRADUATE STUDIES

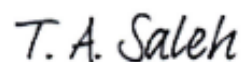
This thesis, written by **ABDULLAHI BIODUN OLABINTAN** under the direction of his thesis advisor and approved by his thesis committee, has been presented and accepted by the Dean of Graduate Studies, in partial fulfillment of the requirements for the degree of **MASTER OF SCIENCE IN CHEMISTRY**.



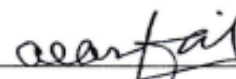
Dr. Khalid R. Alhooshani
Department Chairman



Dr. Suliman Saleh Al-Homidan
Acting Dean of Graduate Studies



Dr. Tawfik A. Saleh
(Advisor)



Dr. Abdulrahman A. Al-Arfaj
(Member)



Dr. Fahd I. AlGhunaimi
(Member)

Date

© Abdullahi Biodun Olabintan

2020

Dedication

[This thesis work is dedicated to Almighty Allah for taking me this far and to my beloved family for their all-round supports.]

ACKNOWLEDGMENTS

All praise is due to Almighty Allah, the Living, the Self-Subsisting and All-Sustaining, the Creator of all creatures, the Cherisher of the entire universe. I express my inestimable gratitude to Him for sparing my life and seeing me through the completion of this work.

It is a matter of immense pleasure to acknowledge my indebtedness to my revered teacher and advisor, Dr. Tawfik A. Saleh. It would never have been possible for me to take this work to completion without his incredible support and encouragement. I sincerely appreciate the members of my committee in persons of Dr. Abdulrahman A. Al-Arfaj and Dr. Fahd I. AlGhunaimi for their invaluable contributions to the success of this work.

I express my special gratitude to the Chairman of Chemistry department and his staff members including the faculties and technicians. I am greatly indebted to the following instructors such as Dr. Abdul Malik Peedikakkal, Dr. Musa Musa, Dr. Mohammed Morsy, Dr. Arief Wibowo and Dr. Basheer Chanbasha, for the knowledge imparted in me during my course work. My hearty appreciation also goes to the lab technicians, Mr. Hassan, Mr. Monsur, Mr. Abdurrashid and Mr. Irshad, for their ever-helping attitudes in the course of this work.

Deep heartedly, I express my unalloyed gratitude to my beloved parents, Mr. and Mrs. Abdurrahman Olabintan, my lovely wife, Mrs. Rofiah Opeyemi, my son, Farhan Temitope and my siblings for their constant prayers, love and care. They have always encouraged me to explore my potential and pursue my dreams. May Allah reward you all endlessly.

TABLE OF CONTENTS

ACKNOWLEDGMENTS	V
TABLE OF CONTENTS.....	VI
LIST OF TABLES.....	X
LIST OF FIGURES.....	XI
LIST OF ABBREVIATIONS.....	XIV
ABSTRACT.....	XVII
ملخص الرسالة.....	XIX
CHAPTER 1.....	1
INTRODUCTION.....	1
1.1 Background	1
1.2 Statements of the problem	4
1.3 Objectives of the study.....	4
1.4 Significance of the study.....	5
1.5 Scheme of the research work	5
1.6 Scheme of research findings reporting	6
CHAPTER 2.....	7
LITERATURE REVIEW.....	7
2.1 Basic factors for hydrocarbons-water separation	7
2.2 Special wettable materials for hydrocarbons-water separation	9

2.2.1	Materials with superhydrophobicity-superoleophilicity	9
2.2.2	Materials with superhydrophilicity-superoleophobicity	10
2.2.3	Materials with superhydrophilicity-underwatersuperoleophobicity.....	11
2.2.4	Smart materials with controllable wettability	12
2.3	Carbon for hydrocarbons-water separation.....	13
2.3.1	Graphene- based sorbents.....	13
2.3.2	Carbon nanotubes-based sorbents	19
CHAPTER 3		21
HYDROPHOBIC AND OLEOPHILIC LAURIC ACID GRAFTED CARBON NANOTUBES FOR EFFICIENT AND RECYCLABLE HYDROCARBONS ABSORPTION.....		21
3.1	Introduction	22
3.2	Experimental section	24
3.2.1	Chemicals and materials	24
3.2.2	Preparation of hydroxylated MWCNTs	25
3.2.3	Synthesis of various hydrophobic MWCNTs Grafted LA absorbents.....	25
3.2.4	Measurements and characterization.....	28
3.2.5	Absorption experiment.....	28
3.2.6	Hydrocarbons-water separation test	29
3.2.7	Reusability test	29
3.3	Results and Discussion	29
3.3.1	Structure analysis of MWCNTs-LA composites	29
3.3.2	Surface morphology	37
3.3.3	Absorption performance of the as prepared MWCNTs-LA absorbents	41
3.3.4	Hydrocarbons- water separation and reusability performance of MWCNTs-LA2	44

CHAPTER 4.....	50
HYDROPHOBIC AND OLEOPHILIC AMINE FUNCTIONALIZED GRAPHENE OXIDE NANOCOMPOSITE FOR EFFICIENT HYDROCARBONS AND ORGANIC SOLVENT RECOVERY.....	50
4.1 Introduction	51
4.2 Experimental section	52
4.2.1 Materials and chemicals	52
4.2.2 GO synthesis	53
4.2.3 Synthesis of amine functionalised GO	54
4.2.4 Characterization.....	54
4.2.5 Hydrocarbons absorption test.....	55
4.3 Results and discussion	55
4.3.1 Chemical Structure and Composition	55
4.3.2 Morphology.....	58
4.3.3 X-ray diffraction analysis.....	65
4.3.4 Absorption performance of the amine functionalized GO absorbents.....	68
4.3.5 Hydrocarbons-water separation	70
CHAPTER 5.....	75
POLYETHYLENE/AMINE FUNCTIONALIZED REDUCED GRAPHENE OXIDE COMPOSITE MATERIALS: MORPHOLOGICAL AND HYDROCARBONS ABSORPTION PROPERTIES FOR REMEDIATION OF HYDROCARBONS SPILLS.	75
5.1 Introduction	76
5.2 Experimental section	79
5.2.1 Materials and chemicals	79

5.2.2	Measurements and characterization.....	79
5.2.3	GO synthesis	80
5.2.4	Dodecylamine functionalization of GO (DDA-GO)	80
5.2.5	Fabrication of DDA-GO/PE Composite	81
5.2.6	Hydrocarbons Absorption and recovery test.....	81
5.3	Results and Discussion	82
5.3.1	FTIR spectra analysis	82
5.3.2	XRD analysis	88
5.3.3	Raman spectra analysis.....	92
5.3.4	SEM analysis	96
5.3.5	Hydrocarbons absorption capacity in DDA-GO/PE composites	98
5.3.6	Hydrocarbons-water separation	101
CHAPTER 6		106
CONCLUSION.....		106
REFERENCES.....		108
VITAE.....		121

LIST OF TABLES

Table 2.1: Carbon-derived superwetting porous absorbents for hydrocarbons-water separation.....	20
Table 3.1: Absorption capacity comparison of various absorbent materials.....	49

LIST OF FIGURES

Figure 2.1: Surfaces and microstructures of biological superwetting materials (a) lotus leaf [52], (b) scales of fish [53].....	8
Figure 2.2: Structure of: (a) graphene, (b) graphene oxide (GO), and (c) reduced graphene oxide (rGO).....	17
Figure 2.3: Schematic representation of covalent functionalization routes targeting the different sites of graphene oxide: (a) acylation, (b) nucleophilic ring-opening, (c) bisocyanate/esterification, (d) diazotization , and (e) cycloaddition reactions [152]...	18
Figure 3.1 : Schematic representation of the synthesis of MWCNTs-LA composites.....	27
Figure 3.2: FTIR spectra of (a) pristine MWCNTs, (b) MWCNTs-OH, (c) MWCNTs-LA 1, (d) MWCNTs-LA 2, (e) MWCNTs-LA 3 and (f) pure LA.....	31
Figure 3.3: Raman spectra of (a) pristine MWCNTs, (b) MWCNTs-OH, (c) MWCNTs-LA 1, (d) MWCNTs-LA 2 and (e) and MWCNTs-LA 3.....	35
Figure 3.4: XRD Patterns of (a) pristine MWCNTs, (b) MWCNTs-OH, (c) MWCNTs-LA 1, (d) MWCNTs-LA 2, (e) MWCNTs-LA 3 and (f) pure LA.....	36
Figure 3.5: Water contact angle measurements for (a) neat MWCNTs, (b) MWCNTs-LA1, (c) MWCNTs-LA 2 and (d) MWCNTs-LA3.....	39
Figure 3.6: Water contact angles for the different absorbents: A-neat MWCNTs, B- MWCNTs-LA1, C-MWCNTs-LA2 and D-MWCNTs-LA3.....	40
Figure 3.7: k values of the three MWCNTs-LA absorbents for various model hydrocarbons samples.....	42
Figure 3.8: Photographs of absorption of hexadecane (coloured with dye) by MWCNTs-LA2 absorbent.....	43
Figure 3.9: Pictures showing the process of selective absorption of hexadecane on	

the water surface (hydrocarbons dyed with Sudan I dye and water coloured methylene blue dye) by MWCNTs-LA2.	45
Figure 3.10 : The separation efficiency of the MWCNTs-LA absorbent for different types of hydrocarbons/water mixture.....	46
Figure 3.11: Absorption capacity of MWCNTs-LA for 5 cycles of hydrocarbons-water separation.....	48
Figure 4.1 : FTIR spectra of (a) GO, (b) FGOHA, and (c) FGODDA.....	57
Figure 4.2: Raman spectra of GO.....	59
Figure 4.3: Raman spectra of GO, FGOHA and FGODDA recorded using 633 nm laser excitation.....	60
Figure 4.4: SEM photos of (a) GO, (b) FGOHA, (c) and FGODDA.....	61
Figure 4.5: Water contact angle measurements for (a) GO, (b) FGOHA, (c) and FGODDA.....	64
Figure 4.6: XRD of grahite flake.....	66
Figure 4.7: XRD patterns of pristine GO, FGOHA and FGODDA.....	67
Figure 4.8: Absorption capacity (weight gain) of the FGO-amine absorption films calculated for engine hydrocarbons and organic solvents.....	69
Figure 4.9: Separation of engine oil from the surface of DI water by FGODDA.....	72
Figure 4.10: Separation of n-hexane from the surface of DI water dyed with Methylene Bue by FGODDA.....	73
Figure 4.11: The separation efficiency of the modified absorbents for different types of hydrocarbons/water mixture.....	74
Figure 5.1: FTIR spectra of GO and DDA-GO nanosheets.....	83
Figure 5.2: FTIR spectra (a) GO, (b) DDA-GO, (c) PE, (d) GO-DDA/PE-1	

and (e) and GO-DDA/PE-2.....	85
Figure 5.3: Contact angle measurements for (a) GO, (b) DDA-GO, (c) GO-DDA/PE-1, (d) DDA-GO/PE-2.....	87
Figure 5.4: XRD of GO	90
Figure 5.5: XRD patterns of (a) GO, (b) DDA-GO, (c) GO-DDA/PE-1, and (d) and GO-DDA/LDPE-2.....	91
Figure 5.6: Raman spectrum of graphite powder.....	94
Figure 5.7: Raman spectra of (a) GO, (b) DDA-GO, (c) GO-DDA/PE-1, and (d) and GO-DDA/LDPE-2.....	95
Figure 5.8: SEM images of (a) GO, (b) GO-DDA, (c) GO-DDA/PE-1 and (d) and GO-DDA/PE-2.....	97
Figure 5.9: Absorption capacities of the GO-DDA/PE-1 and GO-DDA/PE-2 absorbents for the selected hydrocarbons and organic solvents.....	100
Figure 5.10: Pictures showing the process of selective absorption of diesel hydrocarbons (a-f) and decane (g-l) on the water surface (both hydrocarbons dyed with Sudan I dye and water coloured methylene blue dye) by DDA-GO/PE-2.....	102
Figure 5.11: The percentage recovery of the DAA-GO/PE-2 absorbent for different types of hydrocarbons/water mixture.....	104
Figure 5.12: Absorption of DDA-GO/PE-2 for 10 cycles	105

LIST OF ABBREVIATIONS

APTES	:	(3-Aminopropyl)triethoxysilane
cMWCNT	:	carboxyl-functionalized multiwalled carbon nanotubes
CNFs	:	Cellulose nanofibrils
CNTs	:	Carbon nanotubes
CVD	:	Chemical vapour deposition
DDA	:	DodecylamineAcrylamide
DI water	:	Deionized water
DMF	:	Dimethylformamide
EC	:	Ethyl cellulose
μEMWCNT	:	Microemulsified multiwalled carbon nanotubes
FGO	:	Functionalized graphene oxide
FTIR	:	Fourier-Transform Infrared
GE	:	Graphene
GO	:	Graphene oxide
HA	:	Hexylamine
HDTMS	:	Hexadecyltrimethoxysilane

LA	:	Lauric acid
Me-CNT	:	Magnetic carbon nanotube
MWCNTs	:	Multiwalled carbon nanotubes
MWCNTs-OH	:	Hydroxylated multiwalled carbon nanotubes
OCA	:	Hydrocarbons contact angle
ODA	:	Octadecylamine
PC	:	Polycarbonate
PE	:	Polyethylene
PDA	:	Polydopamine
PEI	:	Polyethyleneimine
PETNW	:	Poly(ethylene terephthalate) nonwoven
PTMOS	:	Phenyltrimethoxysilane
PVDF	:	Polyvinylidene fluoride
PTMOS	:	Phenyltrimethoxysilane
SEM	:	Scanning electron microscope
Si-CNTs	:	Silanized carbon nanotubes
THF	:	Tetrahydrofuran

TTEAI	:	Titanium(IV)(triethanolaminate)isopropoxide
UV	:	Ultraviolet
WCA	:	Water contact angle
XRD	:	X-ray diffraction

ABSTRACT

Full Name : [ABDULLAHI BIODUN OLABINTAN]
Thesis Title : [SYNTHESIS AND CHARACTERIZATION OF CARBON-BASED NANOCOMPOSITES FOR EFFICIENT REMOVAL OF HYDROCARBONS FROM WATER]
Major Field : [CHEMISTRY]
Date of Degree : [May, 2020]

Water pollution due to organic chemical leakages has posed a serious environmental threat to aquatic life. Such catastrophes have triggered the need to fabricate novel materials with enhanced sorption capacity for hydrocarbons and organic solvents clean up and recovery. Among the existing techniques, the use of absorbents appears to be promising for removing and recovering hydrocarbons and organic chemicals from less or heavily polluted water. Recently, carbon-based materials have shown potential applications in the area of hydrocarbons-water separation due to their exceptional absorption capacity, high selectivity, chemical stability and acceptable reusability. Herein, we report the fabrications of three set of novel, low cost, efficient, hydrophobic and oleophilic carbon-based composites-lauric acid grafted multiwalled carbon nanotubes (MWCNTs-LA), amine functionalized reduced graphene oxide (FGO-RNH₂) and dodecylamine-amidated graphene oxide/polyethylene (DDA-GO/PE) - as absorbents for effective retrieval of some selected hydrocarbons and organic solvents from the surface of the water. The developed nanocomposites were thoroughly investigated by field emission scanning electron microscopy, X-ray diffraction technique, Fourier transform infrared spectroscopy, Raman spectroscopy and X-ray photoelectron spectroscopy. The prepared carbon-based

absorbents were evaluated for efficient removal of hydrocarbons such as cyclohexane, hexane, decane, dodecane, hexadecane, etc. from water. Spectroscopic studies revealed the successful chemical modifications of the multiwalled carbon nanotubes and graphene oxide leading to the formation of the composites. Absorption experiments with the model samples showed that the composites were efficient absorbents with absorption capacities of 20-33.5, 31.2-64 and 38.5-78 times own weight for MWCNTs-LA, FGO-RNH₂, and DDA-GO/PE absorbents respectively. The separation efficiency of more than 99% was recorded for the prepared absorbents. All the three sets of the modified carbon-derived absorbents showed potential to separate model samples from hydrocarbons–water mixtures with high selectivity, high separation efficiency, stable performance, and acceptable recyclability, which are promising for the applications in the recovery of hydrophobic hydrocarbons and organic solvents from water.

1. ملخص الرسالة

الاسم الكامل: عبد الله بيودون أولابينتتان

عنوان الرسالة: توليف وتوصيف المركبات النانوية القائمة على الكربون لإزالة الهيدروكربونات من الماء

التخصص: كيمياء

تاريخ الدرجة العلمية: مايو 2020

يشكل تلوث المياه بسبب التسربات الكيميائية العضوية تهديدًا بيئيًا خطيرًا للحياة المائية، إلى جانب خسائر فادحة أخرى. وأثارت مثل هذه الملوثات الحاجة إلى تصنيع مواد جديدة ذات قدرة امتصاص محسنة لتنظيف الزيوت والمذيبات العضوية واستعادتها. من بين التقنيات الموجودة، يبدو استخدام المواد الماصة واعدًا لإزالة واستعادة النفط والمواد الكيميائية العضوية من المياه الملوثة. في الآونة الأخيرة، أظهرت المواد القائمة على الكربون تطبيقًا جيدًا في مجال فصل المركبات العضوية الهيدروكربونية عن الماء نظرًا لقدرتها الاستيعابية الاستثنائية والانتقائية العالية والاستقرار الكيميائي وإعادة الاستخدام. في هذا البحث، نقدم تقريرًا عن تصنيع ثلاث مجموعات من مركبات الكربون النانوية الجديدة المصنوعة من الأنابيب النانوية الكربونية متعددة الجدران المعدلة منخفضة التكلفة وعالية الفعالية، مع خصائص مضاد للرطوبة. أيضًا تم تحضير الجرافين المعدل بالبولي إيثيلين كمادة عالية الامتصاص لاسترجاع فعال لبعض الهيدروكربونات والمذيبات العضوية المختارة من سطح الماء. تم فحص المركبات النانوية المطورة بدقة بواسطة عدة أجهزة منها جهاز مطيافية الأشعة تحت الحمراء وجهاز مطيافية الرامان وجهاز الأشعة السينية وجهاز مطيافية الأشعة السينية الضوئية وجهاز مجهر المسح الإلكتروني. تم تقييم المواد الماصة المعتمدة على الكربون للإزالة الفعالة للهيدروكربونات مثل الهكسان الحلقي، الهكسان، الديكان، الدوديكان، الهكساديكان إلخ من الماء. كشفت الدراسات الطيفية عن التعديلات الكيميائية الناجمة للأنابيب النانوية الكربونية متعددة الجدران وأكسيد الجرافين مما أدى إلى تكوين المركبات. أظهرت تجارب الامتصاص على العينات النموذجية العملية أن المركبات كانت فعالة بقدرات امتصاص عالية. تم تسجيل كفاءة الفصل بأكثر من 99%. أظهرت كل المجموعات الثلاث من المواد الماصة المشتقة من الكربون المعدلة إمكانية الفصل بين العينات العملية النموذجية مع الانتقائية العالية وكفاءة الفصل العالية والأداء المستقر وقابلية إعادة التدوير المقبولة، والتي تعد واعدة للتطبيقات في استعادة الهيدروكربونات والمذيبات العضوية من الماء.

1. CHAPTER 1

INTRODUCTION

1.1 Background

Water pollution is a crucial environmental challenge which can cause disastrous effects for aquatic organisms and for humans. The major players in the water pollution are the hydrocarbons and organic spills [1]. The need for fossil fuels has been on the increase sequel to the industrial revolution in the 18th century. This has called for frequent offshore transportation of the hydrocarbon from the place of generation to the point of demand [2]. The prevalent hydrocarbon spill accidents and the huge wastewater discharge from the industries such as petrochemicals, textile and leather, aluminum, steel, metal finishing, palm hydrocarbons and food industries destroy the quality of water. Water contaminated with hydrocarbon is not only detrimental to the human health but also have a destructive effect on aquatic life and almost individual species across the marine food chain is affected [3]. Aside from the aforementioned consequences, hydrocarbon and organic contaminants are potentially hazardous as a result of their high flammability and may eventually cause fire or explosion [4]. To this end, the efficient separation of these contaminants from water has become a matter of urgency and paramount importance in order to shield the ecosystem for the healthy sustainability of the environment. Several conventional methods such as controlled burning [5], bioremediation [6], use of electric field [7], collection by mechanical means [8], use of chemical dispersants [9] and absorbent materials [10-11], have been broadly employed to deal with the hydrocarbons and chemical pollutants. The drawbacks associated with

these techniques are their low efficiency of separation, poor selectivity, high toxicity, lesser recyclability, high operational cost, and the introduction of secondary pollutants [12]. Thus, special attention has been channelled by researchers on the fabrication of numerous low cost functionalized materials which can effectively separate hydrocarbons from water and also be easily produced on a large scale. Materials with either superhydrophilic and superoleophobic or superhydrophobic and superoleophilic surfaces can be efficient to tackle the problem of hydrocarbons separation from water [13]. Here, the water or hydrocarbons swiftly percolates through the superhydrophilic or superhydrophobic materials in which one phase is eventually left behind [14]. Novel materials and methods are currently explored for hydrocarbons/water separation due to some serious limitation of the traditional methods [15, 16, 17]. To achieve effective separation of hydrocarbons from water, designing functional materials with special wettability plays a very crucial role. The realization of this task lies in the construction of superhydrophobic surfaces. Materials with superhydrophobic surfaces are characterized by high contact angle greater than 150° [18]. The fabrication of materials with superhydrophobicity is greatly preferred either for differential absorption, or application for the direct removal of hydrocarbons from water [19]. Among the existing technologies, the use of absorbents appears to be the commonly employed technique for hydrocarbons spill remediation due to its ease of practical applications, low cost, availability and eco-friendliness of the remediation process [20]. Ideal absorbent materials should have high specific surface area, high absorption capacity, suitable pore size, low density, good selectivity, and excellent recyclability [21]. The hydrophobic and oleophilic properties of the absorbent materials are also extraordinarily crucial features since these materials should selectively absorb the hydrocarbons on their surface and at the same time reject the water [22]. Till now, the fabrication of absorbents with remarkable hydrocarbons sorption

properties is a huge challenge for researchers. Over the past few years, several hydrocarbons sorbent materials such as silicas [23], inorganic-organic hybrids [24-25] cross-linked polymers [26-27] macroporous gels [28], nanocomposites [29-30] and carbon-based materials [22], [31-33] have been prepared extensively. Among these, Sorbents from carbon-based materials are drawing the attention of scientists for application in hydrocarbons/water separation due to their unique properties [34]. Activated carbon, CNTs, carbon nanofibres, carbon aerogels, porous carbon nanoparticles, carbon coatings, and graphene sponges have been widely explored in remediation, hydrocarbons/water separation, water filtration, gas purification and separation [35-37]. Compared to the foregoing conventional sorbents, graphene and CNTs have been exhibited to have potential application in the area of hydrocarbons-water separation owing to their robust mechanical properties, high absorption capacity, high surface area, quick absorption rates and well-established surface chemistry tuning [38]. Graphene-derived materials have been used as absorbents for the retrieval of organic pollutants; including hydrocarbons, several organic solvents from water [39-41]. The graphene surface can be improved to obtain an excellent hydrophobic surface as exhibited by silane and other polymeric materials [42]. The ease of synthesis and the processability make graphene oxide (GO) an excellent precursor for graphene and its composites. On the other hand, a few studies have also included CNTs based materials for application in hydrocarbons-water separation. Modification of CNTs surfaces was visualized by many researchers to improve their chemical feature and this can be achieved either by covalent or non-covalent functionalization or by creation of defects [43-44]. Chemical functionalization of CNTs brings about the attachment of chemical functionalities like hydroxyl, carboxyl and amino groups to the sp^2 hybridized carbon frame-work [45]. The anchoring of other chemical molecules to the CNTs surface is made possible

via covalent attachment to these groups in order to achieve desirable properties for hydrocarbons-water separation application.

This work is intended to fabricate novel set of inexpensive, highly effective and environmentally friendly carbon-based nanocomposites as absorbents for removing hydrophobic hydrocarbons from water. This will be followed by extensive characterization of the as-prepared sorbent materials and their assessments for efficient removal of hydrocarbons from water.

1.2 Statements of the problem

Hydrocarbons contaminated water is not only harmful to the human health but also has a destructive effect on aquatic life. Various existing traditional techniques suffer from various drawbacks including low separation efficiency, poor selectivity, high toxicity, lesser recyclability, high operational cost, and the introduction of secondary pollutants. Till now, the fabrication of absorbents with remarkable sorption properties is a huge challenge for researchers. Hence, it is compelling, although also challenging, to fabricate highly efficient absorbent materials with eco-friendliness, low cost, high selectivity and high absorption capacity for applications in different fields.

1.3 Objectives of the study

The aim of the work is to fabricate new set of inexpensive, highly effective and environmentally friendly carbon-based absorbents for removing hydrophobic hydrocarbons from water. The specific objectives of this research are to:

- i. synthesize nanocomposites of lauric acid functionalized multiwalled carbon nanotubes.

- ii. synthesize nanocomposites of amine functionalized graphene oxide and polyethylene.
- iii. characterize the prepared nanocomposites by SEM, XRD, FTIR and Raman spectroscopy.
- iv. investigate the efficiency of the prepared nanocomposites for the removal of some selected hydrocarbons such as cyclohexane, hexane, decane, dodecane, hexadecane and some organic solvents from water.

1.4 Significance of the study

The importance of the carbon-based nanocomposites is due their tunable surface chemistry which makes the anchoring of low surface energy molecules on their surfaces possible by surface modifications. These modifications in turn facilitate the required surface superhydrophobicity and superoleophilicity for efficient separation of hydrocarbons from water.

1.5 Scheme of the research work

The research centers on the three major schemes which are highlighted below:

- Design and synthesis of carbon-based composite materials as absorbents for recovering hydrocarbons from water.
- Extensive characterization of the as-prepared absorbent materials using up-to-date imaging and spectroscopic techniques.
- Assessment of the absorption capacity performance of the novel absorbent materials for application in separation of hydrocarbons from water.

1.6 Scheme of research findings reporting

The following shows the order of this thesis report which has been organized and arranged in chronological manner into five chapters for easy reading and comprehension:

Chapter 1 description of the hydrocarbons spill catastrophes, the need for the carbon-based absorbent materials, highlight of the specific objectives, problem statement, importance of the study as well as the research findings and reporting scheme.

Chapter 2 gave a brief literature survey on basic considerations in water treatment, several kinds of porous materials, their design strategies.

Chapter 3 explained succinctly the fabrication of lauric acid grafted multiwalled carbon nanotubes as absorbents for retrieval of hydrocarbons from the surface of water.

Chapter 4 illustrated the preparation amine functionalized reduced graphene oxide absorbents for effective performance.

Chapter 5 described the preparation of nanocomposites of amine functionalized reduced graphene oxide and polyethylene as absorbents for effective removal of some hydrocarbons and organic solvents from water.

Chapter 6 gave a summary of the conclusions from the work.

2. CHAPTER 2

LITERATURE REVIEW

2.1 Basic factors for hydrocarbons-water separation

Wettability of a surface is an intrinsic feature of a solid surface, and dictates the ultimate wetting behaviours when a liquid makes contact with the solid material. It is one of the most significant considerations when using a material for hydrocarbons-water separation. Over the past few years, expansive researches on the biomaterial surfaces have enhanced a thorough understanding of the mechanism governing superwetting surfaces [46-48]. For example, the “lotus effect” phenomenon reported by Barthlott [49], when the droplets of water sit on the surface of lotus leaves having WCA greater than 150° and easily rolls off transporting the dust during tilting. This unique characteristic is termed self-cleaning and superhydrophobicity [50-51]. Subsequent investigation revealed that lotus leaf is composed of nano or microhierarchical networks endowed with low surface energy wax to decrease the surface energy, thereby conferring the self –cleaning and the superhydrophobic properties (figure 2.1a)[52]. This extraordinary feature can be employed to construct superhydrophobic materials to remove hydrocarbons from water accomplishing hydrocarbons-water separation. Another experience from nature is to mimic the superhydrophilic-underwater superoleophobic architectures exhibited by fish scales (uniform fan-folded microstructures) (figure 2.1b)[53] in designing materials to retrieve water from hydrocarbons-water mixture and keep rejecting hydrocarbons [54]. Motivated by these revelations, the

interconnection between surface wettability and surface roughness has been described by four modes of wetting behaviors such as

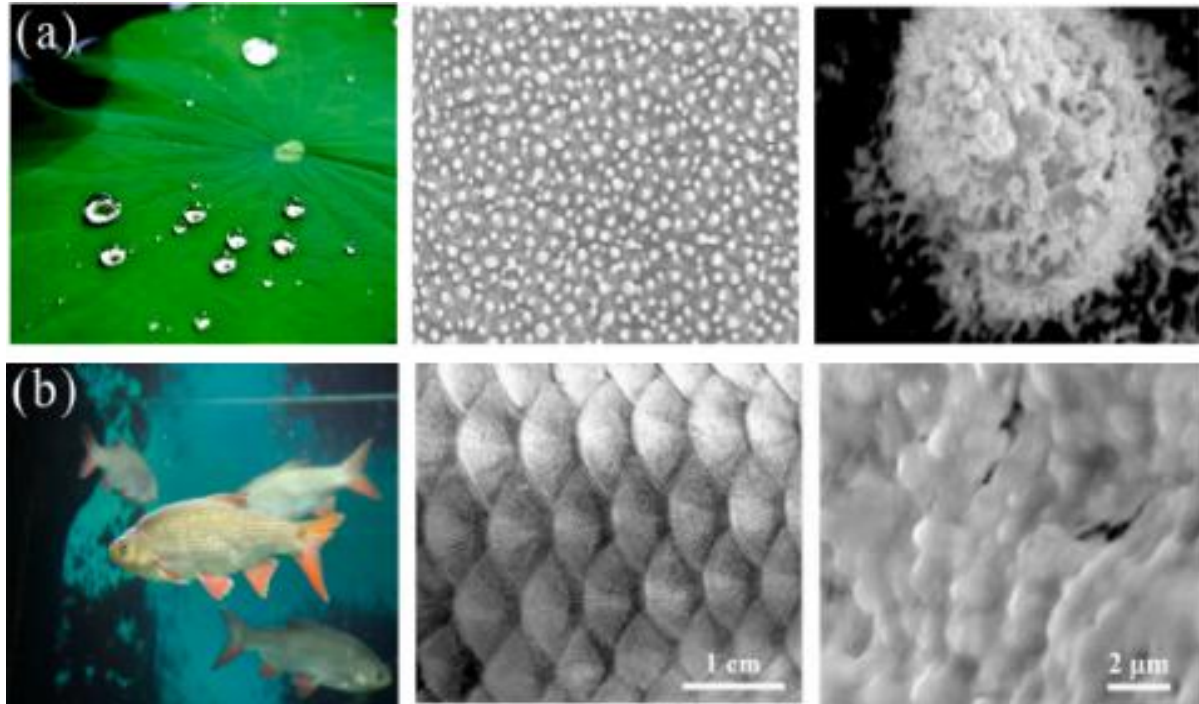


Figure 2.1: Surfaces and microstructures of biological superwetting materials (a) lotus leaf [52], (b) scales of fish [53].

Young's mode [55-56], Cassie's mode [57-58], Wenzel's mode [59-60] and the Cassie-Wenzel intermediate state [61-62]. According to Young's model, a perfectly smooth surface has finite hydrophobic property as only low-surface energy will not suffice to attain the superhydrophobicity in any solid materials without nano or microhierarchical architectures. However, superhydrophobicity can be easily achieved by the creation of a rough surface with structures at the nano or microscale which is the prediction of Cassie and Wenzel models. From the two, Cassie state displays a high contact angle and low contact hysteresis, while the Wenzel mode is wet-contact state. The superhydrophobic Cassie state can be used to describe the lotus effect. Moreover, in real situations, there often occurs an intermediate state between the Cassie and Wenzel's states, when the surface is tilted at a specific angle, the water droplets on the surface slide. Hence, several biomimetic surfaces with unique wettability could be attained by fine-tuning the structures of the surface at nano or micro scales and the chemical constitution [63].

2.2 Special wettable materials.

Furnishing various porous materials with unique wettable features, such as superhydrophobicity-superoleophilicity, superhydrophilicity-underwater superoleophilicity and superhydrophilicity-superoleophobicity, is preferred for separation of hydrocarbons-water mixture. Hence, various types of porous materials with unique wettable properties and their design strategies are briefly discussed as follows.

2.2.1. Materials with superhydrophobicity-superoleophilicity.

Materials with superhydrophobic-superoleophilic wettability are typically hydrocarbons retrieving materials applied in separating hydrocarbons/water mixture either by filtration (two-

dimensional membranes, textiles and metal meshes,) or absorption (three-dimensional foams, sponges and carbon-based materials) [64-65]. These materials reject water and at the same time allow hydrocarbons to pass through them, thus separating hydrocarbons from water. As roughness of the surface and surface chemical constitution are the two main considerations to design unique wettability, materials with superhydrophobic–superoleophilic surfaces can be prepared by two methods: (1) improvement of surface roughness by the creation of nano or micro structures on the substrate; (2) modification of the enhanced rough surfaces with molecules or groups of low surface energy [66-67]. This type of unique wettable material has stimulated great attention due of its high efficiency, suitable selectivity, and special advantages in hydrocarbons filtration or hydrocarbons spill absorption. In recent times, several strategies have been designed to prepare such separation materials, including wet chemical reaction, CVD, spray-dip coating, phase separation, hydrothermal treatment, electrospinning method, freeze-drying method, template technique, *etc.*

2.2.2. Materials with superhydrophilicity–superoleophobicity.

Based on theory, porous materials with superhydrophilicity–superoleophobicity can be used in hydrocarbons-water separation either by absorption or filtration. Although, from the underlying wetting theory, inherent superhydrophobicity is exhibited by a superoleophobic surface since fuel ordinarily demonstrate lower surface free energy. Hence, it is a huge task to accomplish a superhydrophilic–superoleophobic surface in a conventional environment [68-69]. Scientists have discovered that some stimuli-sensitive materials can concurrently exhibit hydrophilic and oleophilic features depending on counter adhesion characteristics toward polar liquids like water and non polar liquids like dodecane. With this approach, Zhang *et al.* used a suitable molecular design to create superhydrophilic–superoleophobic surface by reacting poly

(diallyldimethylammonium chloride) with perfluorooctanoate/SiO₂ in aqueous medium [70]. The incorporation of the SiO₂ nanoparticles created the nano or micro surface roughness which led to the desired special wettable property. The as-prepared polymer coated mesh displayed water penetration and outstanding hydrocarbons rejection behaviours, showing that the treated mesh can be employed in hydrocarbons-water separation. In another similar work by Su and his co-workers, a melamine sponge with superhydrophobic–superoleophilic wettability was fabricated from Fe₃O₄ nanoparticles and sodium perfluorononanoate through dip-coating technique recording OCA of angle of 144° [71]. The modified sponge can readily remove huge amount of water pollutants from bulk hydrocarbons when combined with peristaltic pump.

2.2.3. Materials with superhydrophilicity– underwater superoleophobicity.

Inspired by the superhydrophilic-underwater superoleophobic architectures of fish scales which are believed to shield fish underwater from hydrocarbons contamination, superhydrophilic-underwater superoleophobic porous materials are arousing the interests of researchers and appear to be more preferred in hydrocarbons–water separation [72]. Typically, a mucus layer which chiefly consists of a hydrophilic hydrogel covers the rough fish scales. The fish skin demonstrates air superhydrophilicity and underwater superoleophobicity with an OCA of 156.4 ± 3.0 because of this hydrophilic chemical constitution on the surfaces and hierarchical nano/microscale architectures [73]. Compared to the superhydrophobic porous materials, superhydrophilic-underwater superoleophobic porous materials were designed to overcome the challenge of adhesion of hydrocarbons to the surface of the former by the formation of dense water film. In this type of materials, hydrocarbons is shielded to contact the materials at the surface by the water film and such leaving the surface clean [74-75]. For instance, Dong *et al.* fabricated stainless steel meshes coated GO by dipping the meshes in aqueous solution of GO [76]. After several

consecutive immersions, there was formation of regular nanostructures of GO layers on the steel mesh and this exhibited outstanding superhydrophilic–underwater superoleophobic property. By employing this choice of underwater counter wettability, a variety of hydrocarbons–water-mixtures were effectively separated. Also, Jiang and his co-workers reported the fabrication of a filter paper coated with hydrogel and this showed exceptional separation capability for both hydrocarbons-in-water emulsion and hydrocarbons-water mixtures with efficiency of separation of more than 99% in a complicated environment [77]. Materials with superhydrophilicity–underwater superoleophobicity show more formidable potential in hydrocarbons–water separation application compared to traditional materials with superhydrophilicity–superoleophobicity.

2.2.4. Smart materials with controllable wettability.

Either superhydrophilic or superhydrophobic porous materials possess a single wetting property and can separate or absorb particular liquids. Moreover, high hydrocarbons like crude hydrocarbons tend to adhere easily onto the surface of the superhydrophobic materials leading to the decrease in absorption capability and difficult desorption [78]. Intelligent porous materials with adjustable wettability are gaining ground due to the benefits of their swift response to external stimulation, easy absorption-desorption, self-cleaning, versatile hydrocarbons-water separation under different environment. A variety of porous materials have reported to apply in hydrocarbons-water separation which can swap their wettability under influence of heat [79], light [80], pH [81], magnet [82] and voltage [83], exhibiting ease of desorption after absorbing hydrocarbons and self-cleaning. For instance, Li *et al.* [80] worked on the fabrication of photo-responsive PU sponge by dipping in titania and octadecanoic acid solution under ultrasonication to obtain superhydrophobic composite with WCA of 151°. The superhydrophobic modified PU sponge was turned into superhydrophilic surface of WCA of 0° after irradiation with UV by the generation of Ti^{3+} . This

intelligent TiO₂ coated PU sponge could absorb hydrocarbons of 27 to 60 times own weight and displays specific self-cleaning and anti-fouling properties. Although some accomplishments were recorded in external stimuli-driven controllable surface wettability such as by heat, magnet, light, pH, voltage, etc., they may cause destruction to the intrinsic architectures of the substrate and lead to reduction in their life-time. Hence, more focus should be directed to these more eco-friendly, cheap, harmless external stimuli-sensitive technologies for as needed hydrocarbons–water separation.

2.3. Carbon-based sorbents for hydrocarbons-water separation.

Ideal absorbent materials should have high specific surface area, high absorption capacity, suitable pore size, low density, good selectivity, and excellent recyclability. Microporous polymers [84-85] have been utilized as absorbent materials, but they take a while to degrade, which poses danger to the environment and ecological system. Besides, they have somewhat long and complex fabrication method and brittle mechanical properties. Superhydrophobic carbon-derived materials can be prepared by several techniques [86]. Their excellent chemical stability, high specific surface area, outstanding flexibility, eco-friendliness and great pore volume of carbon materials make them promising candidates for hydrocarbons/water separation, filtration, remediation, treatment of wastewater, gas purification and separation [87]. Activated carbon, carbon nanotubes, carbon nanofibres, carbon aerogels, porous carbon nanoparticles, carbon coatings, and graphene sponges have been widely explored as sorbents due to their exceptional hydrocarbons absorption capability and recyclability [88].

2.3. 1 Graphene-based sorbents

The pristine form of graphene consists of a single layer of carbon atoms organized in a sp^2 -bonded aromatic structure. Graphene is by nature the basic unit of graphite, where the lamellar graphite structure is firmly held in place by the π -stacking of graphene sheets with an interlayer spacing 3.34 Å between the sheets [89]. The exfoliation of graphite to single layers of graphene can be achieved in different ways. Zhu and co-workers first demonstrated the micromechanical exfoliation method by sequentially cleaving graphite to graphene by means of adhesive tapes [90]. It can also be prepared by exfoliation in liquid phase [91], chemical vapour deposition [92], epitaxial growth, solvothermal synthesis, [93] and the reduction of GO [94]. Of all these, the GO reduction seems to be the cheapest method for the graphene synthesis. This involves graphite exfoliation into one-atom-thick sheets by oxidation, producing GO followed by its reduction into a graphene sheet by reducing agents such as hydrazine, sodium borohydride, vitamin C, hydroquinone or by thermal treatments [95-97]. The reduced GO method almost attains the highly preferred characteristics of graphene. One of the most popular methods to graphene-based nanocomposites is to use GO, due to its lower costs of production. GO being the oxidized form of graphene displays several oxygen-containing functionalities. According to the most generally known model of GO structure put forward by Lerf and co-workers, the carboxyl groups populate the GO edges; while the hydroxyl and epoxy are located in the basal plane of GO as shown in Figure 2.2b [98]. Because of the abundant oxygenated functional groups, GO displays excellent hydrophilicity that enables its easy dispersion in polar solvents and functionalization via traditional aqueous chemistry routes (Figure 2.3). For this reason, GO sheets are versatile routes for anchoring secondary nanomaterials to generate graphene-based hybrids.

Graphene-based composites have been employed as absorbents for the retrieval of organic pollutants, such as hydrocarbons, and several organic solvents from water [99-101]. The selectivity

and efficiency of graphene can be enhanced by modulating its surface to acquire an excellent hydrophobic surface, as exhibited by silane and other polymeric materials [102]. The ease of synthesis and the processability make GO an excellent precursor for graphene and its composites. For example, Peng et al. used the surface modification technique to produce superoleophilic and superhydrophobic graphene coated melamine foam for collection and retrieval of pollutants from water [103]. Similarly, Ricky et al. developed superhydrophobic reduced GO modified polyurethane sponges as greatly effective and recyclable sorbents for use in hydrocarbons-water separation [104]. Li and Shi manufactured graphene aerogel (GA) absorbent materials by reducing chemically graphene oxide (GO) dispersion [105-106]. Qu and Xie fabricated nitrogen doped graphene architecture as the absorbents for organic solvents' sorption [107-108]. In another work, a facile dip coating method was employed for the preparation of graphene-based sponges with superhydrophobic and superoleophilic features for the large-scale collection of organic contaminants [109]. Even though the above mentioned graphene-based absorbent materials exhibit high absorption capacity, they have low selectivity for hydrocarbons and water thereby decreasing the efficiency of separation. In order to furnish the neat graphene monolith with superhydrophobicity and superoleophilicity so as to further enhance its efficiency of separation, designing surface structure with low surface energy and high roughness is expected to be a viable and efficient route. Nowadays, incorporation of long alkyl chains has been explored to modulate the GO surface lipophilically. This can facilitate regular GO dispersion in the polymer and weaken its high affinity for water and this is desirable for its application in hydrocarbons-water separation. Jiao et al. grafted alkylamines such as octadecylamine (ODA) to tune the hydrophilic GO into hydrophobic surface, thereby promoting GO application in non-polar polymers [110]. Lee and co-workers functionalized GO with dodecylamine and noticed enhanced mechanical and barrier

characteristics of the polyethylene composites when the modified graphene was added [111]. The interaction mechanism between nanomaterials and organic compounds is a function of their structural properties (e.g. dipole moment, molecular conformation, functional groups present) [112]. Absorption of hydrophobic organic compounds by graphene can be explained in terms of the hydrophobic effects [113]. Hydrophobic interactions were thought to be involved in the mechanism of absorption of non-polar hydrocarbons on modified GO or pristine graphene sheets [114]. The high affinity between graphene sheets and the hydrocarbons could be interpreted in terms of the sieving effect produced by the presence of the grooved regions on the graphene surface [115].

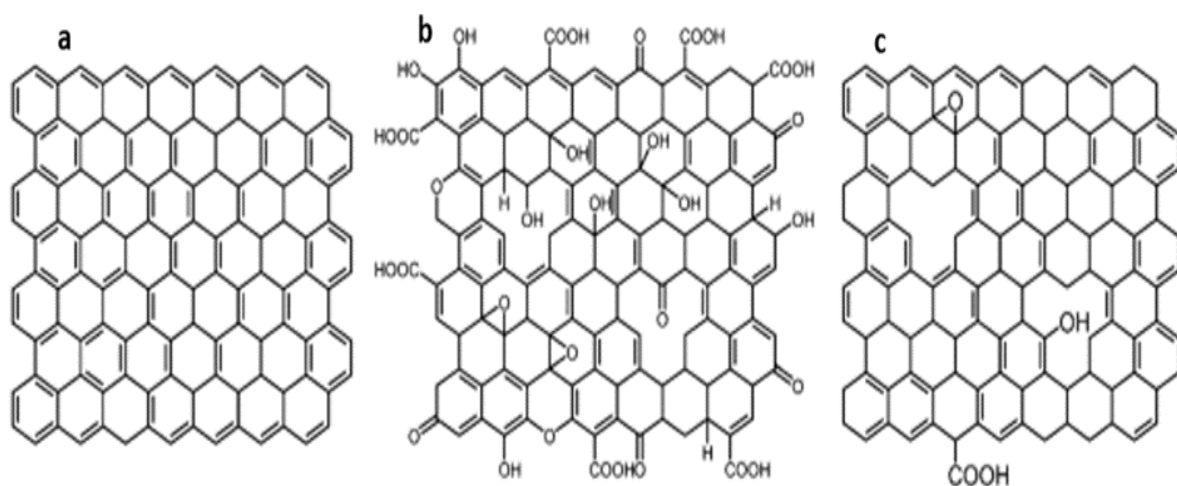


Figure 2.2: Structure of: (a) graphene, (b) graphene oxide (GO), and (c) reduced graphene oxide (rGO)

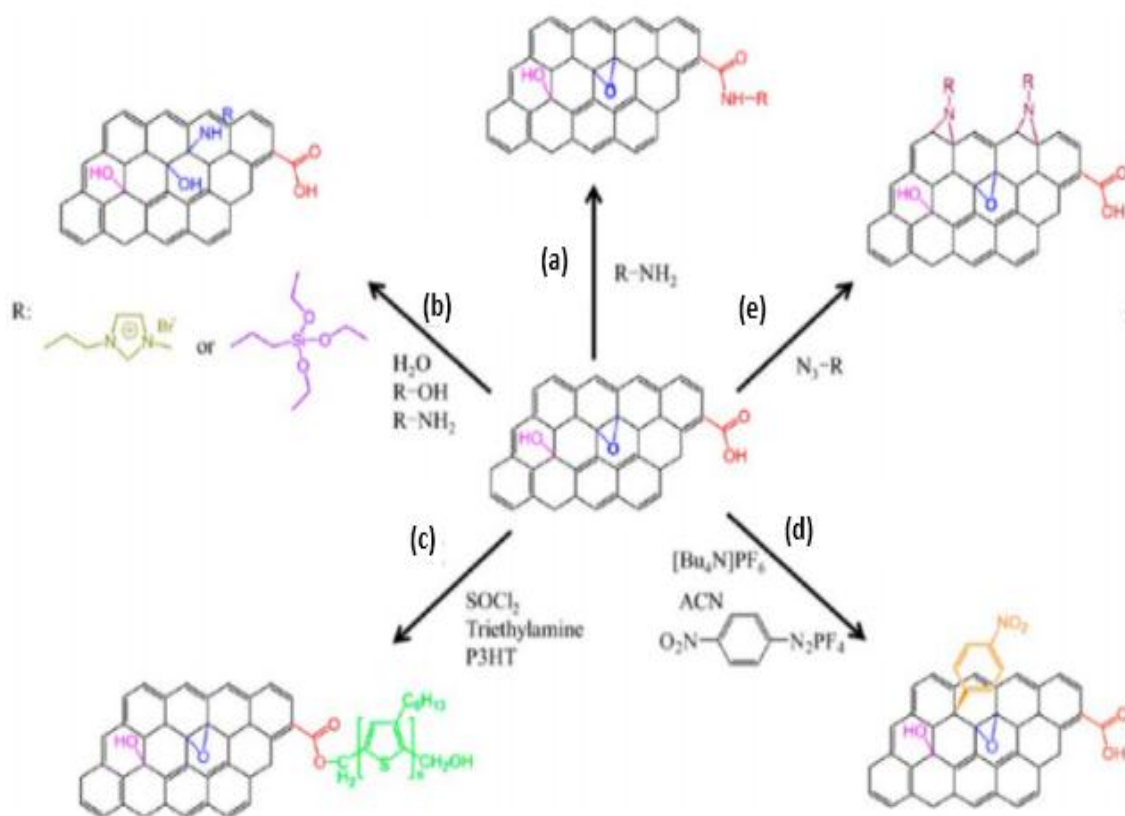


Figure 2.3: Schematic representation of covalent functionalization routes targeting the different sites of graphene oxide: (a) acylation, (b) nucleophilic ring-opening, (c) bisocyanate/esterification, (d) diazotization , and (e) cycloaddition reactions [152].

2.3.2 Carbon nanotubes-based sorbents

Compared to the foregoing conventional sorbents, carbon nanotubes have been exhibited to have potential application in the area of hydrocarbons-water separation owing to their robust mechanical properties, high absorption capacity, high surface area, quick absorption rates and well-established surface chemistry tuning [116-117]. Several methods have been reported to synthesize CNTs, including pyrolysis, electrochemical techniques, laser ablation, CVD and arc discharge techniques. A few studies have included CNTs for application in hydrocarbons-water separation. For example, Al-Jammal *et al.* prepared modified CNTs sorbent by microemulsion method. The microemulsified CNTs attained absorption capacities of 2.48 to 6.07 times own weight for the removal of hydrocarbons water surface [118]. Sun *et al.* demonstrated the functionalization of CNTs with *p*-phenylenediamine (P-CNTs) by diazotization method for hydrocarbons sorption. The P-CNTs show maximum absorption capacity of 3-12 times own weight for hydrocarbons and organic solvents [119]. Gao *et al.* fabricated CNT-coated sponges with exceptional performances for hydrocarbons-water separation. The CNT coating improved the selectivity of the sponges to absorb only hydrocarbons while rejecting water completely. The spongy CNT absorbents exhibited high absorption capacity and the absorbed hydrocarbons could be retrieved by mechanical squeezing [120].

Modification of CNTs surfaces was visualized by many researchers to improve their chemical feature and this can be achieved either by covalent or non-covalent functionalization or by creation of defects [121-122]. Chemical functionalization of CNTs brings about the attachment of chemical functionalities like hydroxyl, carboxyl and amino groups to the sp^2 hybridized carbon frame-work [123]. The anchoring of other chemical molecules to the CNTs surface is made possible via covalent attachment to these groups in order to achieve desirable properties.

sorbents	methods	WCA(°)	sorption capacity (g/g)	ref.
μEMWCNT	microemulsion	-	max. 6.1 (n-octane)	[118]
PS/CNT	electrospinning	>150	max. 16 (n-octane)	[181]
PC/cMWCNTs	TINIPS, freeze drying	159	max. 12.6 (n-hexane)	[40]
EC/Si-CNTs /HDTMS	freeze drying	158.2	max. 35 (n-hexane)	[182]
PU-CNT-PDA -ODA sponge	oxidative self-polymerization	158	max. 34.5 (n-hexane)	[120]
CNT/PVDF	freeze drying	156	max. 7.8 (DCM)	[39]
Me-CNT	CVD	>140	max. 56 (n-octane)	[183]
C ₈ -GONF	solvothermal	147	max. 38 (diesel)	[184]
GE-PETNW-T	dip-spray coating	153.2	max. 34 (engine fuel)	[180]
GO/CNFs/silica hybrid aerogel	Hydrothermal, freeze drying, CVD	157.3	max. 40 (n-octane)	[185]
PTMOS/PEI/GO PU-DW sponge	hydrothermal, dip coating	95.8	max. 8.4 (chain fuel)	[186]
rGO-PU sponge (APTES/TTEAI)	Covalent functionalization	-	max. 46 (diesel)	[104]

Table 2.1: Carbon-derived superwetting porous absorbents for hydrocarbons-water separation

3. CHAPTER 3

4.

HYDROPHOBIC AND OLEOPHILIC LAURIC ACID GRAFTED CARBON NANOTUBES FOR EFFICIENT AND RECYCLABLE ABSORPTION

3.1 Introduction

Nowadays, hydrocarbons/water separation has been a global plight as a result of the alarming rise in the discharge of industrial wastewater as well as frequent accidental pollutants. The world experienced a number catastrophes, which culminated in huge contamination of different water bodies such as seas, oceans, rivers and lakes [2], [124-125]. For example, the disaster which occurred in the Gulf of Mexico in the year 2010- one of the greatest incidents in the history [126]. The enormous amount of water contaminated with hydrocarbons is not only detrimental to the aquatic ecosystem and marine environment but also has a deleterious effect on the human health [127]. Besides, hydrocarbons and organic contaminants are potentially hazardous due to their high flammability and may eventually cause fire or explosion [4]. Compelled by environmental and economic considerations, retrieval of hydrocarbons from wastewater is very crucial, and up-to-date technologies for hydrocarbons/water separation are pressingly required [128-129]. Several conventional methods such as controlled burning [5], bioremediation [6], use of electric field [7], collection by mechanical means [8], use of chemical dispersants [9] and absorbent materials [11],[130], have been broadly employed to deal with the hydrocarbons and chemical pollutants. Most of the traditional treatment techniques suffer from various drawbacks, including low separation efficiency, poor selectivity, high toxicity, lesser recyclability, high operational cost, and the introduction of secondary pollutants [12]. Hence, it is compelling, although also challenging, to fabricate highly efficient absorbent materials having low cost, high selectivity, high absorption capacity and high efficiency. Among the existing technologies, the use of absorbent materials appears to be the commonly employed technique for water remediation due to its ease of practical applications, low cost, availability and eco-friendliness of the remediation process [20]. Ideal absorbent materials should have high specific surface area, high absorption capacity, suitable pore

size, low density, good selectivity, and excellent recyclability [21]. The hydrophobic and oleophilic properties of the absorbent materials are also extraordinarily crucial features since these materials should selectively absorb the hydrocarbons on their surface and at the same time reject the water [22].

Till now, the fabrication of absorbents with remarkable hydrocarbons sorption properties is a huge challenge for researchers. Sorbents from carbon-based materials are drawing the attention of scientists for application in hydrocarbons/water separation due to their unique properties [34]. Activated carbon, carbon nanotubes, carbon nanofibres, carbon aerogels, porous carbon nanoparticles, carbon coatings, and graphene sponges have been widely explored in remediation, hydrocarbons/water separation, water filtration, gas purification and separation [35-37]. Compared to the foregoing conventional sorbents, carbon nanotubes have been exhibited to have potential application in the area of hydrocarbons-water separation owing to their robust mechanical properties, high absorption capacity, high surface area, quick absorption rates and well-established surface chemistry tuning [116-117]. A few studies have included CNTs for application in hydrocarbons-water separation. For example, Al-Jammal *et al.* prepared modified CNTs sorbent by microemulsion method. The microemulsified CNTs attained absorption capacities of 2.48 to 6.07 times own weight for the removal of hydrocarbons water surface [118]. Sun *et al.* demonstrated the functionalization of CNTs with *p*-phenylenediamine (P-CNTs) by diazotization method for hydrocarbons sorption. The P-CNTs show maximum absorption capacity of 3-12 times own weight for hydrocarbons and organic solvents [119]. Gao *et al.* fabricated CNT-coated sponges with exceptional performances for hydrocarbons-water separation. The CNT coating improved the selectivity of the sponges to absorb only hydrocarbons while rejecting water

completely. The spongy CNT absorbents exhibited high absorption capacity and the absorbed hydrocarbons could be retrieved by mechanical squeezing [120].

Modification of CNTs surfaces was visualized by many researchers to improve their chemical feature and this can be achieved either by covalent or non-covalent functionalization or by creation of defects. Chemical functionalization of CNTs brings about the attachment of chemical functionalities like hydroxyl, carboxyl and amino groups to the sp^2 hybridized carbon frame-work. The anchoring of other chemical molecules to the CNTs surface is made possible via covalent attachment to these groups in order to achieve desirable properties.

Herein, we report for the first time a facile approach for fabricating low cost, hydrophobic and oleophilic MWCNTs-LA nanocomposites as highly efficient absorbents for retrieval of hydrocarbons from water. The MWCNTs-LA absorbents were prepared by hydroxylation of MWCNTs and subsequent esterification of the hydroxylated MWCNTs with LA. Different techniques were used to evaluate the morphology and surface features of the absorbent materials. The wetting behaviours of the MWCNTs-LA composites were measured to justify the hydrophobic and oleophilic properties. The absorption of compounds and hydrocarbons–water mixture separation properties of the prepared materials were systematically evaluated.

3.2 Experimental section

3.2.1 Chemicals and Materials.

The chemicals and the reagents purchased were analytical grades and used as received without any further purification. The MWCNTs was commercially procured from Fluka AG, Chemische Fabrik, Buchs (Switzerland). Lauric Acid (LA) was purchased from Merck Schuchardt OHG (Germany). Dimethylformamide (DMF), Tetrahydrofuran (THF),

hexane, decane, dodecane, hexadecane, and ethanol were supplied by Sigma-Aldrich Co. (USA). H_2SO_4 , HCl , NaOH , diesel, colouring agents were obtained from local market and used as received.

3.2.2 Preparation of Hydroxylated MWCNTs

1.5g of MWCNTs and 6M HCl were introduced into a round-bottom flask. The mixture was sonicated for 0.5h and then refluxed at 95°C for 24h. The resulting suspension was filtered; the precipitate was thoroughly washed with DI water to achieve a pH of about 7 and dried overnight at 70°C . Afterward, 0.45g of the dried solid was added to 60mL of newly distilled THF in a round-bottom flask which had been purged with dry nitrogen to eliminate oxygen. Then, NaOH solution (containing 1.2g of NaOH dissolved in 60mL of DI water) was added to the MWCNTs/ THF suspension and stirred for 24h at ambient temperature. After the completion of the reaction, the resulting mixture was poured into 500mL of DI water under continuous stirring and filtered. The black precipitate was then washed with ethanol and DI water for at least three times. The hydroxylated MWCNTs were dried in vacuum oven at 70°C for 1 day and the product is denoted as MWCNTs-OH.

3.2.3 Synthesis of Various Hydrophobic MWCNTs Grafted LA Absorbents

In the typical synthesis of the MWCNTs-LA composite, MWCNTs-OH was dispersed by sonication in DMF. Thereafter, LA was added to the dispersed MWCNTs-OH and sonicated for 0.5h. Afterward, about 1mL of concentrated H_2SO_4 was added to the mixture and then kept under reflux with continuous stirring at 90°C for 6h. Then, resulting composites were placed in oven and dried at 70°C for 3h. The MWCNTs attached to the LA via ester linkage formed by the

esterification reaction between the -COOH groups on the LA chains and the -OH groups incorporated on the MWCNTs surface in the previously described step. To check the effect of LA, three different composites were prepared with varying amounts of LA to give the MWCNTs: LA ratios of MWCNTs-LA1 (1:5), MWCNTs-LA2 (1:10) and MWCNTs-LA3 (1:20). This method helps to produce composites with excellent hydrophobicity. The MWCNTs-LA 2 composite with ratio 1:10 provides best chemical interaction between the MWCNTs and LA. Figure 1 shows the experimental steps for the synthesis of CNTs-LA composite.

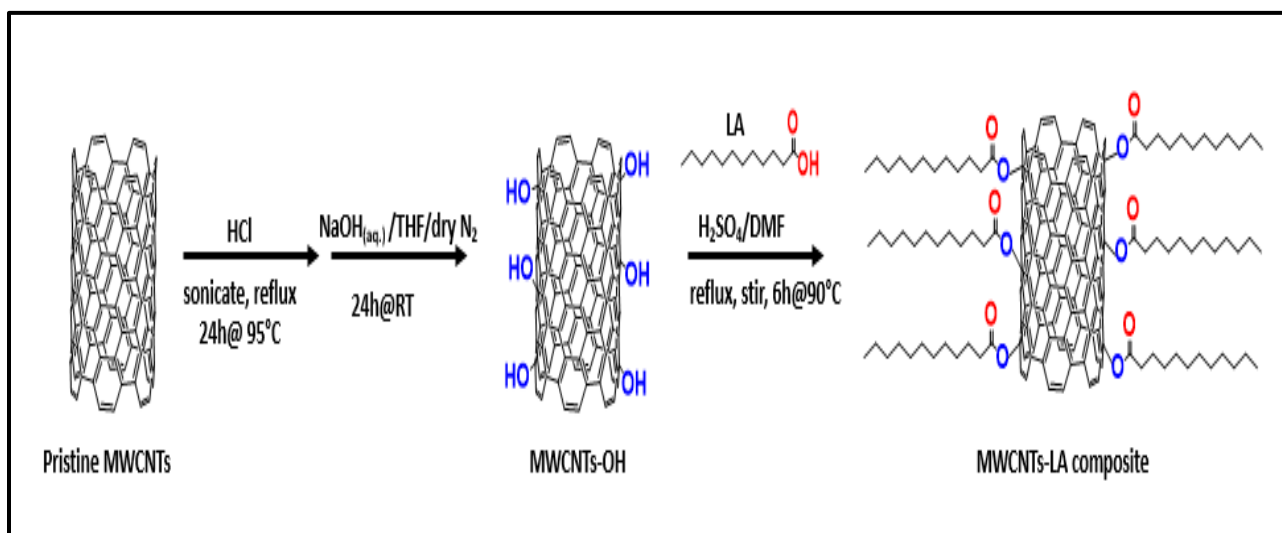


Figure 3.1: Schematic representation of the synthesis of MWCNTs-LA composites.

3.2.4 Measurements and Characterization

The FTIR spectra of the samples were measured using Thermo Scientific Nicolet iS10 FTIR spectrophotometer and the spectra were recorded in the range of 4000-500 cm^{-1} . The Raman spectra were obtained using Horiba Scientific LabRAM HR Evolution Confocal Raman Microscope. The microstructures and surface morphologies of the prepared materials were studied by Field Emission Scanning Electron Microscope (SEM) (JSM-6610LV, Scanning Electron Microscope, JEOL) at 20 kV acceleration voltage. The surface hydrophobicity of the samples was investigated using Biolin Scientific Attension Theta Flex. The WCAs of various samples were measured immediately after the deposition of distilled water on the substrate. The volume of water droplet used was 5 μL and five separate measurements were carried out on the surface of each sample at least. The XRD spectra were recorded by an XRD machine (Rigaku Ultima IV, Kuraray Co. Ltd. Japan).

3.2.5 Absorption Experiment

The model hydrocarbons samples were poured into the beaker and the preweighed absorbent material was dipped in the hydrocarbons samples to be completely absorbed. Once the saturated absorbent material was taken out of the beaker, its weight was immediately measured and recorded. Lastly, the saturated absorbent was repetitively squeezed to expel most of the hydrocarbons absorbed. The mean value of each of the sample tested for at least three trials was recorded. The absorption capacity of the absorbent materials (Q) for different hydrocarbons were calculated using the equation below:

$$\text{Absorption capacity} = \frac{m_c - m}{m} \quad (1)$$

where m_c is the absorbent weight after immersion in hydrocarbons in g, and m is the weight of the dry absorbent in g.

3.2.6 Hydrocarbons-Water Separation Test.

The absorbent sample was placed into the mixture of water and various types of hydrocarbons (or other organic solvents) for absorption until saturation with the liquid. The absorbent material was taken out of the by means of tweezers, drained for a while and then squeezed to expel hydrocarbons (or other organic solvents). The separation efficiency of the absorbent is calculated using the equation:

$$\text{Separation efficiency (\%)} = \frac{m_r}{m_0} \times 100 \quad (2)$$

where m_r is the weight of the retrieved hydrocarbons (or organic solvent) while m_0 is the original weight of the hydrocarbons sample in the mixture.

3.2.7 Reusability Test.

The reusability of the prepared absorbent materials was assessed by squeezing mechanically. In the first place, the weight of the dried absorbent was taken and recorded. Thereafter, the absorbent was placed in the sample hydrocarbons until it was saturated with the hydrocarbons and the weight of the absorbent was again measured. The absorbed hydrocarbons was expelled by hand squeezing. Then, the weight of the absorbent was again taken and noted. A total of 5 sorption–desorption tests were carried out to evaluate the reusability of the prepared sorbent material.

3.3 Results and Discussion

3.3.1 Structure Analysis of MWCNTs-LA Composites.

The synthesis of CNTs-LA composites is schematically shown in Figure 3.1. The neat CNTs were first dispersed in concentrated hydrochloric acid solution and subsequently treated with

sodium hydroxide solution to anchor hydroxyl groups on the surface of the tubes. The carboxylic acid groups on the LA chains chemically react with the hydroxyl groups on the tube's surface via esterification reaction, thereby conferring hydrophobic properties to MWCNTs with their 12-carbon long hydrocarbon chain. The MWCNTs-LA composites with hydrophobic-oleophilic surface become a major consideration to ensure that the as-synthesized composites achieve hydrocarbons sorption while rejecting water.

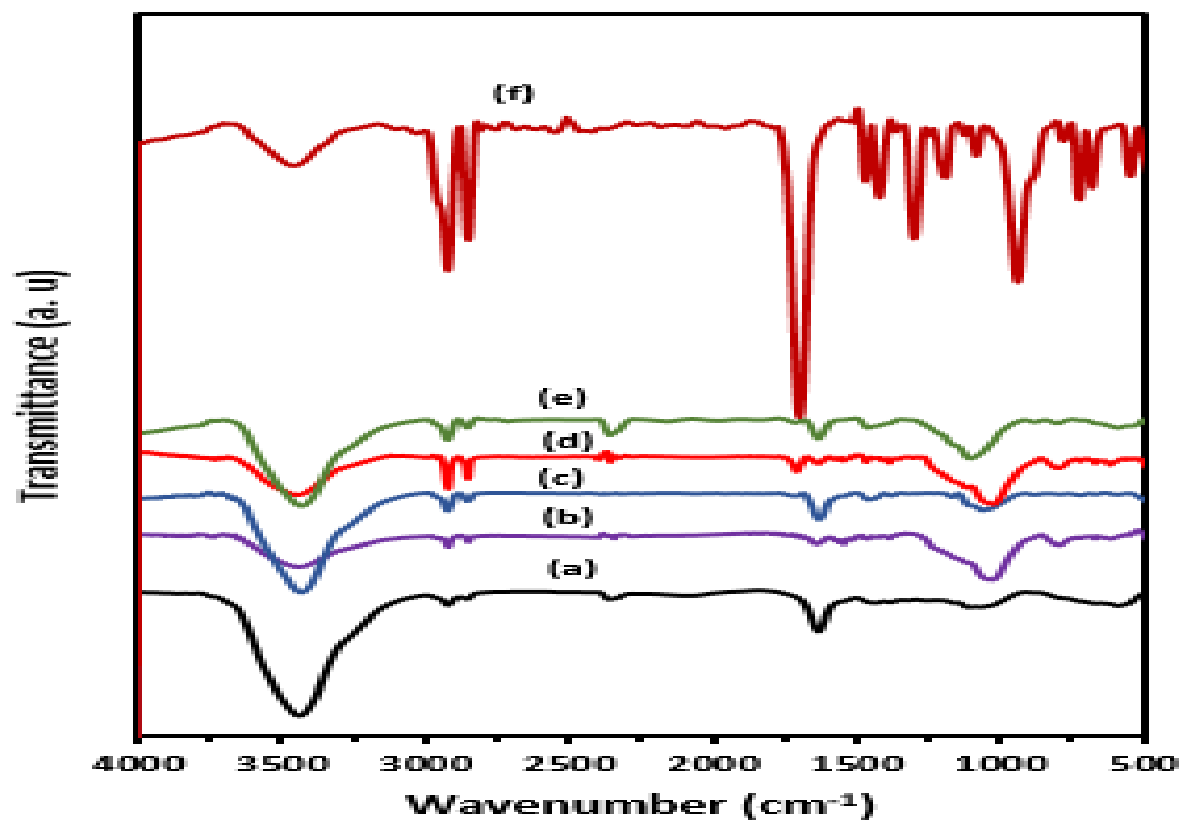


Figure 3.2 : FTIR spectra of (a) pristine MWCNTs, (b) MWCNTs-OH, (c) MWCNTs-LA 1, (d) MWCNTs-LA 2 , (e) MWCNTs-LA 3 and (f) pure LA.

In order to establish qualitatively the chemical grafting of the LA chains onto the pristine CNTs surface, FTIR measurement was employed. The FTIR results of neat MWCNTs, pure LA, MWCNTs-OH, and MWCNTs-LA composites are shown in Figure 3.2. The intensities of the groups introduced onto the surface of CNTs are somewhat weaker as a result of the low concentrations of these groups as well as the high absorbance of the pristine MWCNTs backbone. For the pristine CNTs, the broad band at 3435cm^{-1} shows O-H absorption vibration from oxygenated groups remaining after acid treatment for the enhancement of purity of CNTs, the peaks at 2916 and 2854cm^{-1} show the existence of CH_3 and CH_2 mainly emanated from the defect of pure CNTs, and the peak around 1625 cm^{-1} represents the extending vibrations of $\text{C}=\text{C}$ in aromatic ring [131-132]. For MWCNTs-OH, the peaks at 3444 , 1386 , and 1020cm^{-1} respectively indicate the O-H absorption, C-OH bending and C-O stretching vibrations [133]. In the LA spectra, the FTIR peaks around 3446 and 1699cm^{-1} are assigned respectively to the O-H and $\text{C}=\text{O}$ extending vibrations, which together indicate the carboxylic acid groups. Also, the two sharp peaks at 2922 and 2852 cm^{-1} can be ascribed respectively to the tensile vibration of the aliphatic CH_3 and CH_2 groups on the LA chains, the peaks in the range $1300\text{-}1070\text{cm}^{-1}$ are due to C-O stretching absorptions and a broad peak of moderate intensity centered at 941cm^{-1} is ascribed to out-of-plane O-H bending vibration. For the composites, there are formations of new peaks or shifts of some peaks, showing that there is chemical reaction between hydroxylated CNTs and LA. A new peak around 1720 cm^{-1} ($\text{C}=\text{O}$ stretch of ester) is noticed in the three composites after LA grafting, whereas the peaks at 1699 , $1300\text{-}1000$ and 941cm^{-1} disappeared due to the esterification reaction between the –

COOH group of LA and O-H groups of the hydroxylated CNTs. In addition, the grafting of LA is further confirmed by the significant pronounced peaks at 2920 and 2850 cm^{-1} (C-H extending vibration). The results above show the successful incorporation of LA chains to the surface of CNTs.

Raman measurement was carried to further assess integrity of the pristine MWCNTs and the prepared composites because the Raman spectroscopy is responsive to slight change of structural disorder in CNTs. The synthesis of the functionalized MWCNTs absorbents employed in this work includes some chemical reaction steps which are anticipated to confer more defects in the structure of the pristine MWCNTs. There are three prominent bands observable in the higher frequency region of the Raman spectrum of MWCNTs, such as the D band (1200–1400 cm^{-1}), the G band (1500-1600 cm^{-1}) and the 2D band (2500-2900 cm^{-1}) [134]. The disorder or D band is ascribed to the A_{1g} breathing modes of the sp^3 carbon atoms indicating structural defects in CNTs, the graphite or G band emanates from the first order scattering of the E_{2g} mode for sp^2 carbon domains and can be related to the graphite structure, while the 2D band is a second overtone of the disorder induced D band and it is known to be responsive to the increasing disorder density of CNTs [135]. Figure 3.3 displays the Raman spectra of the pristine and functionalized MWCNTs. The existence of the D and G bands in all the functionalized samples indicate the conservation of the graphitic structure. The ratio of intensities of the D and G bands (I_D / I_G), can be used to assess defect density in the structure of the CNTs. Higher value I_D / I_G ratio indicates the breaking of the sp^2 bonds and forming of the new sp^3 bonds and therefore greater defect density. The I_D / I_G ratio of MWCNTs is 0.75 while the I_D / I_G ratios of MWCNTs-OH, MWCNTs-LA1, CNTs-LA 2 and CNTs-LA 3 are 1.20, 1.36, 1.42 and 1.3 respectively. As evident in Figure 3.3, the I_D / I_G values for the

modified CNTs are greater than that of the pristine CNTs, the highest ratio being noticed for the CNTs-LA-2. The results reveal that the integrity of CNTs-LA 2 is the least meaning that the organic groups covalently attached on the surface of CNTs-LA-2 are the most. The fractional increase in the ratio of I_D / I_G for the functionalized MWCNTs is anticipated as chemical functionalization of MWCNTs leads to the breaking some bonds and making of others by inserting some chemical groups and this can be explained as defects on the structure.

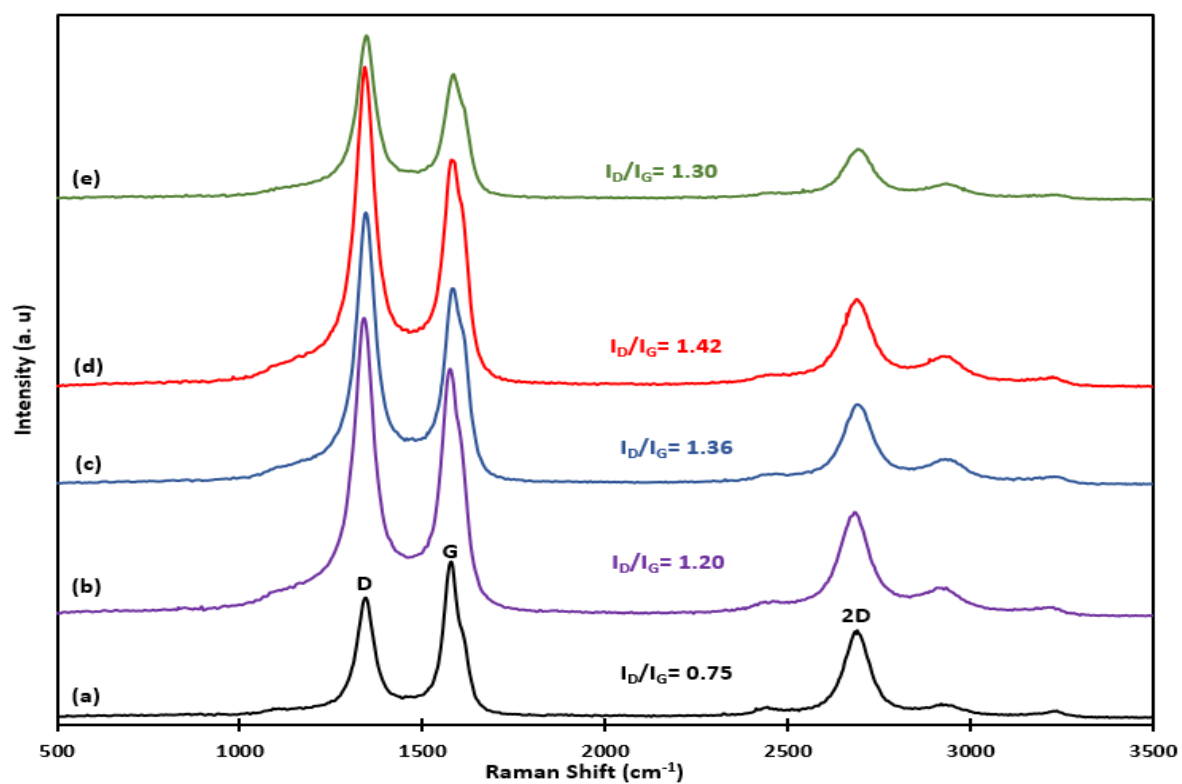


Figure 3.3: Raman spectra of (a) pristine MWCNTs, (b) MWCNTs-OH, (c) MWCNTs-LA 1, (d) MWCNTs-LA 2 and (e) MWCNTs-LA 3.

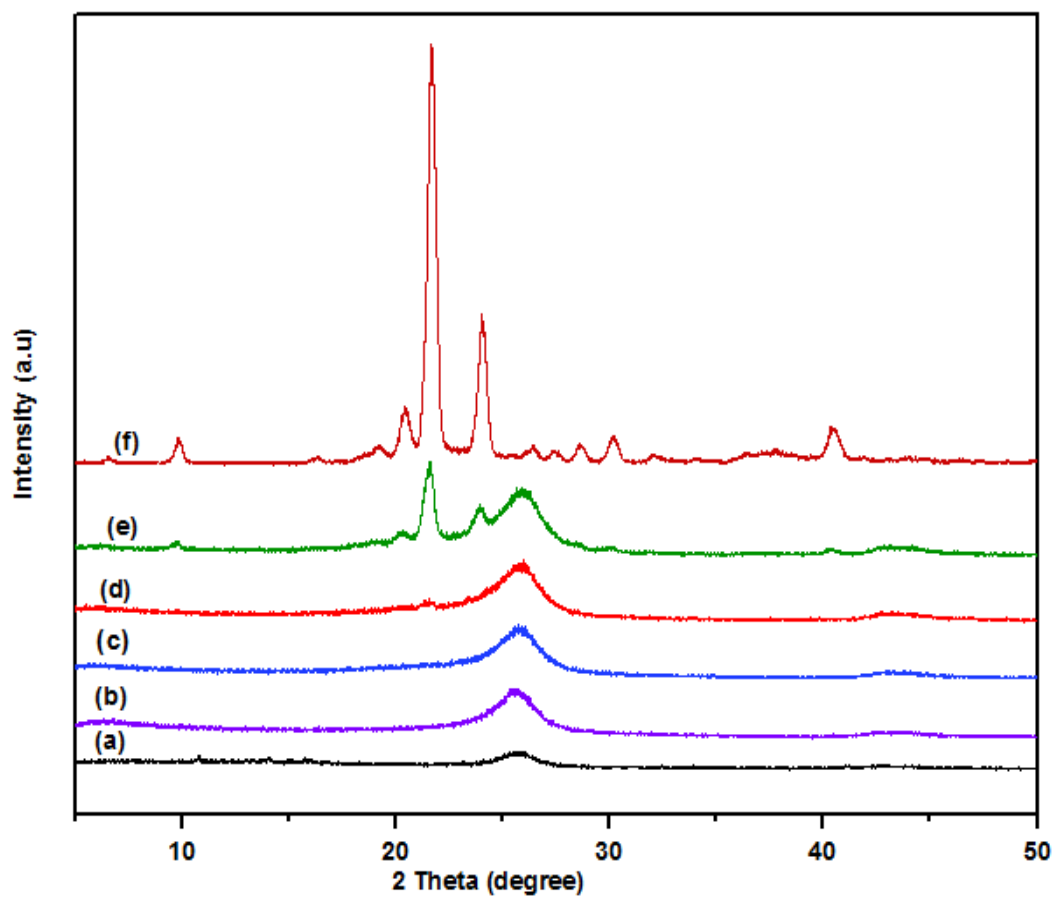


Figure 3.4: XRD Patterns of (a) pristine MWCNTs, (b) MWCNTs-OH, (c) MWCNTs-LA 1, (d) MWCNTs-LA 2, (e) MWCNTs-LA 3 and (f) pure LA.

The crystal structures of the pristine MWCNTs, neat LA and the functionalized MWCNTs were investigated by XRD. As evident from Figure 3.4 (a) and (b), pure CNTs shows two distinctive diffraction peaks ($2\theta = 26.1^\circ$ and $2\theta = 43.5^\circ$) relating to the hexagonal graphite structure with corresponding (002) and (001) lattice planes respectively. Pure LA shows two main characteristic peaks ($2\theta = 22.6^\circ$ and $2\theta = 24.9^\circ$) which correspond respectively to the lattice planes of (002) and (100) [136]. The pristine MWCNTs and the functionalized MWCNTs show somewhat similar XRD patterns, implying the retention of the identical tubular structures by the composites when compared with the as received CNTs. Therefore, the chemical functionalization does not have a pronounced effect on the CNTs tube-like structure. However, there is gradual surfacing of peaks attributive of the grafted LA in the composites which increase in intensities for higher LA concentrations. Moreover, the diffraction change in position of peaks around 22.6° and 24.9° due LA grafting in MWCNTs is not too obvious indicating that the finite space in the pristine MWCNTs does not alter the crystal structure of LA.

3.3.2 Surface Morphology

The effects of surface roughness and surface energy on the wettability characteristics of MWCNTs were established by contact angle measurements, which are presented in Figure 3.5. The different surfaces were evaluated for hydrophobicity by measuring their various water contact angles (WCAs). After five measurements at separate points on the surface each sample, the WCA was shown to have a mean value of $5.54 \pm 1.26^\circ$ on the MWCNTs (see fig 5a) while MWCNTs-LA1, MWCNTs-LA2 and MWCNTs-LA 3 composites exhibit average WCAs of $141.02 \pm 1.46^\circ$, $145.26 \pm 1.57^\circ$ and $140.08 \pm 1.75^\circ$ respectively (as shown in fig 5b-c). The raw MWCNTs displays a very low WCA due to the existence of the hydrophilic oxygenated groups on its surface, whereas the WCAs of all the three composites reach mean values of at least 140° with MWCNTs-LA 2

exhibiting the highest WCA as presented in Figure 3.6. The long alkyl LA chains causes impairment in the water permeability of the pristine MWCNTs and thus higher WCAs of the MWCNT-LA nanocomposites. Hence, chemical grafting of the MWCNTs with a low surface energy LA successfully switches its surface hydrophilicity to hydrophobicity, which is more desirable for application in hydrocarbons/water separation.

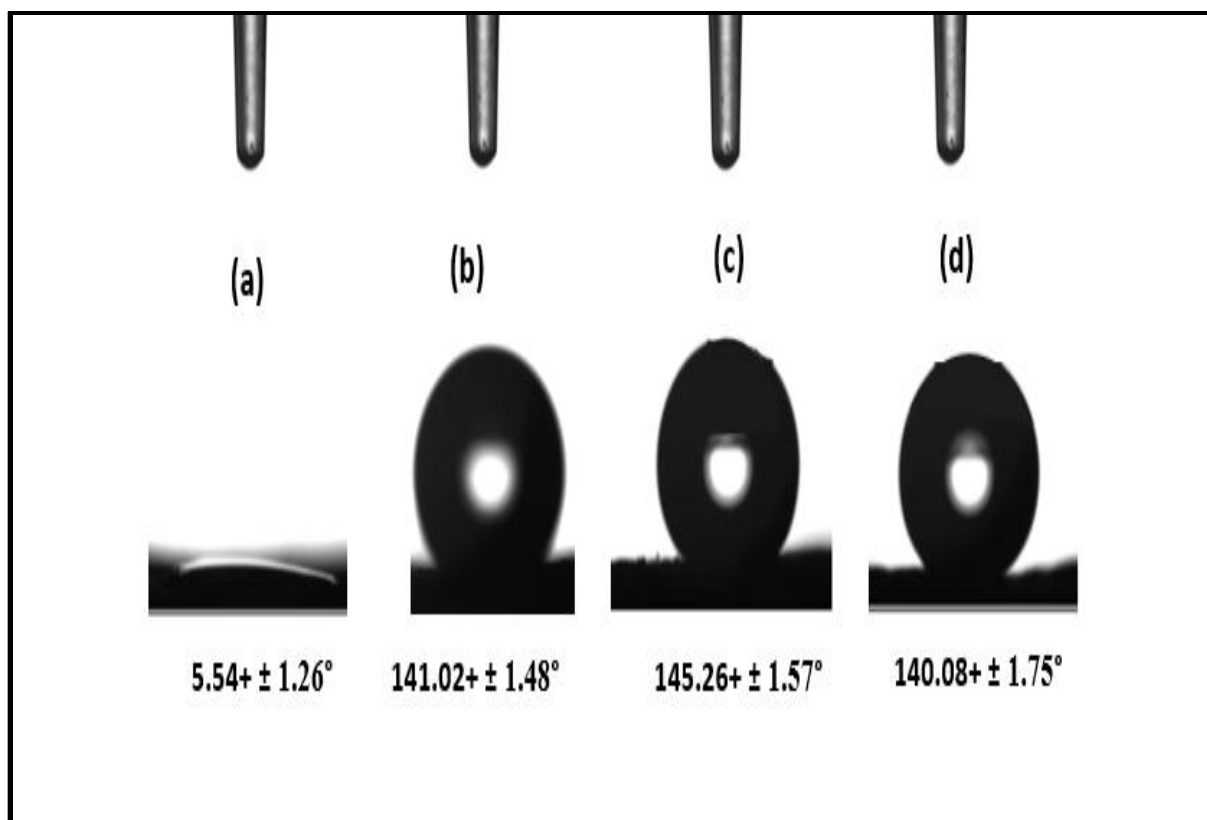


Figure 3.5: Water contact angle measurements for (a) neat MWCNTs, (b) MWCNTs-LA1, (c) MWCNTs-LA 2 and (d) MWCNTs-LA 3.

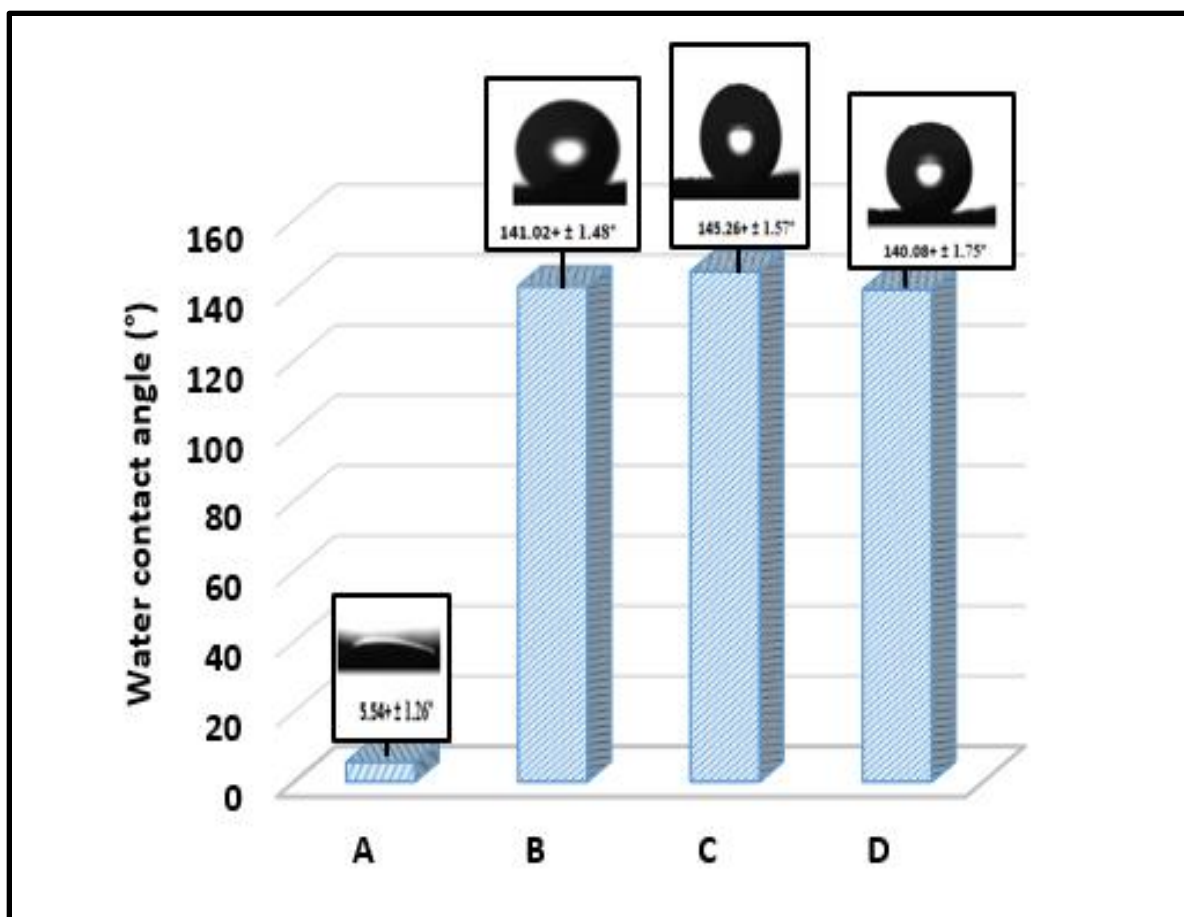


Figure 3.6: Water contact angles for the different absorbents: A- neat MWCNTs, B- MWCNTs-LA1, C-MWCNTs-LA 2 and D- MWCNTs-LA 3.

3.3.3 Absorption Performance of the as prepared MWCNTs-LA Absorbents

A simple batch experiment was done out at ambient temperature to determine quantitatively the hydrocarbons absorption performance of the three MWCNTs-LA absorbents. In typical absorption capacity measurements, hexane, decane, dodecane and hexadecane were selected as absorbing targets. In this test, the absorbents were placed in a beaker containing model hydrocarbons to be absorbed. Each absorbent was introduced into 10 mL of the test hydrocarbons sample and forced in the liquid for maximum hydrocarbons absorption. The absorbents were then taken out and manually squeezed with the aid of a quick-grip clamp. The results of the absorption capacities of all the functionalized MWCNTs absorbents in the diesel and in the organic liquid media are presented in Figure 3.7. The absorption capacity is greatly dependent on the absorbent's porosity. More porous structures will afford a higher liquid absorption. Therefore, absorbents with greater hydrophobicity will absorb hydrocarbons more readily and retrieve hydrocarbons from water more efficiently. Hence, MWCNTs-LA2 displayed best absorption capacity of all the three composite absorbents with the k value (from 24.0 to 33.5 times its own weight) for various model hydrocarbons tested. Earlier reports from the literature also revealed the k value of an absorbent material could be correlated with the hydrocarbons viscosity, density and surface tension [137]. In the course of absorption, the liquid hydrocarbons or the hydrocarbons percolated the pores of the 3D network of the MWCNTs-LA. The density of the percolated hydrocarbons determined the k value of the absorbent when its porosity was saturated by the hydrocarbons. Significantly, the MWCNTs-LA2 showed greater absorption capacity than many CNTs based sorbents in previous reports as presented in Table 1. The simple, cheap and easily large scale preparation technique make MWCNTs-LA absorbent a promising candidate to be used as a sorbent for hydrocarbons spill remediation and organic pollutants.

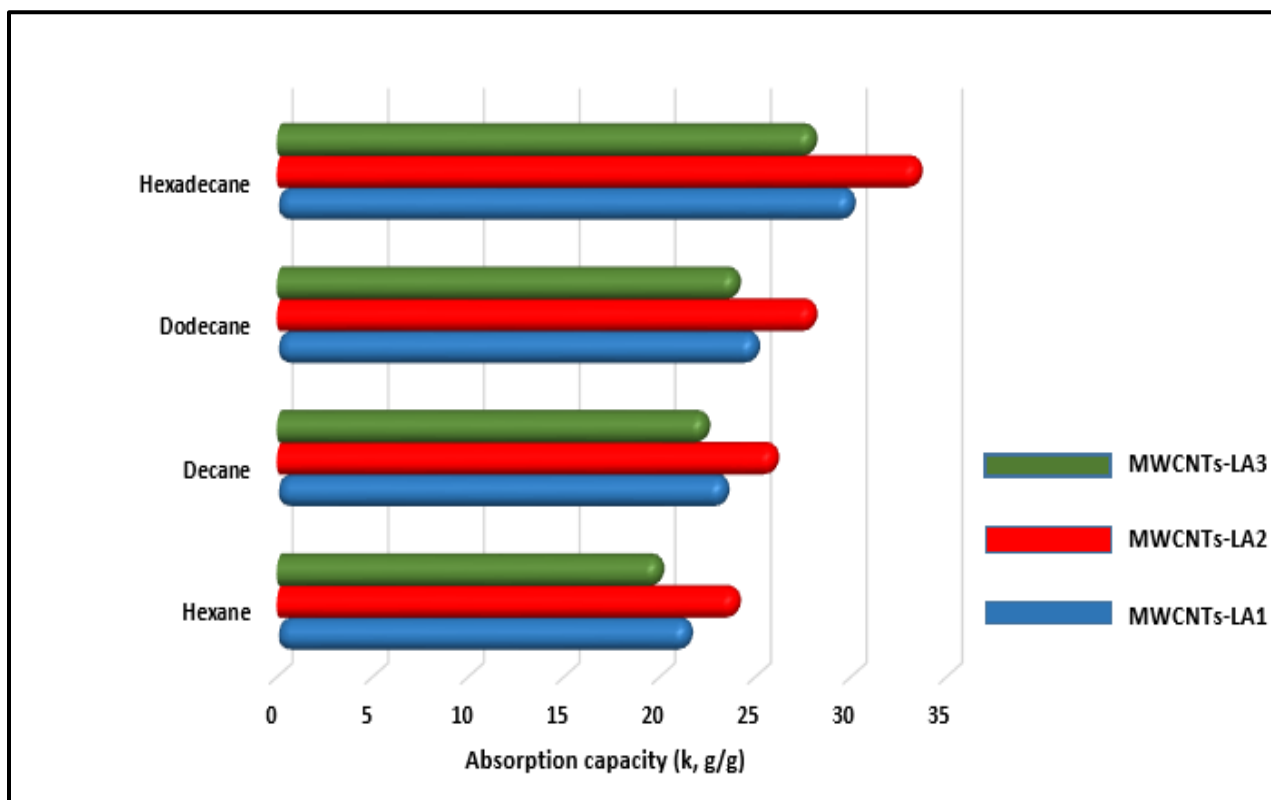


Figure 3.7: k values of the three MWCNTs-LA absorbents for various model hydrocarbons samples

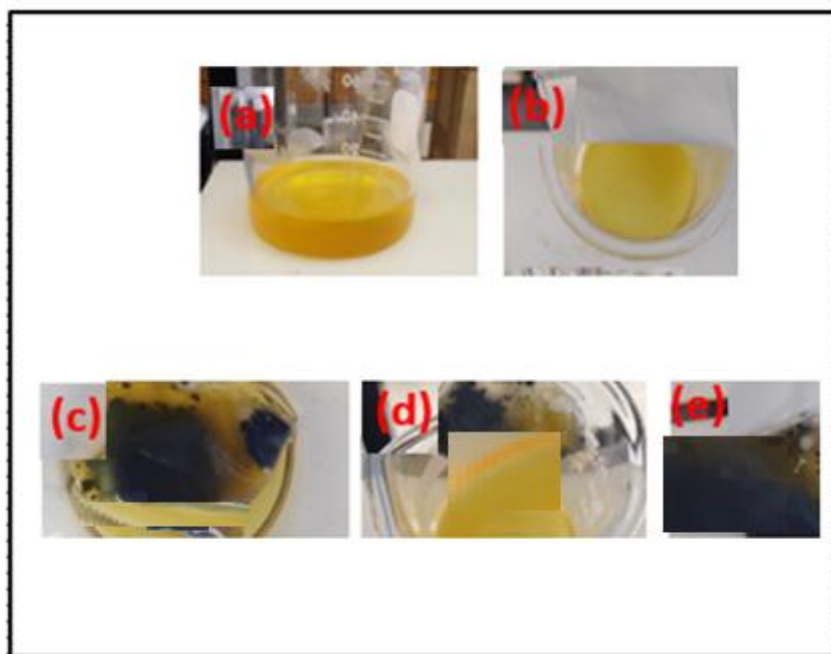


Figure 3.8: Photographs of absorption of hexadecane (coloured with dye) by MWCNTs-LA2 absorbent.

3.3.4 Hydrocarbons water separation and Reusability Performance of MWCNTs-LA2

The MWCNTs-LA2 absorbent showed high repulsion for water from the hydrocarbons or liquid hydrocarbons efficiently due its hydrophobic characteristics. To demonstrate its potential for application as sorbent for hydrocarbons spill cleanup, an hydrocarbons-water selective absorption test was important. As displayed in Figure 3.9, when a filter bag containing a desired amount of MWCNTs-LA2 was introduced to the surface of hexadecane/ water mixture, the hydrocarbons sample on the surface of water was swiftly absorbed into the 3D network pores of MWCNTs-LA2 and was wholly removed by the absorbent within a short period of time. For a clear visual observation, the hexadecane and water were respectively coloured with Sudan I and methylene blue. After the separation, no trace of red hydrocarbons was seen in the water by visual inspection, thereby showing high separation ability. Similar experiment was conducted for the separation of other hydrocarbons sample from water using MWCNTs-LA2 and the separation efficiency obtained is presented in Figure 3.10. The separation efficiency of MWCNTs-LA2 for all the tested sample hydrocarbons was from 97% in hexane up to 99% in hexadecane.

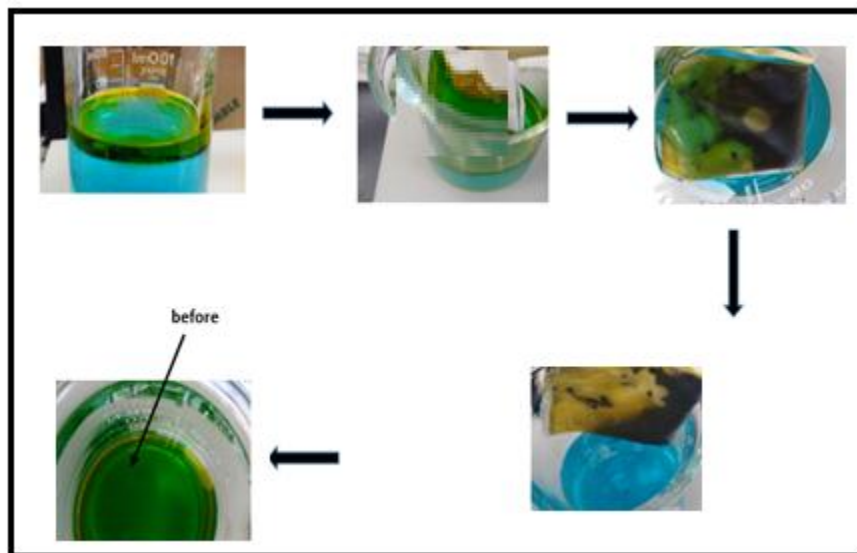


Figure 3.9: Pictures showing the process of selective absorption of hexadecane on the water surface (hydrocarbons dyed with Sudan I dye and water coloured methylene blue dye) by MWCNTs-LA2.

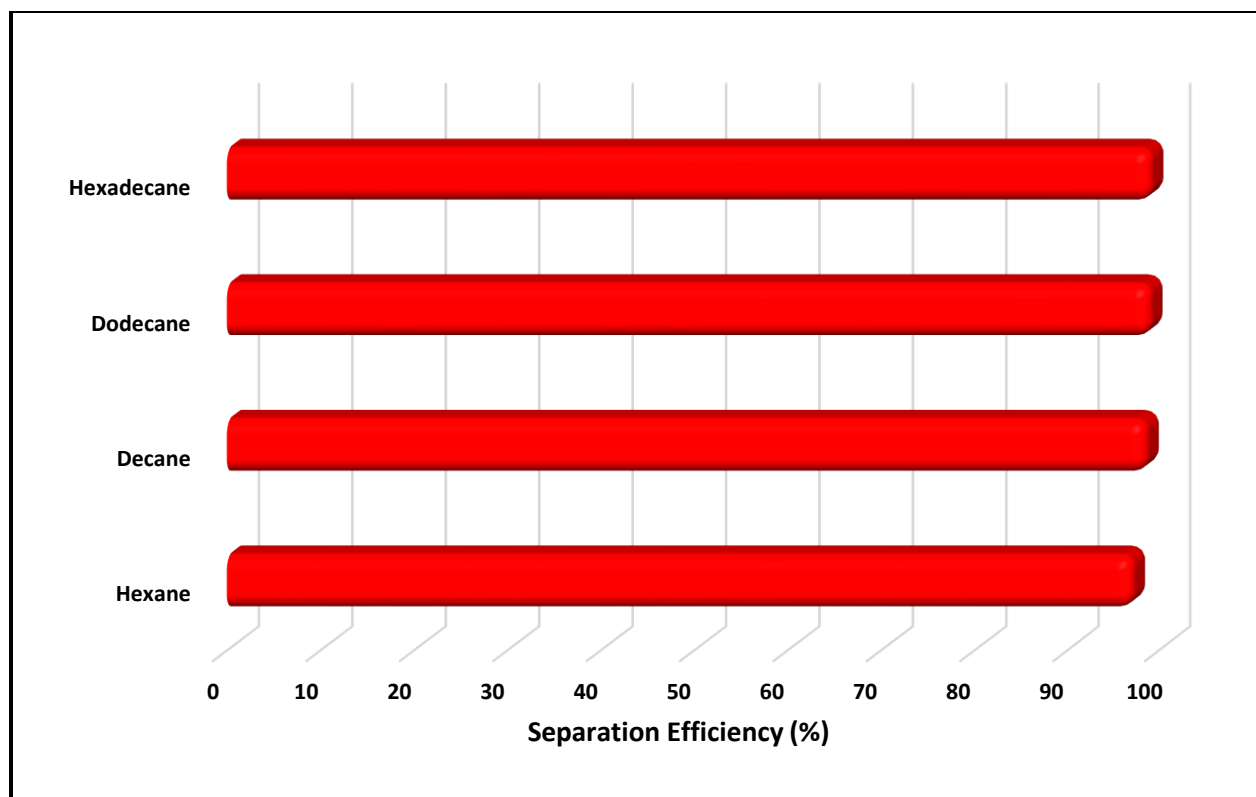


Figure 3.10: The separation efficiency of the MWCNTs-LA absorbent for different types of hydrocarbons/water mixture.

The oleophilic-hydrophobic feature of the as-prepared MWCNTs-LA2 can be noticed from these images. Together with outstanding hydrocarbons selectivity, MWCNTs-LA2 exhibits a huge promising application for highly efficient hydrocarbons or organic solvent collection.

From the application perspective, absorbent's reusability is another key prerequisite for hydrocarbons-spill cleanup. To evaluate this, absorption-desorption tests was carried out on the MWCNTs-LA2 absorbent for at least 5 cycles and the outcomes are shown in Figure 3.11. The hydrocarbons-laden absorbent was desorbed by squeezing. The reusability experiment revealed a very stable absorption capacity of MWCNTs-LA2 absorbent in which the absorption capacity of over 90% was sustained for at least 5 cycles of absorption-desorption experiments.

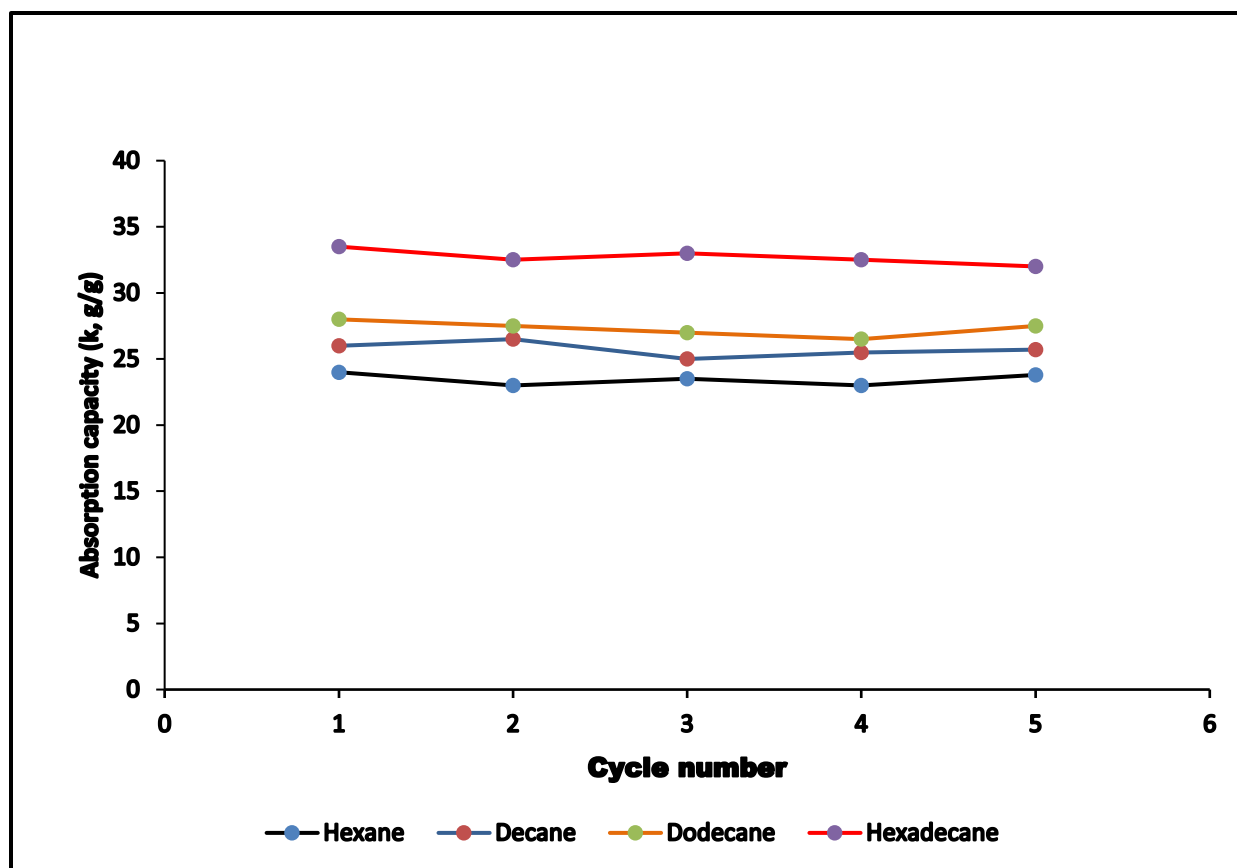


Figure 3.11: Absorption capacity of MWCNTs-LA for 5 cycles of hydrocarbons-water separation.

absorbent material	saturated absorption capacity (g/g)	ref.
CNT/PVDF composite	3.3-7.8	[39]
PC/cMWCNTs monolith	8.1 – 12.6	[40]
CNTs/ <i>p</i> -phenylenediamine	3-12	[27]
CNTs coated sponges	22-35	[28]
MWCNTs-LA composite	20-33.5	this work

Table 3.1 Absorption capacity comparison of various absorbent materials

5.

6.

7. CHAPTER 4

HYDROPHOBIC AND OLEOPHILIC AMINE FUNCTIONALIZED GRAPHENE OXIDE NANOCOMPOSITE FOR EFFICIENT HYDROCARBONS AND ORGANIC SOLVENT RECOVERY.

4.1 Introduction

Water pollution originating from hydrocarbons spills, chemical leakages and organic solvents frequently used in the syntheses of chemicals and pharmaceuticals have generated serious ecological concerns around the globe[1], [138-139]. Hence, to combat this pollution plight, it is crucial to design an economical, efficient and fast clean-up methodology for the recovery of the hydrocarbons and organic pollutants from water. Several methods such as controlled burning [5], bioremediation [6], collection by mechanical means [8], use of chemical dispersants [9] and absorbent materials [10-11] have been broadly employed to deal with the hydrocarbons and chemical pollutants. However, except for absorbent materials, those methods are either time-demanding, expensive or not environmentally friendly [140]. With fascinating attributes of buoyancy, porosity, lightweight, and/or elasticity, several absorbents, namely cellulosic materials [141], zeolites [142], silica aerogels [143], modified organophilic clays [144], exfoliated graphite [125], activated carbon [145] and graphene [22], have been extensively applied in the removal of hydrocarbons spills and organic contaminants in water. Yet, these widely used absorbents still suffer from some drawbacks like low absorption efficiency, poor selectivity, low recyclability or poor hydrophobicity [146]. Thus, collective efforts are crucially needed to fabricate perfect materials with remarkable selectivity, high absorption capacity, remarkable recyclability and high hydrophobicity that could efficiently retrieve hydrocarbons from water. Nowadays, a huge number of advanced materials, including versatile graphene frameworks, are gradually becoming ideal adsorbents owing to their unique properties [147]. Graphene is comprised of sp^2 -hybridized carbon atoms organised in a 2D honeycomb lattice [89]. It can be prepared by CVD [38], mechanical exfoliation of graphite, liquid-phase exfoliation [91], epitaxial growth, solvothermal synthesis [93] and the reduction GO. Of all these, the GO reduction seems to be the cheapest technique for

graphene synthesis. This involves graphite exfoliation into one-atom-thick sheets via oxidation, producing GO followed by its reduction into a graphene sheet by reducing agents such as sodium borohydride, hydrazine, vitamin C, hydroquinone etc. The reduced GO method relatively attains the highly desired graphene properties. Where the graphene is extensively oxidized, it is more appropriately referred to as graphene oxide. It is not feasible to use graphene as selective and efficient hydrocarbons absorbent in water because of its somewhat low hydrophobicity. However, the graphene surface can be improved to obtain a good hydrophobicity as displayed with silane and other polymeric materials [42].

In this study, we report an approach for fabricating efficient, low cost, highly hydrophobic graphene oxide based absorbents functionalized with alkylamines for hydrocarbons and organic solvent recovery. The modified Hummer's method was used to prepare GO via graphite flakes chemical oxidation. The as-synthesised GO was thus functionalized with three alkylamines by amidation reaction followed by chemical reduction. The prepared absorbents were characterized using several characterization techniques, whereas some selected organic solvents and hydrocarbons samples were used to assess the sorption capacity of the prepared absorbents.

4.2 Experimental Section

4.2.1 Materials and Chemicals

The natural graphite powder (99.9%) was commercially purchased from Fluka AG, Chemische Fabrik, Buchs (Switzerland). Sulphuric acid (98%), hydrochloric acid (35%), sodium nitrate (98%), hydrogen peroxide (30%), hydrazine hydrate (80%), and potassium permanganate (99%) were obtained from Sigma-Aldrich Co. (USA) and were used as received. Hexylamine (HA) and dodecyl amine (DDA) were purchased from Merck Schuchardt OHG (Germany) and were used as

received. Cyclohexane, n-hexane, n-decane, n-heptane, absolute ethanol (99.8%) were supplied Sigma-Aldrich Co. (USA) and used as received. Engine hydrocarbons (obtained from Gulf Start Factory for Petroleum Industries Co. Saudi Arabia) was used as absorbate. Deionised water (DI) was used throughout the research.

4.2.2 GO Synthesis

GO nanosheets were produced by modified Hummer's method described by Paulchamy *et al.* [148]. Succinctly, graphite powder (2 g) and sodium nitrate (2 g) were added to 90ml of concentrated sulphuric acid (98%) in an ice bath (0-5°C) with constant stirring. After 4hrs of stirring the mixture at this temperature, potassium permanganate (12 g) was slowly added to the suspension with care keeping the temperature below 15°C. Afterward, 184ml of water was slowly added to dilute the mixture and stirred continuously for 2 hrs. The mixture was then stirred for 2 hrs at 35°C after removing the ice bath. The above mixture was refluxed for 10-15 min at 98°C. After 10 min, the temperature was changed to 30°C which gave a brown coloured solution. The solution was eventually treated with 40 ml hydrogen peroxide by which the colour changed to bright yellow. 200 ml of water was added and stirred for 1 hr. It was then kept without stirring for 3-4 hrs, where the particles settled at the bottom and left over water was poured to filter. The resulting mixture was washed many times by centrifugation (7000rpm for 15mins) with 10% HCl and then followed by DI water several times until it formed gel like material with pH of about 7, and the supernatant was decanted away. After centrifugation the gel like substance was dried in vacuum at 60°C for at least for 6 hrs to obtain GO powder.

4.2.3 Synthesis of Amine Functionalised GO

The as-synthesised GO powder was dispersed in DI water (500mg GO/100mL DI water), followed the sonication of the suspension for 1hr prior to subsequent surface modification. HA (about 1.2g) was dissolved in 200mL ethanol, and then the GO water suspension was introduced to the HA-ethanol solution. The mixture was stirred continuously for a day at room temperature [149]. For the functionalization experiments, the ratio of GO to alkylamines- $\text{CH}_3(\text{CH}_2)_{11}\text{NH}_2$ (DDA), $\text{CH}_3(\text{CH}_2)_5\text{NH}_2$ (HA) -was fixed at 500mg of GO to 0.01 mol of alkyl amine [150]. The reduction of DAH functionalized graphene oxide was done by adding 5mL hydrazine hydrate, and the mixture was refluxed for 3 h at 95°C. The final product was washed by filtration with ethanol-water mixture (1:1) to eliminate unreacted hydrazine hydrate or excess HA adsorbed on the surface of the functionalized graphene oxide (FGOHA). The black powder was dried under vacuum at 60 °C for at least a day. The resulting solid was vacuum dried at 60 °C for at least 24h to obtain FGOHA black powder. Similar synthesis procedure was used to obtain dodecylamine - (FGODDA)-grafted GO absorbents.

4.2.4 Characterizations

The FTIR spectra of the absorbents were obtained using Thermo Nicolet 6700 FT-IR spectrophotometer in the range of 400–4000 cm^{-1} . The Raman spectra were obtained using a Jobin Yvon Horiba LabRAM spectrometer from Raman shift of 700 to 2000 cm^{-1} . The contact angles of the various hydrophobic materials were measured using Biolin Scientific Attension Theta Flex. The XRD spectra were recorded by an XRD machine (Rigaku Ultima IV, Kuraray Co. Ltd. Japan).

4.2.5 Hydrocarbons Absorption test

The weight measurements before and after hydrocarbons absorption were used to assess the absorption capability of the prepared absorbents for an engine hydrocarbons and the selected organic solvents. The initial weight of the sample was taken and recorded as M_i . Then, the sample was dipped into the test hydrocarbons for absorption. The sample was weighed when, with the increase of absorption time, its weight was unchanged; this weight was recorded as M_t . The absorption capacity of materials (Q) for hydrocarbons and various organic solvents was determined by the equation below:

$$Q(g/g) = \frac{M_t - M_i}{M_i}$$

where M_t and M_i are the weights of the hydrocarbons absorbents dispersed in hydrocarbons or organic solvents for time t and the dry weight of the hydrocarbons absorbent, respectively. The separation efficiency of various absorbents was also assessed by measuring the weight percentage of the collected hydrocarbons or solvent in hydrocarbons-water or organic solvent-water mixture. Methylene blue dye was used to colour water layer in order to make it distinct from the organic layer.

4.3 Results and Discussion

4.3.1 Chemical Structure and Composition

The FTIR results of pristine GO, FGOHA, and FGODDA are shown in Figure 4.1. For the pristine GO, the broad absorption peak at 3426 cm^{-1} is attributed to the O–H extending vibrations which confirms the presence of hydroxyl and carboxyl functionalities on the hydrophilic surface of GO

and a small amount of adsorbed water molecules. This corroborates the fact that GO is a greatly absorptive material, as proven by its tendency to become a gel-like solution. The peak at 1720 cm^{-1} is assigned to the C=O extending vibrations in the carboxylic groups at the edges of the basal graphene GO planes. The GO also displays two intense peaks at 1224 and 1055 cm^{-1} that are respectively attributed to the C–O (alcohol) and C–O (epoxide) extending vibrations [151]. The peak at 1626 cm^{-1} corresponds to C=C bond which shows the retention of sp^2 hybridized carbon even after the oxidation of the graphite [148]. After the grafting of alkylamines, two new peaks which surfaced at 1640 cm^{-1} (amide C=O stretching) and 1463 cm^{-1} (amide C–N stretching) are observed, while the peaks at 1055 and 1720 cm^{-1} disappear, due to the nucleophilic substitution and the amidation reactions between –COOH/C–O–C groups of GO and –NH₂ group of the HA and DDA [152]. Moreover, the incorporation of the alkylamines is substantiated by the significant pronounced peaks at 2919 and 2848 cm^{-1} (C–H stretching) as well as the new CH₂ absorption peak at 720 cm^{-1} . In addition, the broad band at 3384 cm^{-1} in GO shifts somewhat to 3448 cm^{-1} with symmetric peak shape and less intense peak, which may be indicative of the N—H stretching of the grafted amine onto GO surface [153].

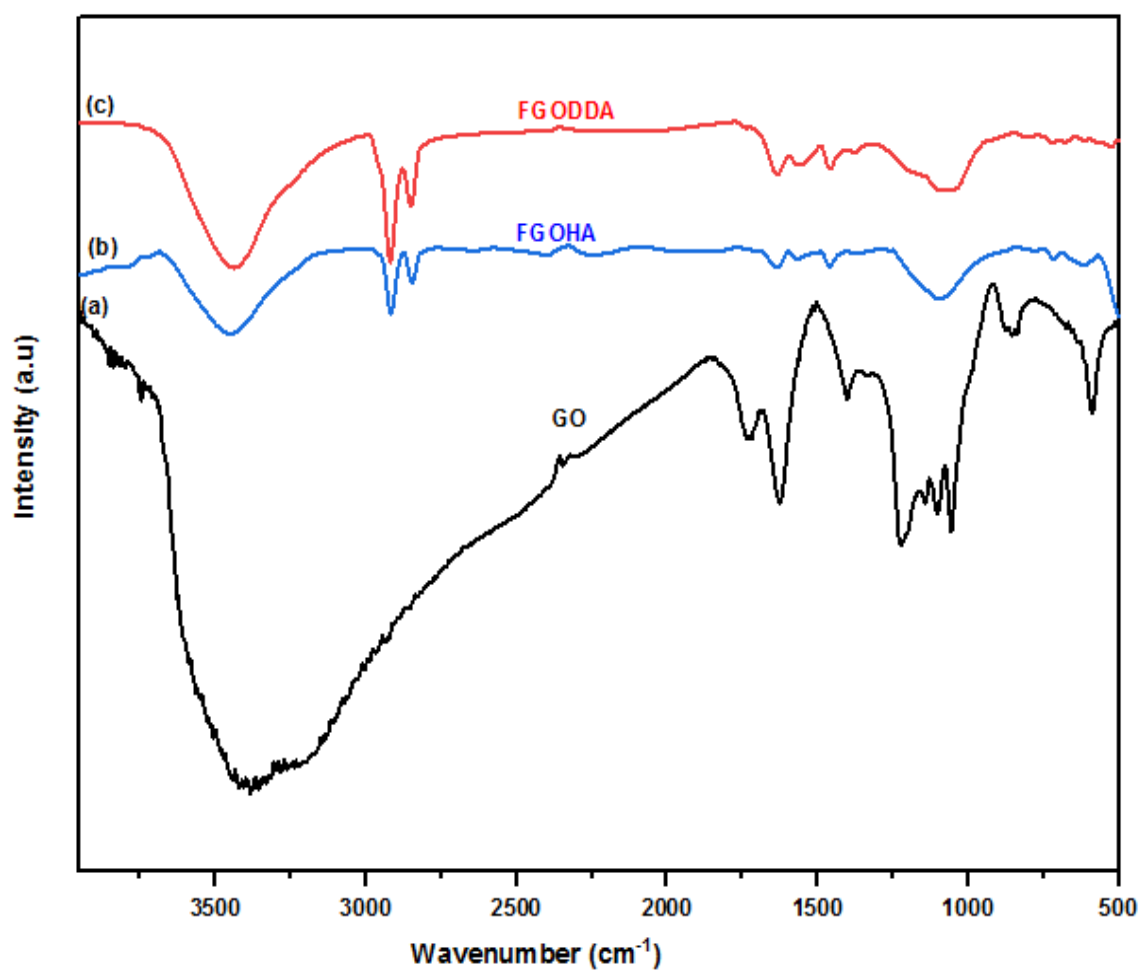


Figure 4.1 : FTIR spectra of (a) GO, (b) FGOHA, and (c) FGODDA.

4.3.2 Morphology

Raman spectroscopy presents an insight on the morphology of carbon-based materials. There are two prominent bands for such materials such as the D and G bands as shown in Figure 4.2. The G mode which is peaked at 1587 cm^{-1} corresponds to the in-plane vibrations of the sp^2 hybridized carbon atoms present in both rings and chains. The disorder band (D band) at 1331 cm^{-1} is indicative of the structural disorder caused by the sp^3 carbon atoms covalently bonded to the epoxide and hydroxyl functionalities in the GO basal plane. The ratio of the peak intensity of D to G bands (I_D/I_G) is used to evaluate the extent of disorder in the graphene-based material. Higher D band indicates the breaking of the sp^2 bonds and forming of the new sp^3 bonds [154]. Figure 4.3 displays the Raman spectra of GO and amine-functionalized GO. The peak intensity ratio (I_D/I_G), for FGODDA ($I_D/I_G = 1.41$) and FGOHA ($I_D/I_G = 1.46$) increased when related to that of GO ($I_D/I_G = 1.14$). This fractional increase in peak intensity ratio demonstrates that new defects are produced during the functionalization of the GO.

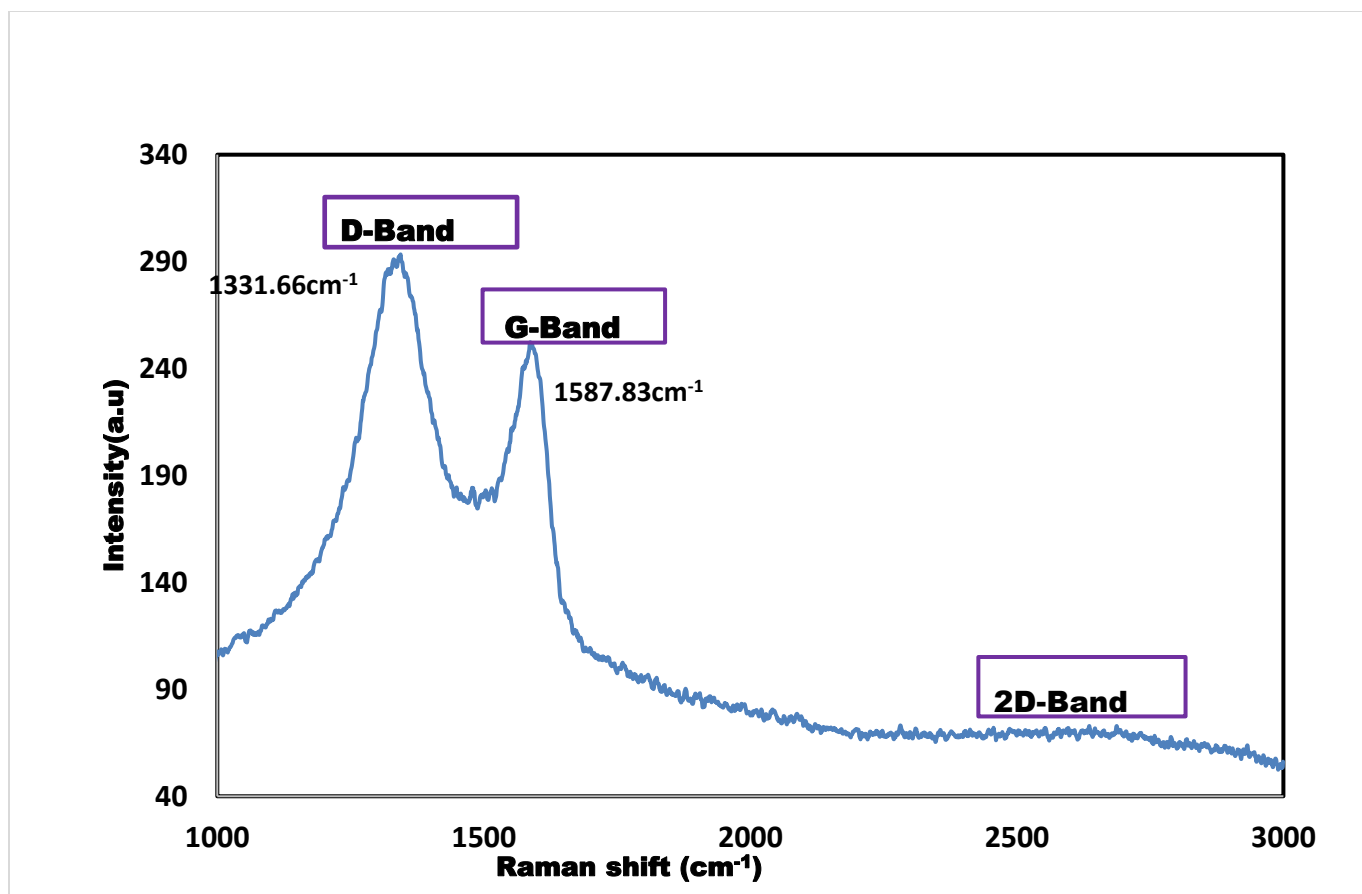


Figure 4.2: Raman spectra of GO

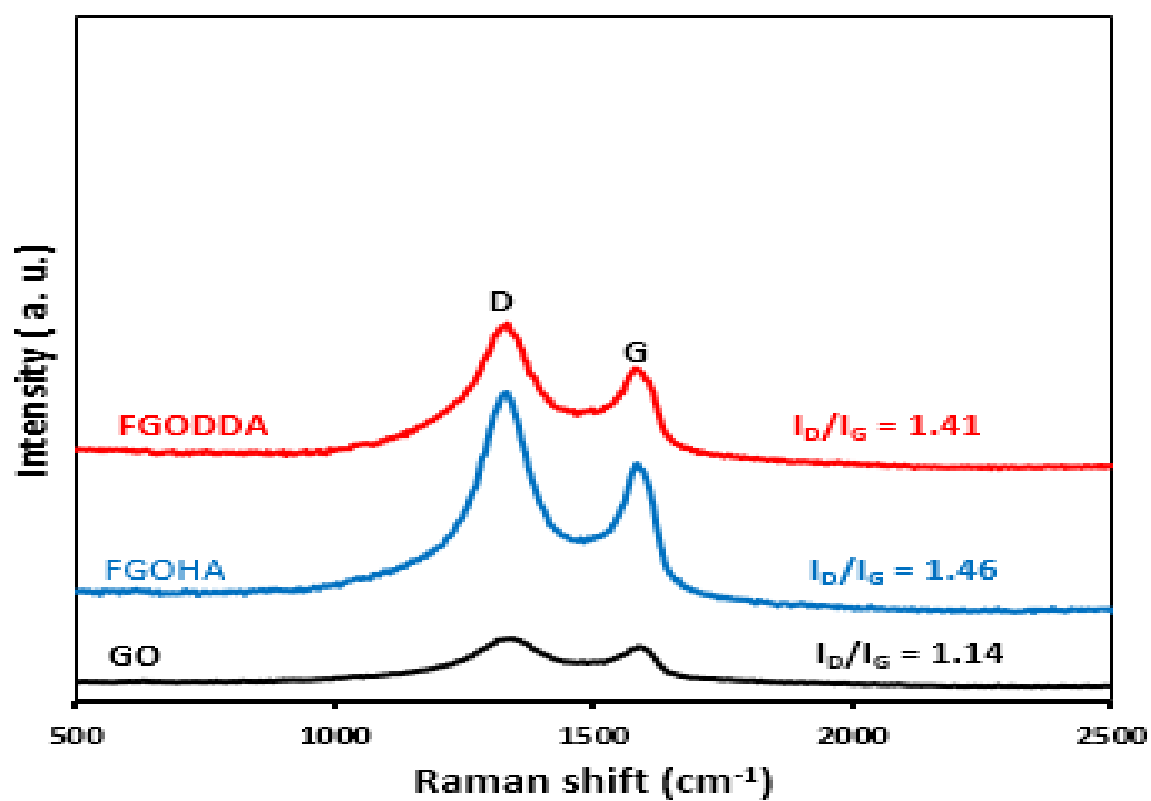


Figure 4.3: Raman spectra of GO, FGOHA, and FGODDA recorded using 633 nm laser excitation.

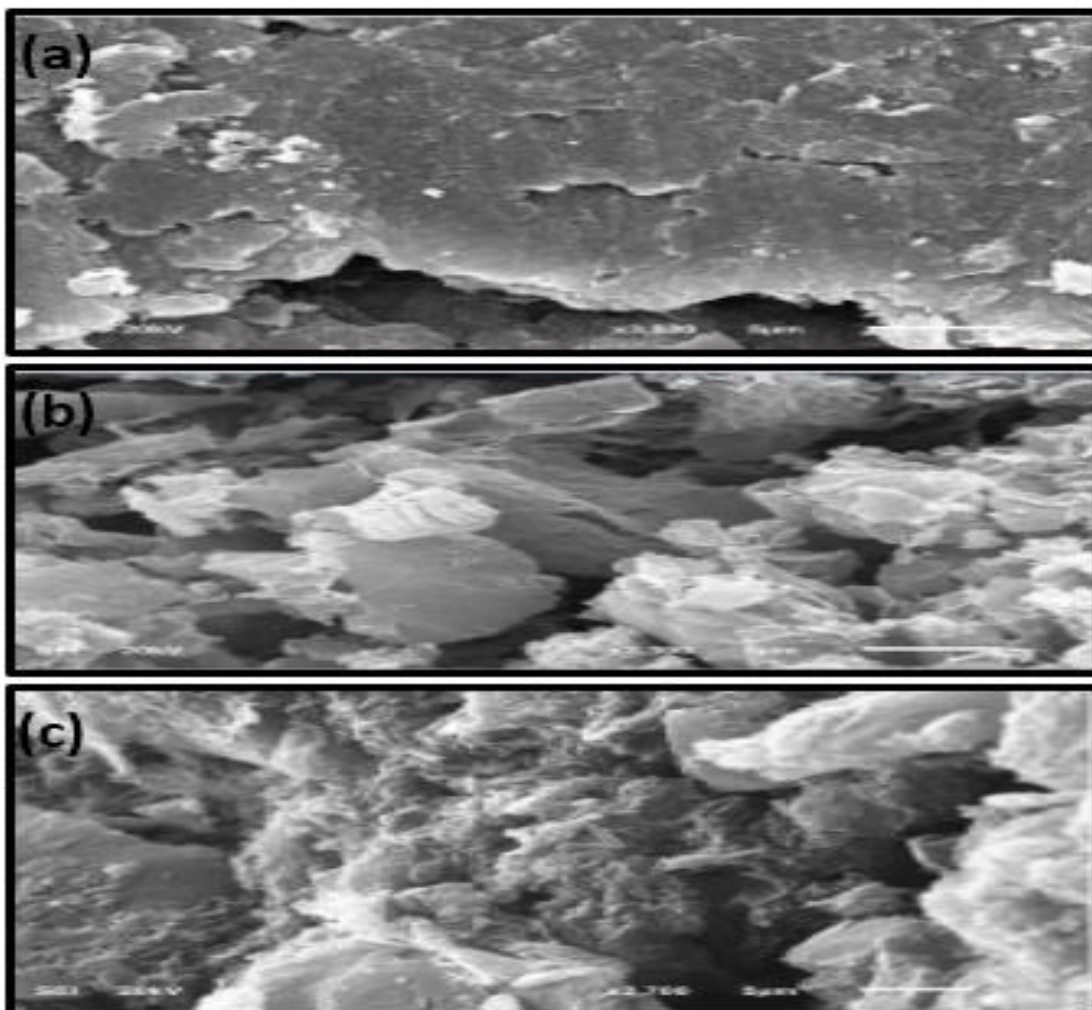


Figure 4.4: SEM photos of (a) GO, (b) FGOHA, (c) and FGODDA.

The morphologies of the pure GO and the modified GO surfaces were studied by using SEM and the micrographs are presented in Figure 4.4. The pristine GO revealed the adjacent stacking of the sheets with somewhat uniform surfaces together with very sharp edges relative to the amine-functionalised GO [155]. However, the alkyl amine functionalized GO absorbents displayed crimple flakes with wrinkles and some groove regions orienting randomly. Increasing the number of chain length of the alkylamine from six (FGOHA) to twelve (FGODDA) led to the generation of many large and more conspicuous thick domains with higher surface roughness indicating that this long-chain alkylamine was well grafted onto surface of GO. The distinction in the surface characteristics between the pristine GO and modified GO can be elucidated in terms of their chemical features. GO being hydrophilic in nature, can disperse readily in water to produce individual sheets with flat surfaces due to the slow vacuum-filtration process. The introduction alkyl chains onto the GO altered it to a hydrophobic substance, causing poor dispersion in a polar solvent. The modified GO also formed large aggregated domains due to a swift vacuum-filtration process. These unique morphological characteristics not only increased the surfaces roughness, but also substantially altered the surface wettability and the dispersion behaviours of the samples [156].

The effects of surface roughness and surface energy on the wettability characteristics of GO are established by WCA measurements, which are presented in Figure 4.5. The different surfaces were evaluated for hydrophobicity by measuring their various WCAs. The hydrophobicity of the GO alone was found to be low with WCA of $51.20 \pm 2.66^\circ$ due to the existence of oxygen bearing hydrophilic groups on the GO sheets. A drastic increase in the WCA was noticed relative to that of GO as different molecules of aliphatic amines were grafted on the GO sheets. The FGOHA and FGODDA display WCAs of $97.98 \pm 2.36^\circ$ and $128.37 \pm 1.89^\circ$, respectively. This could be

explained by hydrophobic hydrocarbon chains conferred on the GO film by its functionalization with the aliphatic amines and subsequent chemical reduction with hydrazine hydrate which removed the hydrophilic labile oxygen containing moieties on the amine functionalized GO films. Moreover, the grafting of the alkylamines appeared to have enhanced the surface roughness of the GO as evident in the SEM results and thereby increasing the hydrophobicity of GO. The amine functionalised GO molecule with a longer hydrocarbon chain is expected to have the least surface energy since it can spread over larger area on GO sheet and has a greater free volume. Hence, the surface energy of FGOHA is greater than that of FGODDA. The concerted effect of surface roughness and surface energy resulted in different WCAs of functionalized GO.

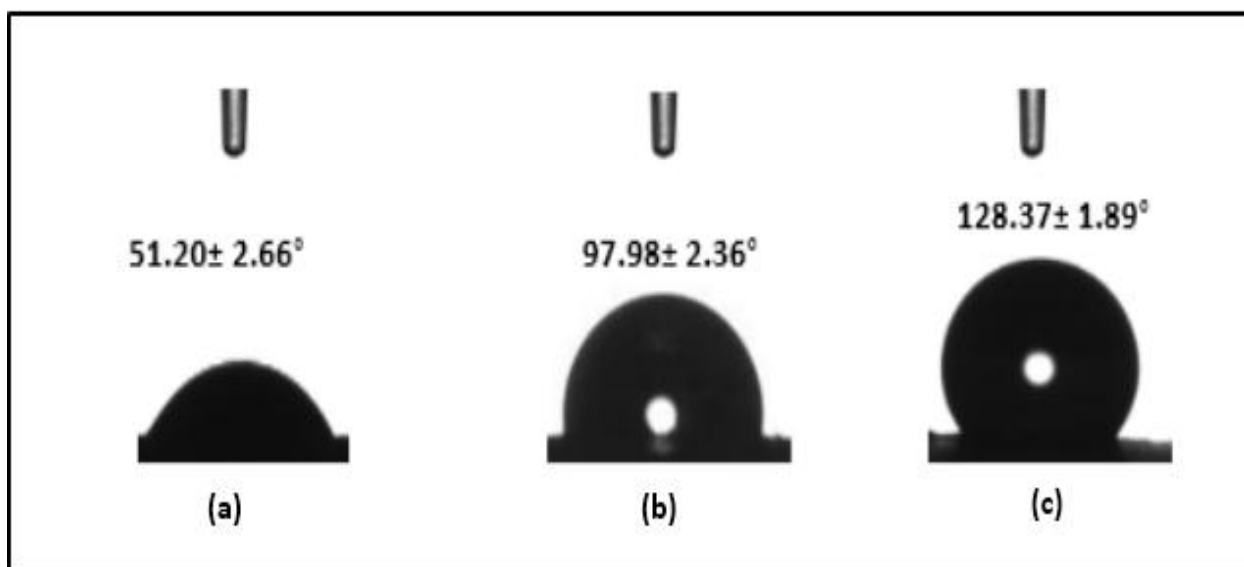


Figure 4.5: Water contact angle measurements for (a) GO, (b) FGOHA, (c) and FGODDA.

4.3.3 X-ray diffraction analysis

Figure 4.6 displays the XRD diffractogram of graphite flake and as synthesized GO. The graphite flakes shows a sharp and strong peak at 26.6° indicating a highly ordered layered structure, which corresponds to the interlayer spacing of 0.336nm between the graphite layers with 002 lattice planes. On the other hand, the XRD pattern of GO shows a reflection at $2\theta = 8.22^\circ$ corresponding to *d*-spacing of 1.075nm which is shown in Figure 4.7. The peak shift from 26.5° to a broader peak at 8.22° corresponding to the increase in *d*-spacing from 0.336nm to 1.075nm is an indication that the pristine graphite flakes is wholly oxidized after chemical oxidation and exfoliation. The introduction of the oxygen containing functionalities in GO via chemical oxidation disrupts the highly ordered lattice structure in the graphite flakes. These functional groups and the intercalated water molecules increase the interlayer distance between the GO sheets. This greater distance between the GO sheets shifts the XRD peak position to a smaller angle, thereby responsible for the broad peak observed around 8.22° . After grafting of GO with HA and DDA, the interlayer spacing was again increased by the intercalation of the long-chain HA and DDA between the graphene layers. XRD patterns of FGOHA and FGODDA are also presented in Figure 4.7. The interaction of the GO and alkylamine may reduce the order of graphite crystallinity, which causes the major diffraction peak to become wider and shift to a slightly lesser angle [187]. Upon functionalization, there was a further peak shift to 6.95° . (FGOHA) and 6.92° (FGODDA), corresponding to the GO sheets interlayer extension from 1.075nm to 1.271nm (FGOHA) and to 1.276nm (FGODDA). In addition to this, the broad peak around $17\text{--}24^\circ$ emanated from the reaggregation of graphene sheets [188].

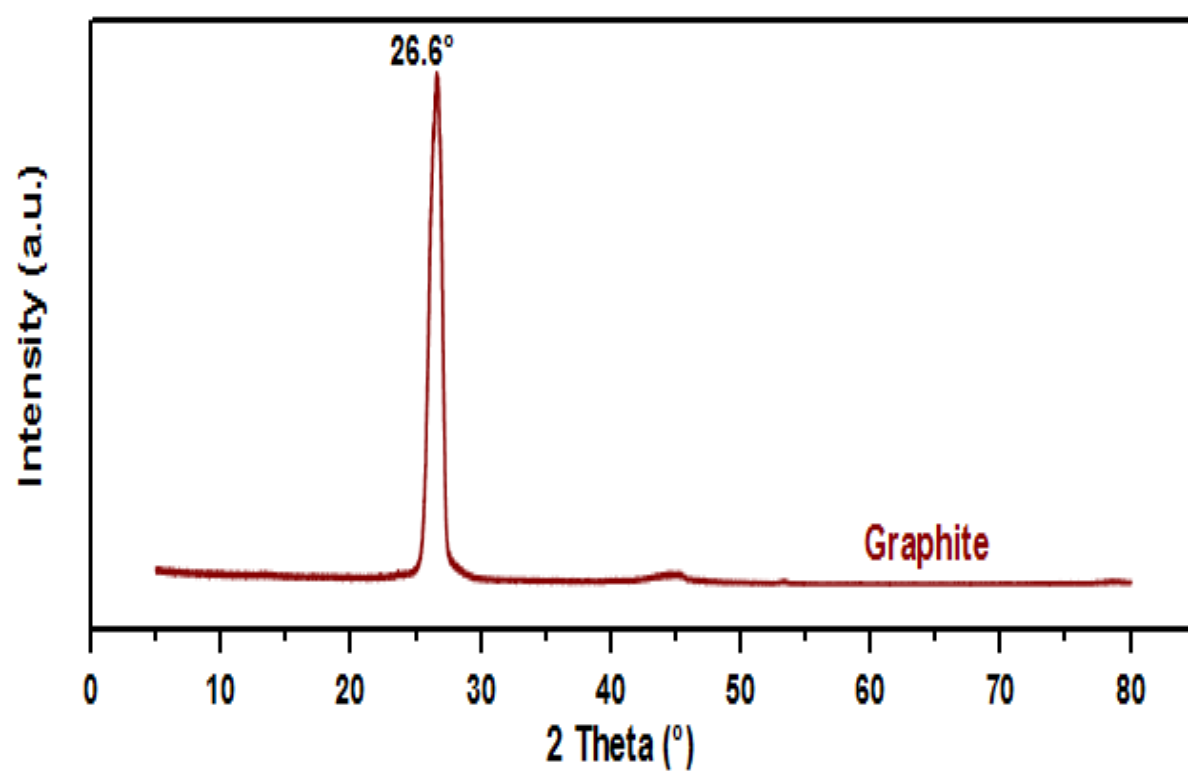


Figure 4.6: XRD of graphite flake

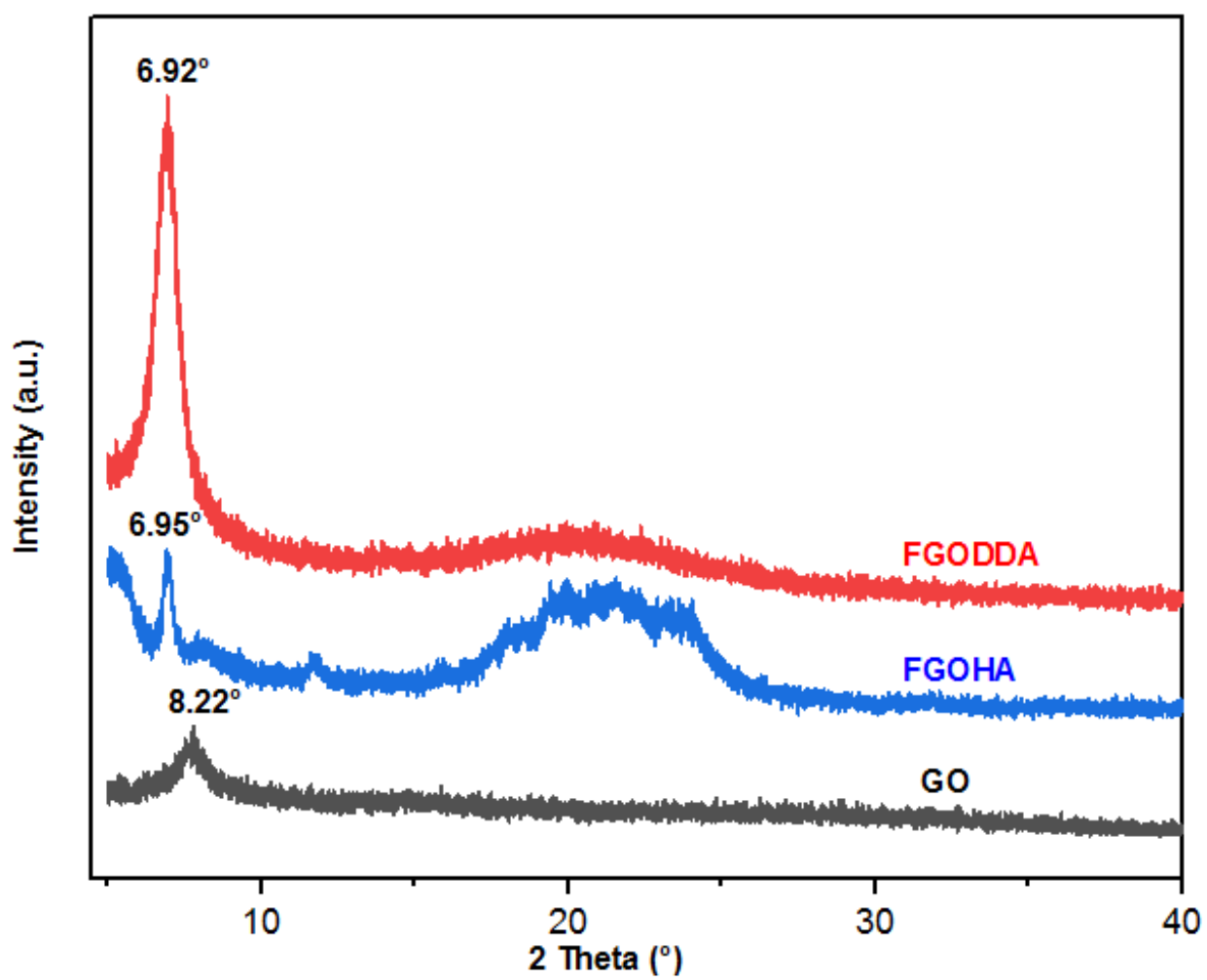


Figure 4.7 : XRD patterns of pristine GO, FGOHA and FGODDA.

4.3.4 Absorption Performance of the Amine Functionalized GO Absorbents

A simple experiment was carried out to assess quantitatively the hydrocarbons absorption capability of the three amine-functionalized GO absorbents. In typical absorption capacity measurements, engine hydrocarbons and common organic solvents such as decane, cyclohexane and hexane were selected as absorbates. In this test, the absorbents were placed in a beaker containing hydrocarbons or organic solvents to be absorbed. Each absorbent was dipped into 10 mL of the absorbate and forced in the liquid for maximum hydrocarbons sorption. The absorbents were then taken out and compressed manually with the aid of a quick-grip clamp. The outcomes of the absorption capacities of all the modified GO absorbents in the engine hydrocarbons and in the organic liquid media are presented in Figure 4.8.

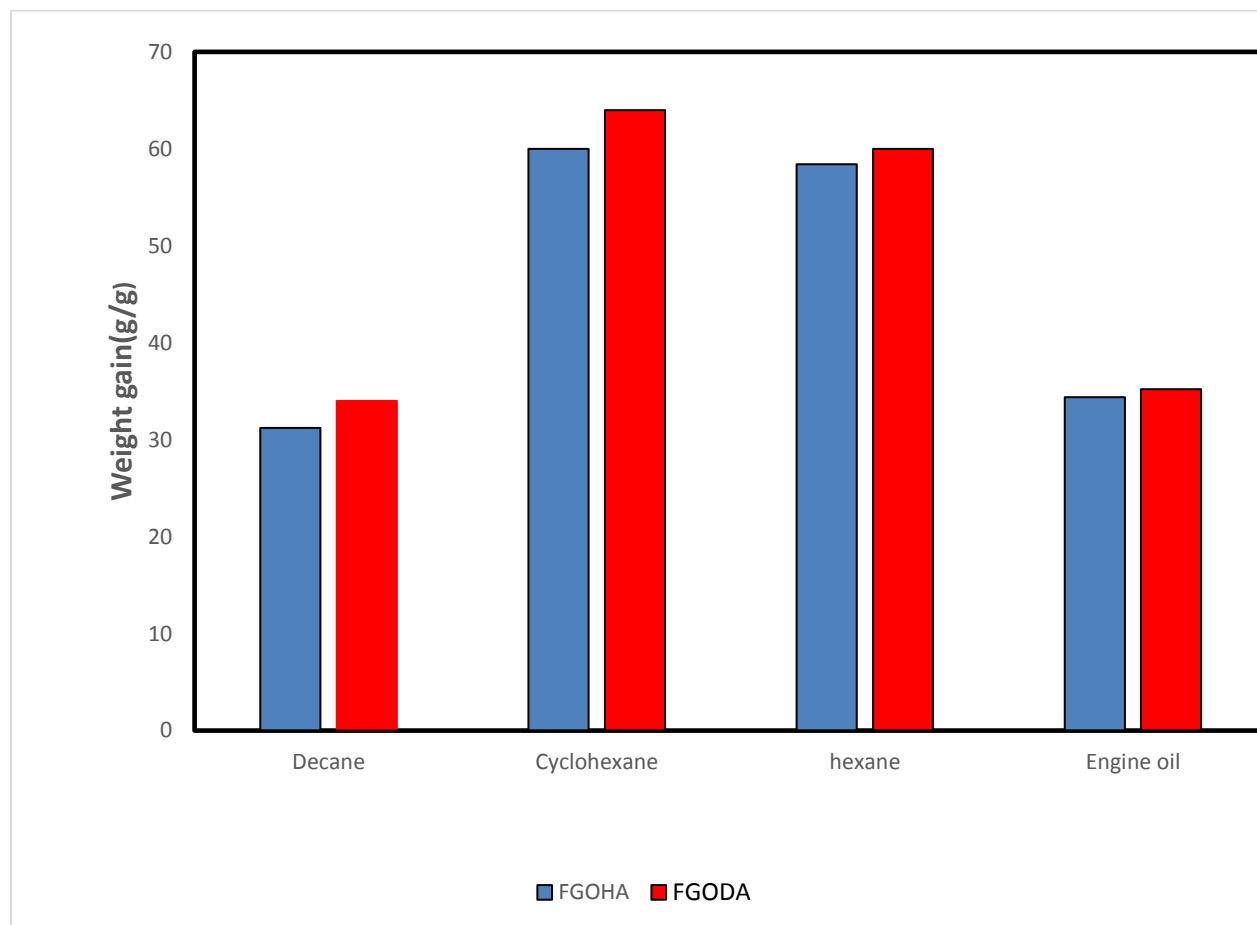


Figure 4.8: Absorption capacity (weight gain) of the FGO-amine hydrocarbons absorption films calculated for engine hydrocarbons and organic solvents.

The absorption capacity is greatly dependent on the the absorbent's porosity. More porous structures will afford a higher liquid absorption. Therefore, absorbents with greater hydrophobic property will absorb hydrocarbons more readily and retrieve hydrocarbons from water more efficiently. Figure 4.8 presents the absorption capacities, q (g/g) of the amine-functionalized absorbents for the engine hydrocarbons and the non-polar solvents which are 31.2 –64 times its original weight, based on the density and viscosity of the hydrocarbons and solvents. The hydrocarbons absorption performance and high selectivity are associated with the porous structures and superoleophilic and superhydrophobic nature of the FGODDA hydrocarbons absorption films, which show four times higher than FGOHA films most especially for cyclohexane. The FGODDA displays excellent absorption capacities ranging from 34 to 64 times its original weight (Figure 4.8) for all the absorbates used. Significantly, the FGODDA showed greater absorption capacity than many sorbents in previous reports, such as polymers (5-25)[157], polydimethylsiloxane sponge (4–11 times)[158], reduced GO foams (5–40 times)[159], and chitin sponge (30–60 times)[160]. However, the absorption capacity in other absorbents is higher than that of FGODDA such as graphene modified foam (60- 140 times)[11], CNF aerogel (106-312 times)[161] and ultra-flyweight aerogel (215–913 times)[146]. The simple, low cost and easily large scale fabrication method make FGODDA a promising candidate to be used as a sorbent for hydrocarbons spill remediation.

4.3.5 Hydrocarbons-Water Separation

The hydrocarbons-water separation test of the prepared absorbents was done by dipping the material in the hydrocarbons or solvent/water mixture (5ml: 45ml). As the absorbent approached the mixture, it selectively and quickly absorbed the floating solvent or hydrocarbons on the surface of the water, leaving behind water in the system. The absorbent tended to float on the surface

despite being immersed by an external force in order to achieve higher separation efficiency. The GO-modified absorbent instantly absorbed the organic phase once the absorbent was in contact with the hydrocarbons or the solvent. The differential affinity to the organic layer (hydrocarbons or solvent phase) clearly showed that the GO-modified absorbent had oleophilic and hydrophobic characteristics, where the organic solvent or hydrocarbons could flow into the absorbent pores easily and rapidly as evident in Figures 4.9d and 4.10c. This clearly showed the superhydrophobic nature of the FGODDA. The hydrocarbons could be retrieved by simple mechanical squeezing method and the absorbent could be reused repeatedly. After the separation, no trace water was seen in recovered hydrocarbons by visual inspection, thereby showing high separation ability. The efficiency of separation of the hydrophobic and oleophilic FGODDA for the organic solvents and engine hydrocarbons is all above 99% (Figure 4.11).

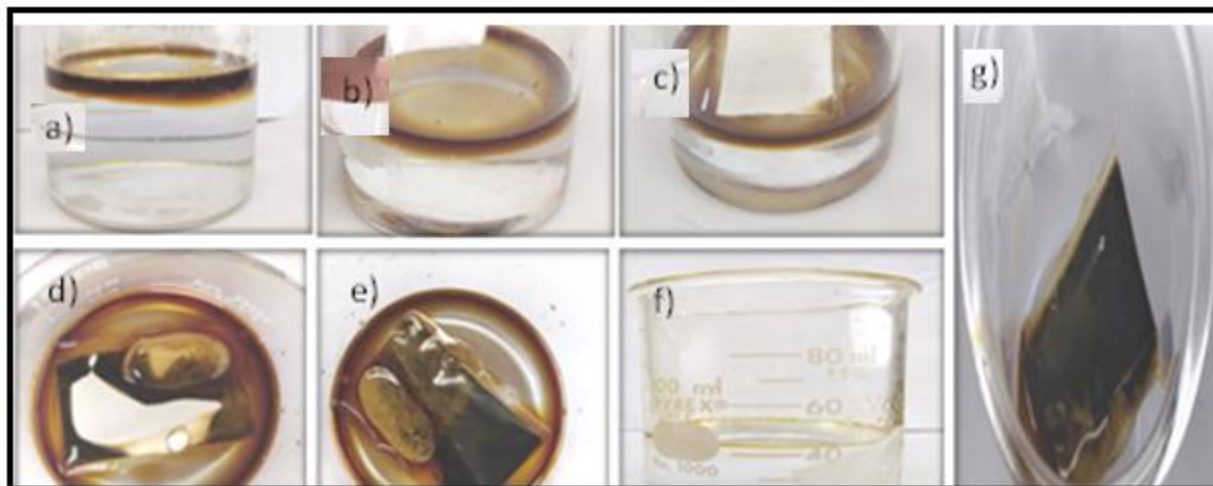


Figure 4.9: (a–g) Separation of engine hydrocarbons from the surface of DI water by a-FGODDA.



Figure 4.10 :(a–e) Separation of n-hexane from the surface of DI water dyed with Methylene Blue by a-FGODDA

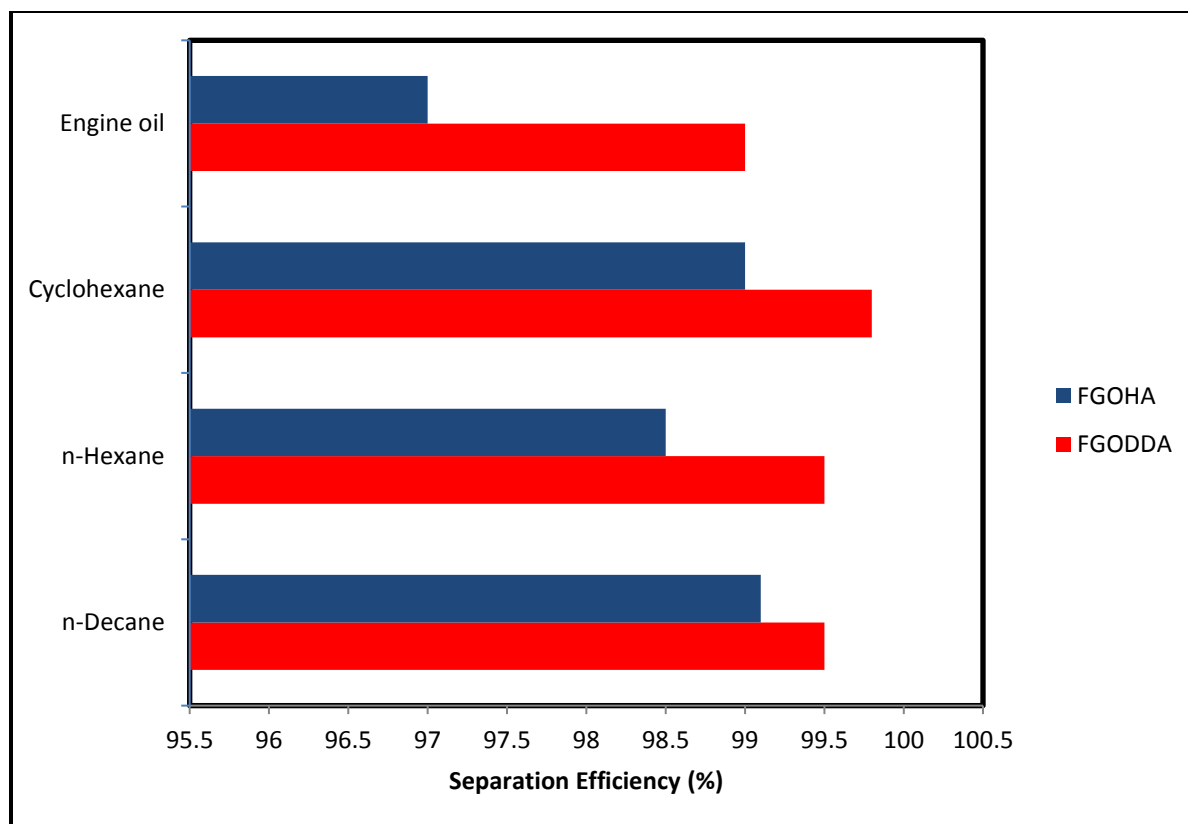


Figure 4.11: The separation efficiency of the modified absorbents for different types of hydrocarbons/water mixture.

8. CHAPTER 5

9. POLYETHYLENE/AMINE FUNCTIONALIZED REDUCED

GRAPHENE OXIDE COMPOSITE MATERIALS:

MORPHOLOGICAL AND HYDROCARBONS ABSORPTION

PROPERTIES FOR REMEDIATION OF HYDROCARBONS

SPILLS

5.1 Introduction

Water pollution is a crucial environmental challenge which can cause disastrous effects for aquatic organisms and humans. The major players in the water pollution are the hydrocarbons and organic spills [1]. The need for fossil fuels and crude hydrocarbons by-products has been on the increase sequel to the industrial revolution in the 18th century. This has called for frequent offshore transportation of the hydrocarbons from the place of generation to the point of demand [2]. The prevalent hydrocarbons spill accidents and the huge hydrocarbons wastewater discharge from the industries such as petrochemicals, textile and leather, aluminum, steel, metal finishing, palm hydrocarbons and food industries destroy the quality of water. Water contaminated with hydrocarbons is not only detrimental to the human health but also have a destructive effect on aquatic life and almost individual species across the marine food chain is affected [3]. Aside from the aforementioned consequences, hydrocarbons and organic contaminants are potentially hazardous due to their high flammability and may eventually cause fire or explosion [4]. To this end, the efficient separation of these contaminants from water has become a matter of urgency and paramount importance in order to shield the ecosystem for the healthy sustainability of environment. Several conventional methods such as controlled burning [5], bioremediation [6], use of electric field [7], collection by mechanical means [8], use of chemical dispersants [9] and absorbent materials [10-11], have been broadly employed to deal with the hydrocarbons and chemical pollutants. The drawbacks associated with these techniques are their low efficiency of separation, poor selectivity, high toxicity, lesser recyclability, high operational cost, and the introduction of secondary pollutants [12]. Thus, special attention has been channelled by researchers on the fabrication of numerous low cost functionalized materials which can effectively separate hydrocarbons from water and also be easily produced on a large scale. Materials with

either superhydrophilic and superoleophobic or superhydrophobic and superoleophilic surfaces can be efficient to tackle the problem of hydrocarbons separation from water [13]. Here, the water or hydrocarbons swiftly percolate through the superhydrophilic or superhydrophobic materials in which one phase is eventually left behind [14]. Novel materials and methods are currently explored for hydrocarbons/water separation due to some serious limitation of the traditional methods [15, 16, 17]. To achieve effective separation of hydrocarbons from water, designing functional materials with special wettability plays a very crucial role. The realization of this task lies in the construction of superhydrophobic surfaces. Materials with superhydrophobic surfaces are characterized by high contact angle greater than 150° [18]. The fabrication of materials with superhydrophobicity is greatly preferred either for differential absorption, or application for the direct retrieval of hydrocarbons from water [19]. Several methods and materials have been developed to produce superhydrophobic surfaces [162-164]. In recent times, carbon-derived materials such as CNTs, CNFs and graphene are receiving considerable interest for the fabrication of several hydrophobic materials for hydrocarbons remediation [165]. The carbon-based materials are easy to come by, cheap and exhibit good hydrophobic behavior [22]. Graphene has attracted a great deal of interests in several applications due to its high surface area, outstanding thermal, electrical and mechanical properties [166-168]. Among the new sorbent materials, graphene is promising because of its low cost and excellent hydrophobicity and oleophilicity. These features make it suitable for use in applications where liquid-liquid separation is desirable [169]. Nowadays, graphene oxide (GO) based nanocomposites are gaining ground as nanoabsorbents for hydrocarbons spill clean-up. GO is the oxidized form of graphene functionalized by reactive oxygen having functional groups. The ease of synthesis and the processability make GO an excellent precursor for graphene and its composites [170]. For example, Peng et al. used the surface

modification method to produce superoleophilic and superhydrophobic graphene coated melamine foam for collection and retrieval of hydrocarbons from water [103]. Similarly, Ricky et al. developed superhydrophobic reduced GO modified polyurethane sponges as highly effective and recyclable sorbents for use in hydrocarbons-water separation [104]. Li and Shi manufactured graphene aerogel (GA) absorbent materials by reducing chemically graphene oxide (GO) dispersion [105], [106]. Qu and Xie fabricated nitrogen doped graphene architecture as the absorbents of hydrocarbons and organic solvents [107], [108]. In another work, a facile dip coating method was employed for the synthesis of graphene-based sponges with superhydrophobic and superoleophilic features for the large-scale collection of organic contaminants [109]. Even though the above mentioned graphene-based absorbent materials exhibit high absorption capacity, they have low selectivity for hydrocarbons and water thereby decreasing the efficiency of separation. In order to furnish the neat graphene monolith with superhydrophobicity and superoleophilicity so as to further enhance its efficiency of separation, designing surface structure with low surface energy and high roughness is expected to be a viable and efficient route. Nowadays, incorporation of long alkyl chains has been explored to modulate the GO surface lipophilically. This can facilitate regular GO dispersion in polymer and weaken its high affinity for water and this is desirable for its application in hydrocarbons-water separation. Jiao et al. grafted octadecylamine on GO surface to tune its hydrophilic surface into hydrophobic one, thereby promoting GO application in non-polar polymers [110]. Lee and co-workers functionalized GO with dodecylamine and noticed enhanced mechanical and barrier characteristics of the polyethylene composites when the modified graphene was added [111]. In this work, we report the superhydrophobic and superoleophilic amine functionalized GO/PE system prepared by dodecylamine (DDA) functionalization of GO via nucleophilic substitution and amidation reaction followed by subsequent hydrophobic

enhancement by polyethylene through solution mixing technique. Different techniques were used to evaluate the morphology and surface features of the absorbent materials. The wetting behaviours of the amine functionalized GO/PE composites were measured to justify the superhydrophobic and superoleophilicity properties. The absorption of hydrocarbons compounds and hydrocarbons–water mixture separation properties of the prepared materials were systematically evaluated.

5.2 EXPERIMENTAL SECTION

5.2.1 Materials and Chemicals

The chemicals and the reagents purchased were analytical grades and used as received without any further purification. The natural graphite powder (99.9%) was commercially purchased from Fluka AG, Chemische Fabrik, Buchs (Switzerland). Sulphuric acid (98%), hydrochloric acid (35%), sodium nitrate (98%), hydrogen peroxide (30%), hydrazine hydrate (80%), and potassium permanganate (99%) were obtained from Sigma-Aldrich Co. (USA). Dodecyl amine (DDA) was purchased from Merck Schuchardt OHG (Germany). Low-density PE pellets were obtained from Scientific Polymer Products. Cyclohexane, silicone hydrocarbons, Tetrahydrofuran (THF), toluene, n-hexane, n-decane, absolute ethanol (99.8%) were supplied Sigma-Aldrich Co. (USA). Engine hydrocarbons and diesel were obtained from Gulf Start Factory for Petroleum Industries Co. Saudi Arabia. The deionised water (DI) was used during the experiment. The laboratory assembled deionizer was used to produce the deionized water.

5.2.2 Measurements and Characterization

The FTIR spectra of the synthesized materials were obtained using Thermo Scientific Nicolet iS10 FTIR spectrophotometer. The contact angles of the various hydrophobic materials were measured

using Biolin Scientific Attension Theta Flex. The Blue M Oven was used for drying purposes. The microstructures and surface morphologies of the prepared materials were studied by Field Emission Scanning Electron Microscope (SEM) (JSM-6610LV, Scanning Electron Microscope, JEOL) at 20 kV acceleration voltage. The Raman spectra were obtained using Horiba Scientific LabRAM HR Evolution Confocal Raman Microscope. The XRD spectra were recorded by an XRD machine (Rigaku Ultima IV, Kuraray Co. Ltd. Japan).

5.2.3 GO Synthesis

GO nanosheets were prepared by modified Hummer's method described by Paulchamy et al. [148] which has been stated in the previous chapter.

5.2.4 Dodecylamine Functionalization of GO (DDA-GO)

In a typical experiment, the as-synthesized GO powder was dispersed in DI water (500mg GO/100mL DI water), and the resulting suspension was sonicated for 1hr prior to subsequent surface modification. Dodecylamine (1.52g) was dissolved in ethanol (70mL) and then the GO water suspension was added to the DDA-ethanol solution. The mixture was stirred continuously for a day at room temperature. The mixture was then refluxed for 1h at 110°C. The reduction of DDA-GO was done by adding 5mL hydrazine hydrate to the mixture. The final product was washed by filtration with ethanol-water mixture (1:1) to eliminate unreacted hydrazine hydrate or excess DDA adsorbed on the surface of the functionalized reduced GO (DDA-RGO). The black powder was dried under vacuum at 60 °C for at least a day.

5.2.5 Fabrication of DDA-GO/PE Composite

The DDA-RGO (100mg) was dispersed in xylene (150mL) and this was sonicated for 1h. The resulting solution was then heated to a temperature of 140 °C and the desired amount of LDPE pellets were slowly introduced into the xylene solution with constant stirring. After a complete dissolution of the LDPE particles, the mixture was slowly added into a considerable volume of stirred ethanol (200mL). The coagulation of DDA-RGO/PE composite was obtained. The resulting composite material was separated via filtration and this was washed with ethanol-water mixture (1:1) for several times, dried at 60 °C for 24h to eliminate the residual solvent. The composites containing 1wt % and 2wt % of DDA-GO were denoted as DDA-RGO/PE-1 and DDA-RGO/PE-2 respectively.

5.2.6 Hydrocarbons Absorption and Recovery Tests

The weight measurements before and after hydrocarbons absorption were used to assess the absorption capacity of the prepared absorbents for the model hydrocarbons. The original weight of the absorbent sample was taken and recorded as M_i . Then, the sample was placed into the mixture of water and various types of hydrocarbons (or other organic solvents) for absorption until saturation with the liquid. The absorbent material was taken out of the by means of tweezers, drained for a while and then squeezed to expel hydrocarbons. The absorption capacity of materials (Q) and the percentage recovery (R %) for various hydrocarbons were determined using the equations below:

$$Q (g/g) = \frac{M_t - M_i}{M_i} \dots\dots\dots (1)$$

$$R_{\%} = \frac{M_c}{M_t - M_i} \times 100 \dots\dots\dots (2)$$

The sample was weighed when, with the increase of absorption time, its weight was unchanged; this weight was recorded as M_t . M_c is the weight of the retrieved hydrocarbons (or organic solvent). Q evaluates the weight of the absorbed liquid relative to the weight of the absorbent, and R measures the amount the hydrocarbons in the liquid taken up in the absorbent material. The sorption–desorption tests were repeated for 10 times to evaluate the reusability of the prepared sorbent material.

5.3 Results and Discussion

5.3.1 FTIR Spectra Analysis

Figure 5.1 shows the FTIR spectra of GO and DDA-GO. The broad absorption peak at 3384 cm^{-1} is assigned to the O–H extending vibrations which confirms the presence of hydroxyl and carboxyl functionalities on the hydrophilic surface of GO and a small amount of adsorbed water molecules. This corroborates the fact that GO is a greatly absorptive material, as proven by its tendency to become a gel-like solution. The peak at 1720 cm^{-1} is ascribed to the C=O extending vibrations in the carboxylic groups at the edges of the basal graphene GO planes. The GO also displays two intense peaks at 1224 and 1055 cm^{-1} that are respectively attributed to the C–O (alcohol) and C–O (epoxide) extending vibrations [151]. The peak at 1626 cm^{-1} corresponds to C=C bond which shows the retention of graphitic sp^2 hybridized carbon even after the oxidation of the graphite [148]. After the grafting of DDA, a new peak surfaced at 1463 cm^{-1} (amide C–N stretching) is observed, while the peaks at 1055 and 1720 cm^{-1} disappear, due to the nucleophilic substitution and the amidation reactions between –COOH/C–O–C groups of GO and –NH₂ group of DDA. Moreover, the incorporation of DDA is substantiated by the significant pronounced peaks at 2919

and 2848 cm^{-1} (C-H stretching) as well as the new CH_2 absorption peak at 720 cm^{-1} . The results above show the DDA chains are successfully grafted to the GO surface [171-172]. In addition, the broad band at 3384 cm^{-1} in GO shifts somewhat to 3448 cm^{-1} with symmetric peak shape and less intense peak, which may be indicative of the N—H stretching of the grafted amine onto GO surface.

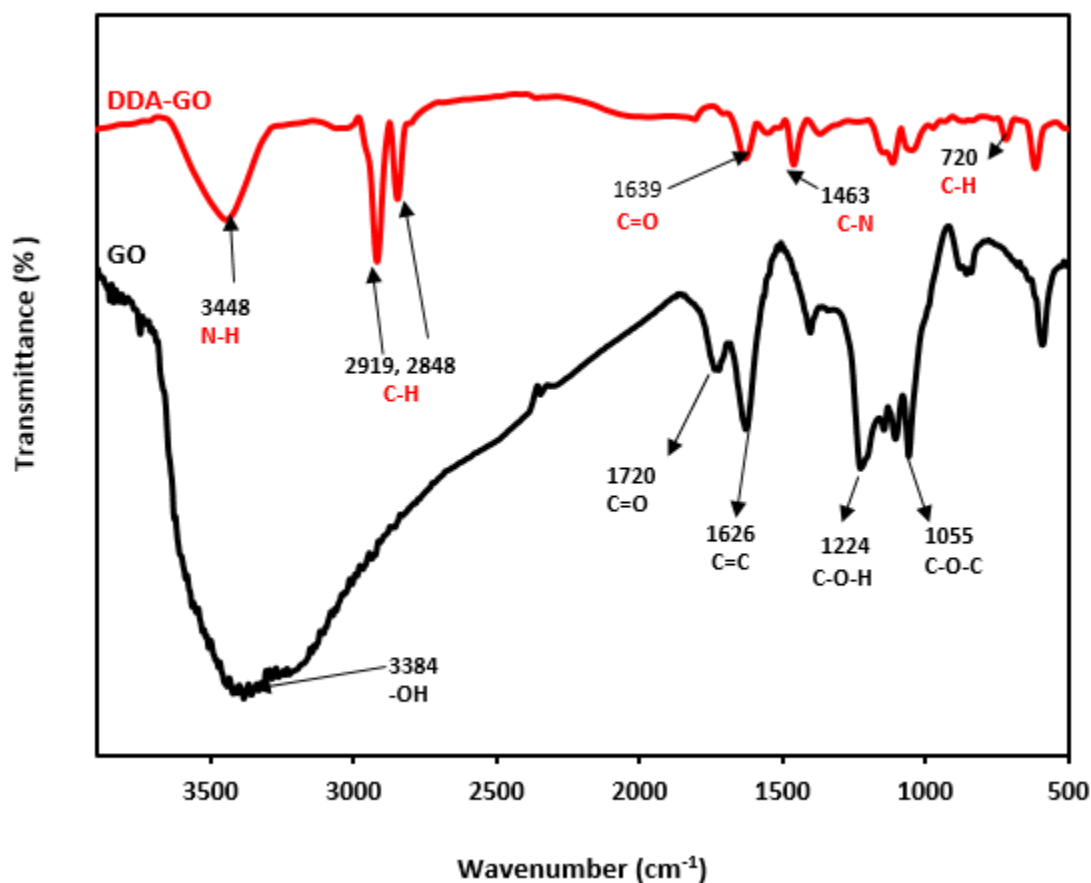


Figure 5.1: FTIR spectra of GO and DDA-GO nanosheets.

Figure 5.2 shows the typical FTIR spectrum for the GO, DDA-GO, PE, DDA-RGO/PE-1 and DDA-RGO/PE-2 absorbents. The neat PE spectrum agrees well with other PE spectra previously reported in the literature, having the characteristic peaks for PE, namely, peaks at 1470, 1381 and 720 cm^{-1} which are due to $-\text{CH}_2$ bending, $-\text{CH}_3$ symmetric and $-\text{CH}_2$ rocking deformations respectively. Also, the peaks at 2928 and 2839 cm^{-1} are respectively assigned to the $-\text{C-H}$ bond asymmetric and symmetric stretching in the neat PE [173]. With the incorporation of the DDA-GO into LDPE matrix, the peaks at 1470 and 1381 cm^{-1} in the neat LDPE were shifted slightly to 1479 and 1385 cm^{-1} in GO-DDA/LDPE composites, which could be a consequence of probable interaction between the two blended components. The observed difference in peak positions may be due to the little amount of DDA-GO relative to the polymer matrix. Although the shift is very small (about 4~9 cm^{-1}), likely interaction between the DDA-GO and LDPE matrix cannot be impossible because the presence of long hydrocarbon chain on DDA-GO helped to increase the compatibility and facilitate good interfacial interaction with the LDPE matrix. The spectral features of the two GO-DDA/PE composites (Figure 1d and e) are similar but with different peak intensities which is expected due to the different composition of DDA-GO. The spectra of the composites obviously combine the spectral characteristics of DDA-GO entity and the LDPE polymer matrix thereby confirming the formation of the DDA-GO/PE system.

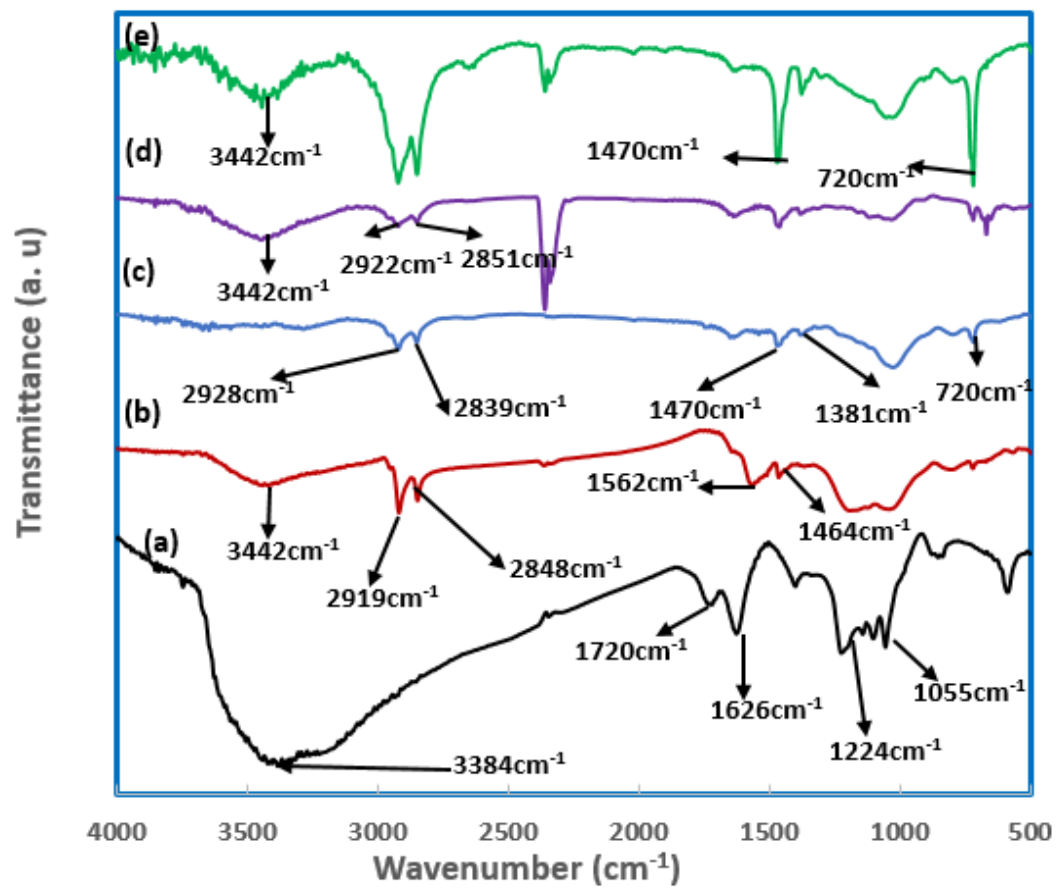


Figure 5.2: FTIR spectra (a) GO, (b) DDA-GO, (c) PE, (d) DDA-GO/PE-1, and (e) and DDA-GO/PE-2.

The effects of surface roughness and surface energy on the wettability characteristics of GO are established by contact angle measurements, which are presented in Figure 5.3. The different surfaces were evaluated for hydrophobicity by measuring their various WCA. The GO hydrophobicity was found to be low with CA of $51.20 \pm 2.66^\circ$ due to the existence of oxygen-bearing hydrophilic groups on the GO sheets. A drastic increase in the WCA was noticed as the DDA was grafted on the GO sheets. The contact angle of GO-DDA was found to be $128.37 \pm 1.89^\circ$ and this could be explained by hydrophobic long hydrocarbon chains conferred on the GO film by its functionalization with DDA and subsequent chemical reduction with hydrazine hydrate which removed the hydrophilic labile oxygen containing moieties on the GO-DDA films. However, the superhydrophobic property was not achieved until further modification with PE was carried out. The WCAs of the DDA-GO/PE-1 and DDA-GO/PE-2 were found to be $151.62 \pm 2.25^\circ$ and $153.12 \pm 2.37^\circ$ respectively. The results indicate significant enhancement in the wettability characteristics of the DDA-GO. The long alkyl chains of the DDA facilitates the homogenous dispersion of DDA-GO in the PE matrix causing impairment in its water permeability and thus higher WCAs of the DDA-GO/PE nanocomposites.

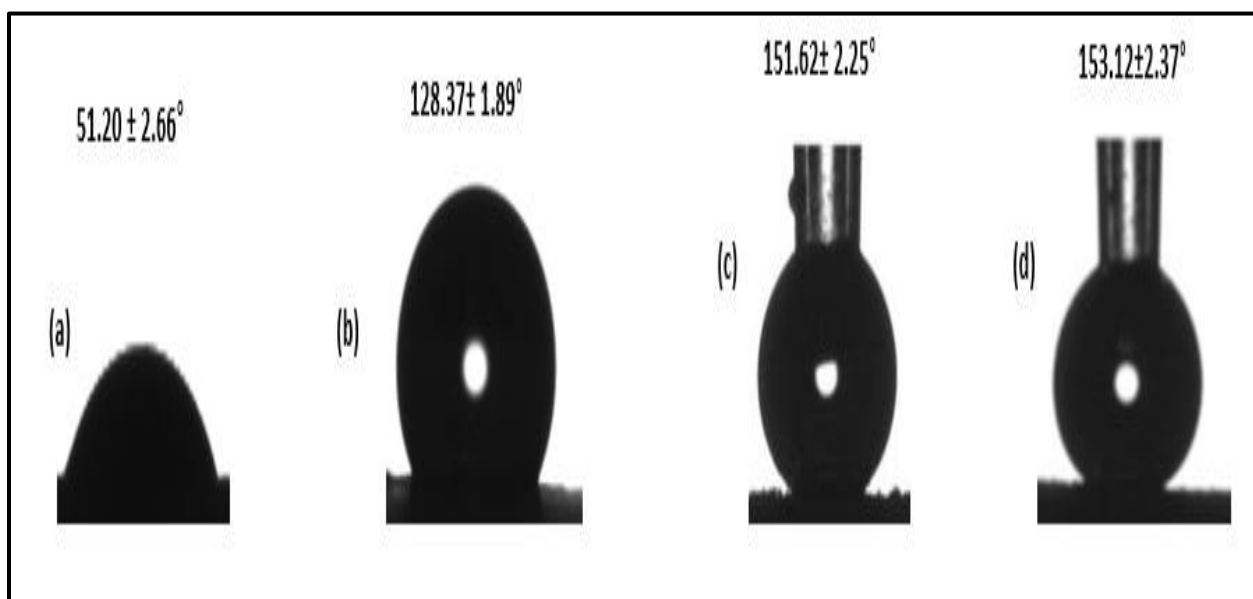


Figure 5.3: Contact angle measurements for (a) GO, (b) DDA-GO, (c) GO-DDA/PE-1, (d) DDA-GO/PE-2

5.3.2 X-Ray Diffraction Analysis

Figure 5.4 displays the XRD diffractograms of graphite flake and as synthesized GO. The graphite flakes shows a sharp and strong peak at 26.5° in Fig.4b showing a highly arranged layered structure, which corresponds to the interlayer spacing of 0.336nm between the graphite layers. On the other hand, the XRD pattern of GO shows a reflection at $2\theta = 8.22^\circ$ corresponding to d-spacing of 1.075nm. The peak shift from 26.5° to a broader peak at 8.22° corresponding to the increase in d-spacing from 0.336nm to 1.075nm is an indication that the pristine graphite flakes is wholly oxidized after chemical oxidation and exfoliation. The introduction of the oxygen containing functionalities in GO via chemical oxidation disrupts the highly ordered lattice structure in the graphite flakes. These functional groups and the intercalated water molecules increase the interlayer distance between the GO sheets. This greater distance between the GO sheets shifts the XRD peak position to a smaller angle, thereby responsible for the broad peak observed around 8.22° . The XRD pattern of DDA-GO shows two distinctive broader peaks ($2\theta = 6.4^\circ$ and $2\theta = 21.46^\circ$). The first diffraction peak ($2\theta = 6.4^\circ$) which is slightly lower than GO peak position indicates the grafting of the DDA moiety increased the interlayer distance of between the reduced GO-DDA sheets. The second broad amorphous peak at ($2\theta = 21.46^\circ$) is indicative of the structural disruption and less crystallinity of the incorporated DDA [174]. Also, this diffraction peak substantiates the removal of most oxygenous moieties from the GO sheet and the graphitic content restoration in the DDA-GO sheets via reduction process. This is also established by the great difference in hydrophilic–hydrophobic characteristics between GO and GO-DDA. GO displays a low water contact angle of 51.2° because of the numerous oxygen-containing functionalities, whereas the GO-DDA water contact reaches 128.37° . Thus, the grafting process switches the nanofillers from hydrophilic to hydrophobic, which is more fascinating for hydrocarbons-water

separation application. Figure 5.5c and d present the XRD patterns of GO-DDA/PE-1, and GO-DDA/PE-2 composites respectively. The two GO-DDA/PE composites displayed sharp diffraction peaks almost at $\sim 2\theta = 22^\circ$ and $\sim 2\theta = 24^\circ$ which can be attributed to the (110) and (200) lattice planes of LDPE in the prepared composites [175]. The XRD peaks due to the GO-DDA are not obvious in the composite XRD pattern, suggesting uniform dispersion of GO-DDA in the polymer matrix. Also, the diffraction peak intensities of the composites slightly appreciated with an increase in the loadings of GO-DDA. This is as a result of the nucleating effect of GO-DDA in the composites.

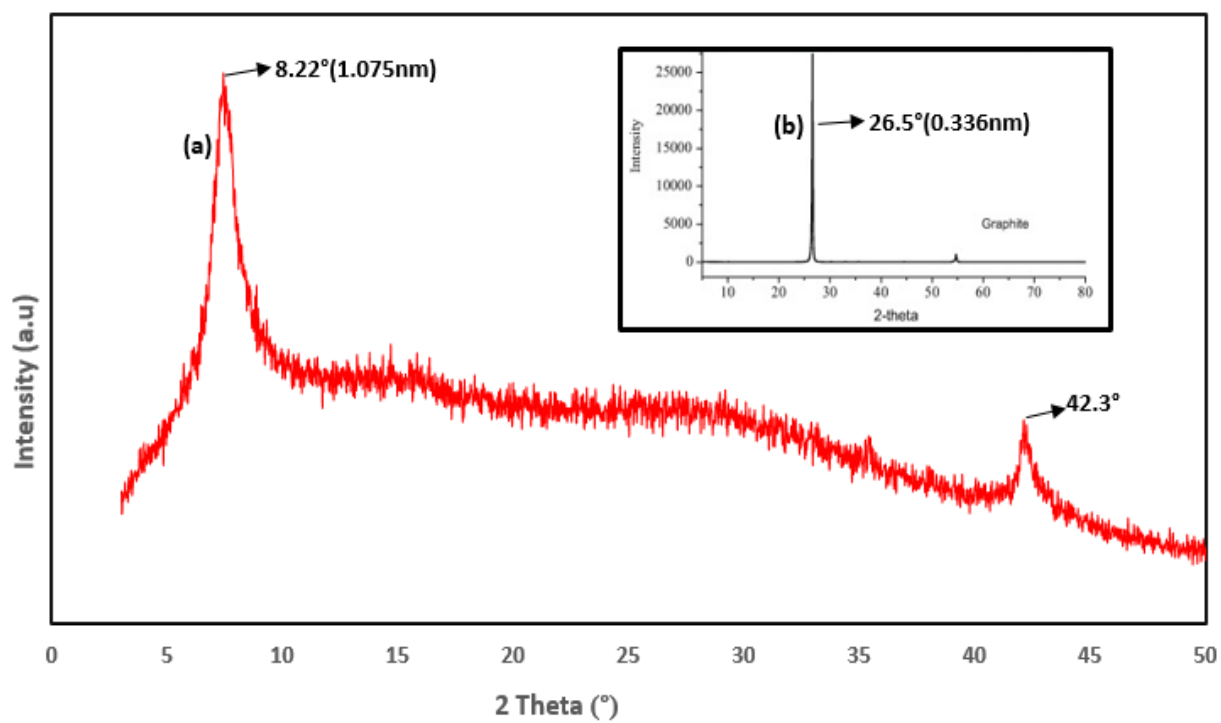


Figure 5.4: XRD of GO (inset shows the XRD of graphite flake).

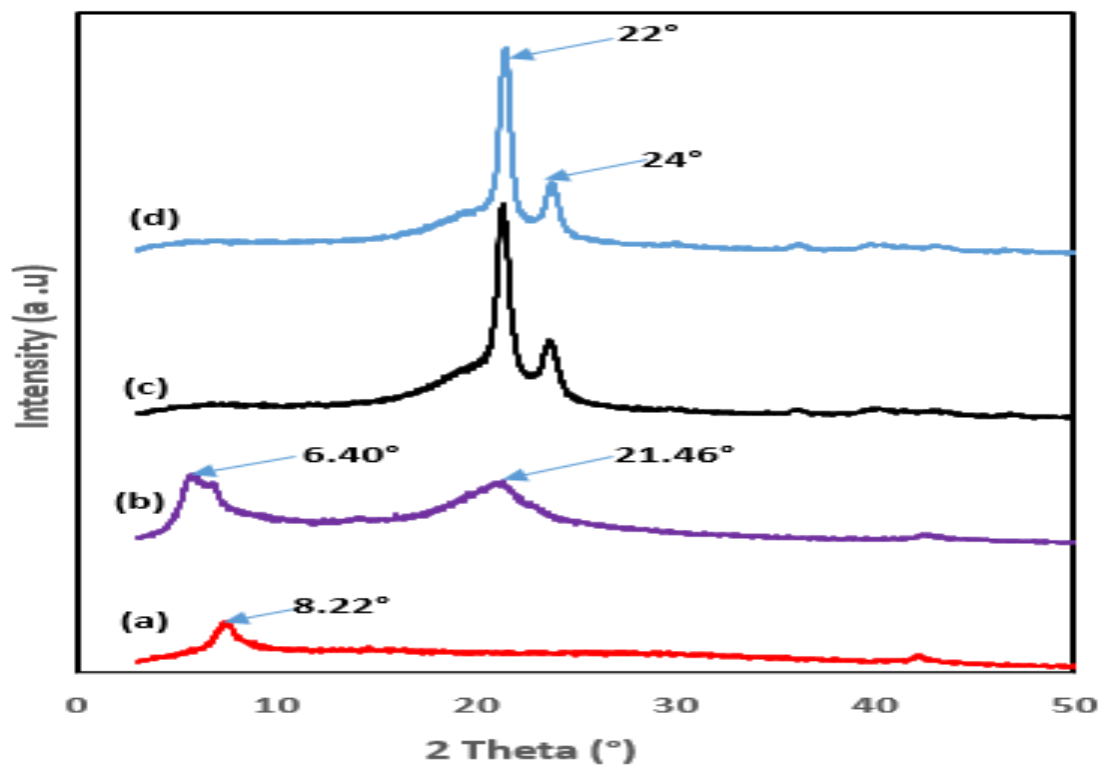


Figure 5.5: XRD patterns of (a) GO, (b) DDA-GO, (c) DDA-GO/PE-1, and (d) and DDA-GO /PE-2.

5.3.3 Raman Spectra Analysis

Raman spectroscopy presents a summary of the morphology of carbon- based materials. Figure 5.6 presents the Raman spectrum of the neat natural graphite powder, which indicates a principal G band at 1578cm^{-1} indicating the first order scattering of the E_{2g} mode for sp^2 carbon domains and the 2D band at 2700cm^{-1} . The D band which is peaked at 1352cm^{-1} reveals the presence of structural disorder and its small intensity relative to the G band ($I_D/I_G = 0.21$) indicates a high quality graphitic structure [176]. The 2D band (second order spectra) implies greatly crystalline nature of the pristine graphite powder [177]. The Raman spectra of GO, DDA-GO and the two composites are presented in figure 5.7a-d. The Raman spectrum of GO (Fig. 5.7a) shows a wider and somewhat shifted (to 1613 cm^{-1}) G band relative to graphite. The GO disorder D band which is marginally shifted (to 1366 cm^{-1}) is indicative of the structural disorder caused by the sp^3 carbon atoms covalently bonded to the epoxide and hydroxyl functionalities in the GO basal plane sequel to graphite oxidation. The ratio of the peak intensity of D to G bands (I_D/I_G) is used to evaluate the extent of disorder in the graphene-based material. Higher D band indicates the breaking of the sp^2 bonds and forming of the new sp^3 bonds. Figure 5.7b displays the Raman spectra of DDA-GO, the peak intensity ratio (I_D/I_G), for DDA-GO ($I_D/I_G = 1.05$) increased compared to that for GO ($I_D/I_G = 0.81$) and graphite ($I_D/I_G = 0.21$). This fractional increase in peak intensity ratio demonstrates that new defects are produced during oxidation of graphite to GO and functionalization of the GO. Figure 5.7c-d presents the Raman spectra of DDA-GO/PE-1 and DDA-GO/PE-2 respectively. Raman shifts of the composite with DDA-GO loadings of 2wt% (DDA-GO/PE-2) give the distinctive peak values that indicate suitable combination of the reduced functionalized graphene and the LDPE. The main characteristics of chemical bond in PE are C-C stretching at $\sim 1063\text{ cm}^{-1}$ and $\sim 1127\text{ cm}^{-1}$, H-C-H mixing at 1441 cm^{-1} and the two bands at ~ 2848 and $\sim 2878\text{ cm}^{-1}$ can be

ascribed to the methyl C–H extending vibrations. These results are consistent with the previously reported values for LDPE in the literature [178]. In addition to the bands attributed to LDPE in the composite, the three more peaks noticed around 1300, 1600, and 2700 cm^{-1} are attributed to D, G, and 2D bands of the blended functionalized graphene, respectively.

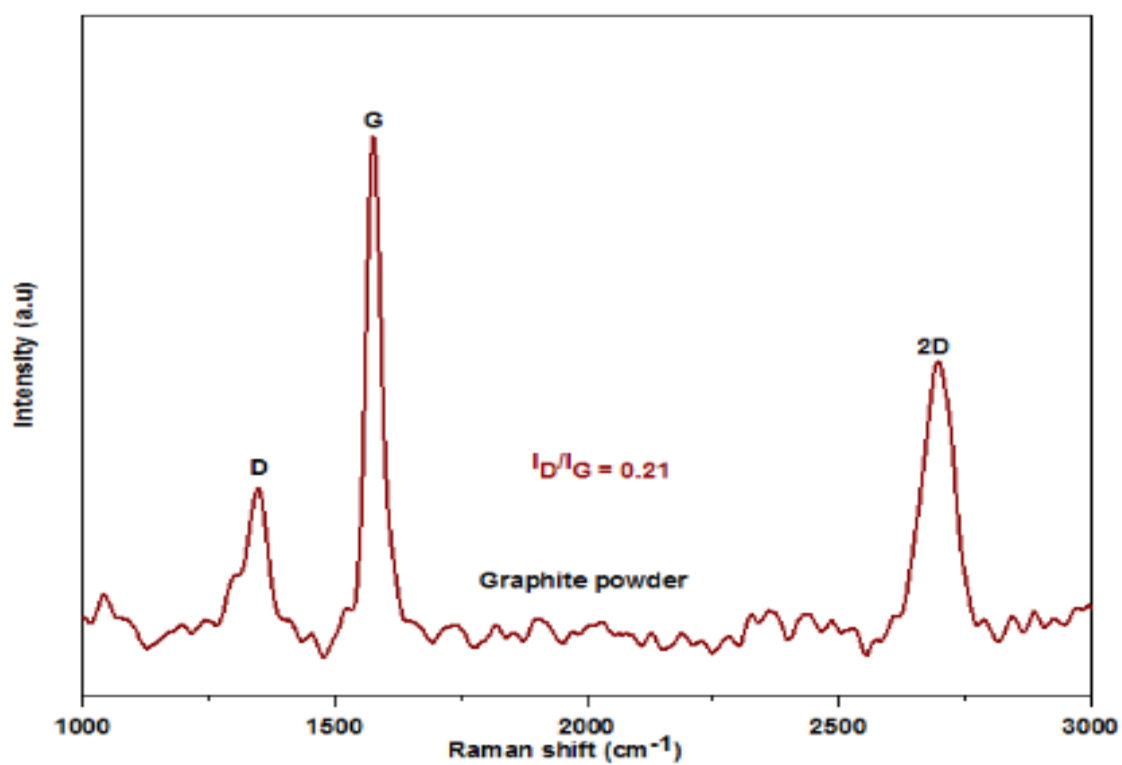


Figure 5.6: Raman spectrum of graphite powder.

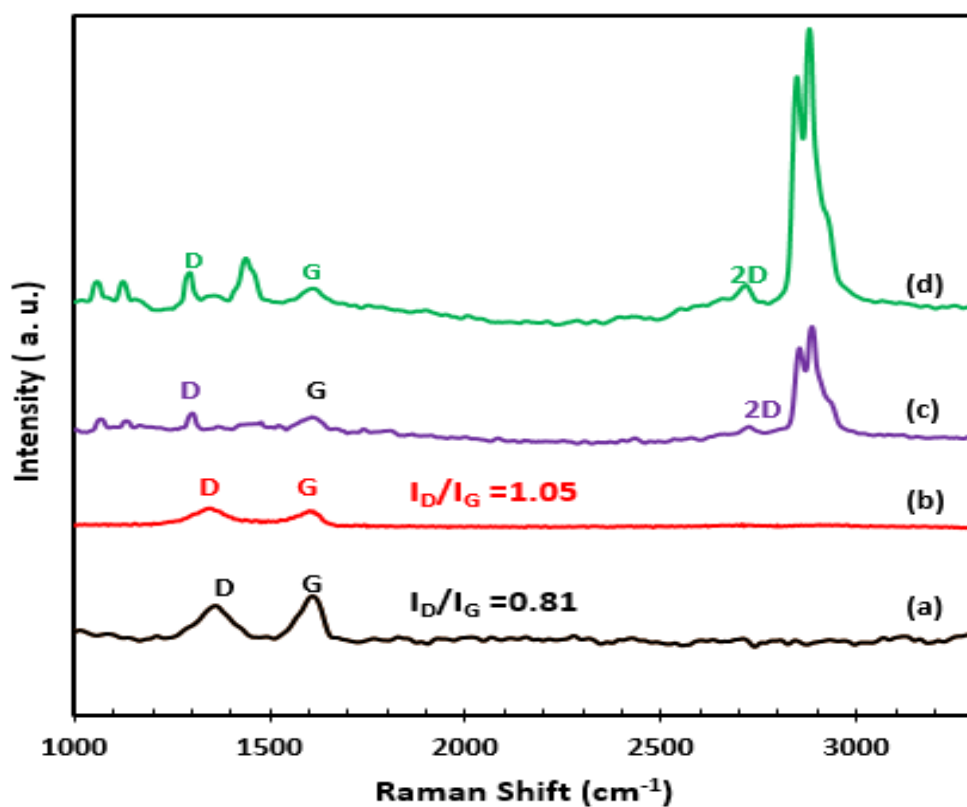


Figure 5.7: Raman spectra of (a) GO, (b) DDA-GO, (c) GO-DDA/PE-1, and (d) and GO-DDA/LDPE-2.

5.3.4 SEM Analysis

The morphology of the surfaces of the neat GO and its composites were investigated by using SEM and the results are presented in Figure 5.8. The as-produced ultrathin neat GO displayed an adjacent stacking of the sheets with somewhat uniform surfaces together with very sharp edges and several wrinkled ridges. These wrinkles of GO emanated from the hydrogen bonding interaction between the hydrophilic moieties on the edges and the basal planes of the GO sheets. Such hydrogen bonding altered the way in which the tangled GO sheets were agglomerated and thereby contributing to the wrinkles. However, the surface morphology of the GO-DDA showed more crimple flakes with wrinkles and some groove regions orienting randomly. The incorporation of DDA molecule onto GO surfaces led to the production of many large and more conspicuous thick domains with greater surface roughness as obvious in figure 5.6b. This indicates that the long-chain alkylamine was successfully grafted onto the GO surfaces. The surface morphologies of the two GO composites in figure 5.6c and d indicate that the GO-DDA is well encapsulated into the LDPE matrix and combined strongly. This considerable interfacial interaction between the nanofiller and the polymer matrix may be ascribed to the presence of similar alkyl chains in the two molecules. The entrapment and noncovalent interaction (π - π or van der Waal's) among the alkyl chains and the LDPE molecules facilitated homogeneous dispersion and the excellent interfacial bonding. The SEM images of DDA-GO/PE-1 shows comparatively less uniformity and more roughness than DDA-GO/PE-2 which is important for application in hydrocarbons- water separation.

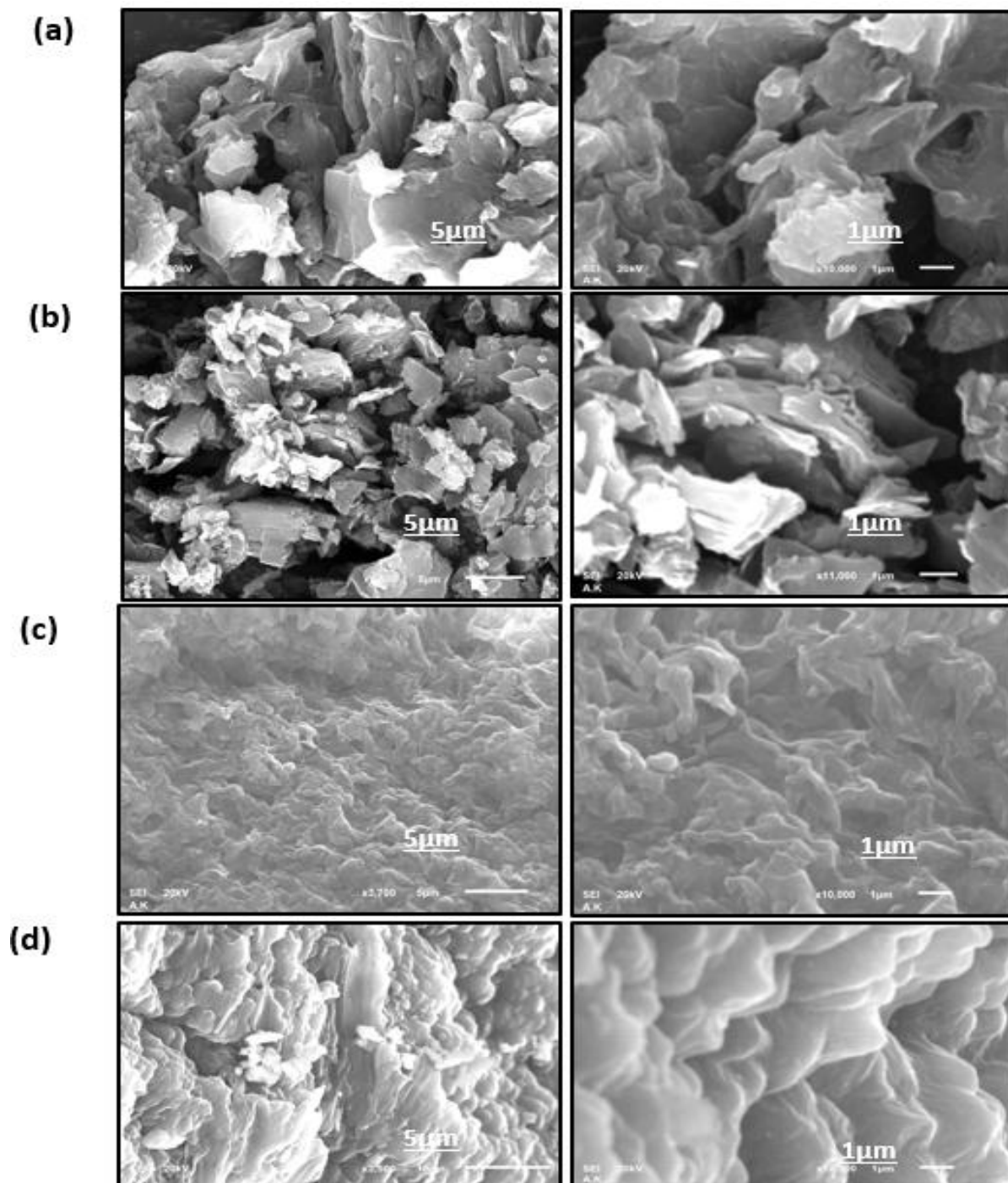


Figure 5.8: SEM images of (a) GO, (b) GO-DDA, (c) GO-DDA/PE-1 and (d) and GO-DDA/PE-2.

5.3.5 Hydrocarbons Absorption Capacity in DDA-GO/PE Composites

Diesel, silicone hydrocarbons, engine hydrocarbons, and some other selected organic solvents were used to determine the absorption capacity of the composite absorbents. All the absorption tests were carried out at room temperature. The maximum absorption capacities of the absorbents for the organic solvents were reached in few seconds whereas it took few minutes for those of the tested hydrocarbons. The Q value is a key parameter for an absorbent for collection of hydrocarbons. The Q values of DDA-GO/PE-1 and DDA-GO/PE-2 (including silicone hydrocarbons, engine hydrocarbons, diesel, THF, toluene, cyclohexane, hexane and decane, heptane, hexane, cyclohexane, toluene, and xylene) were determined and the results were presented in Figure 5.9. The absorption capacity is greatly dependent on the porosity of the absorbent. More porous structures will afford a higher liquid absorption. Therefore, absorbents with greater hydrophobicity will absorb hydrocarbons more easily and retrieve hydrocarbons from water more efficiently. The prepared DDA-GO/PE-2 displayed better absorption capacity than the DDA-GO/PE-1 with the former Q value (from 40 to 78 times its original weight) while the latter showed Q value (ranging from 38.5 to 71 times its own weight) for various organic liquid samples tested. Earlier reports from the literature also revealed the Q value of an absorbent material could be correlated with the absorbate viscosity and density [179]. In the course of absorption, the organic solvents or the hydrocarbons percolated the pores of the 3D network of the DDA-GO/PE. The density of the percolated hydrocarbons determined the absorbent Q value when its porosity was saturated by the absorbates. Significantly, the DDA-GO/PE-2 showed greater absorption capacity than many sorbents in previous reports, such as polymers (5-25)[157], polydimethylsiloxane sponge (4-11 times)[158], graphene coated Poly(ethylene terephthalate)(18-34 times)[180], reduced GO foams (5-40 times)[159], and chitin sponge (30-60

times)[160]. However, the absorption capacity in other absorbents is higher than that of DDA-GO/PE-2 such as graphene modified foam (60- 140 times) [8], CNF aerogel (106-312 times) [161] and ultra-flyweight aerogel (215–913 times) [146]. The simple, cheap and and easy large scale preparation technique make DDA-GO/PE absorbent a promising candidate to be used as a absorbent for hydrocarbons spill cleanup and organic pollutants.

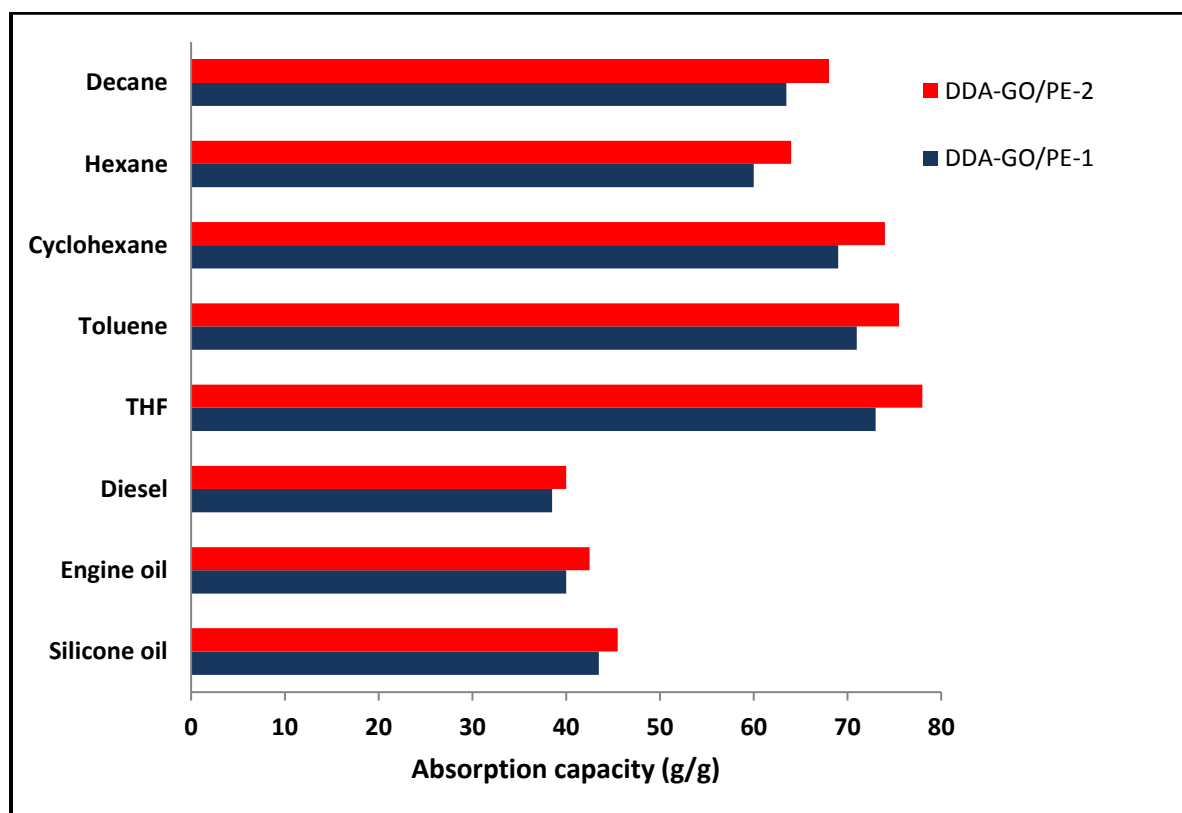


Figure 5.9: Absorption capacities of the GO-DDA/PE-1 and GO-DDA/PE-2 absorbents for the selected hydrocarbons and organic solvents.

5.3.6 Hydrocarbons-Water Separation

The GO-DDA/PE-2 absorbent showed high repulsion for water from hydrocarbons or organic solvents efficiently due its hydrophobic characteristics. To show its potential for application as sorbent for hydrocarbons spill cleanup, an hydrocarbons-water selective absorption test was important. As displayed in Figure 5.10, when a filter bag containing a desired amount of GO-DDA/PE-2 was introduced to the surface of diesel/ water mixture, the diesel on the surface of water was swiftly absorbed into the 3D network pores of GO-DDA/PE-2 and was wholly removed by GO-DDA/PE-2 within a short period of time. For a clear visual observation, the organic solvent and water were respectively coloured with Sudan I and methylene blue. After the separation, no trace of red hydrocarbons was seen in the water by visual inspection (Figure 5.10 a-f), thereby showing high separation ability. Similar experiment was conducted for the separation of decane/water mixture (Figure 5.10g-l).The superoleophilic-superhydrophobic feature of the as-prepared DDA-GO/PE-2 can be noticed from these images. Together with outstanding hydrocarbons selectivity, DDA-GO/PE-2 exhibits a huge promising application for highly efficient hydrocarbons or organic solvent collection.

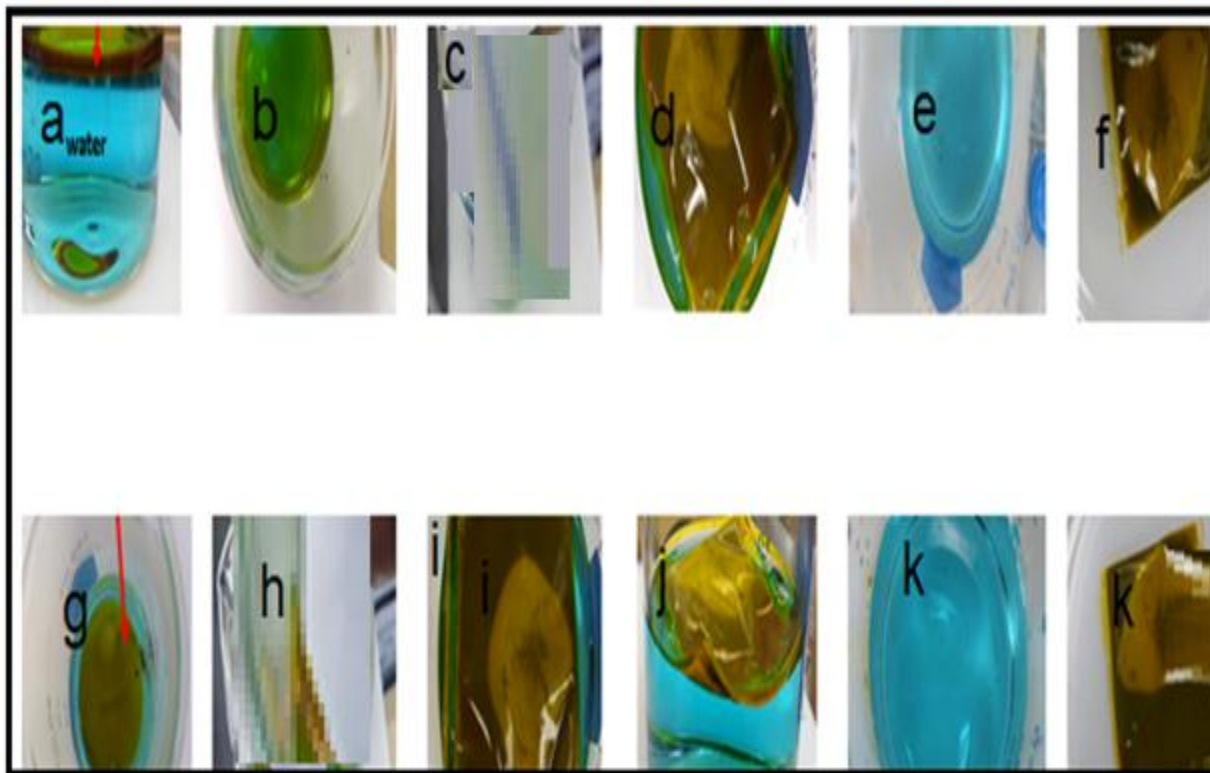


Figure 5.10: Pictures showing the process of selective absorption of diesel hydrocarbons (a-f) and decane (g-l) on the water surface (both hydrocarbons dyed with Sudan I dye and water coloured methylene blue dye) by DDA-GO/PE-2.

To further elucidate the hydrocarbons retrieval process with DDA-GO/PE-2 absorbent, the percentage recovery of hydrocarbons or organic solvent from water was measured and the outcomes are presented in Figure 5.11a. The recovery percentages of DDA-GO/PE-2 for all the tested sample hydrocarbons and organic solvents were from 92% in hexane up to 99% in silicone hydrocarbons. From the application perspective, absorbent's reusability is another key prerequisite for hydrocarbons-spill cleanup. To evaluate this, absorption-desorption tests was carried out on the DDA-GO/PE-2 absorbent for at least 10 cycles and the outcomes are shown in Figure 5.12. The hydrocarbons or organic solvent-laden absorbent was desorbed by squeezing. The reusability experiment revealed a very stable absorption capacity of DDA-GO/PE-2 absorbent in which the absorption capacity of over 90% was sustained for at least 10 cycles of absorption-desorption experiments.

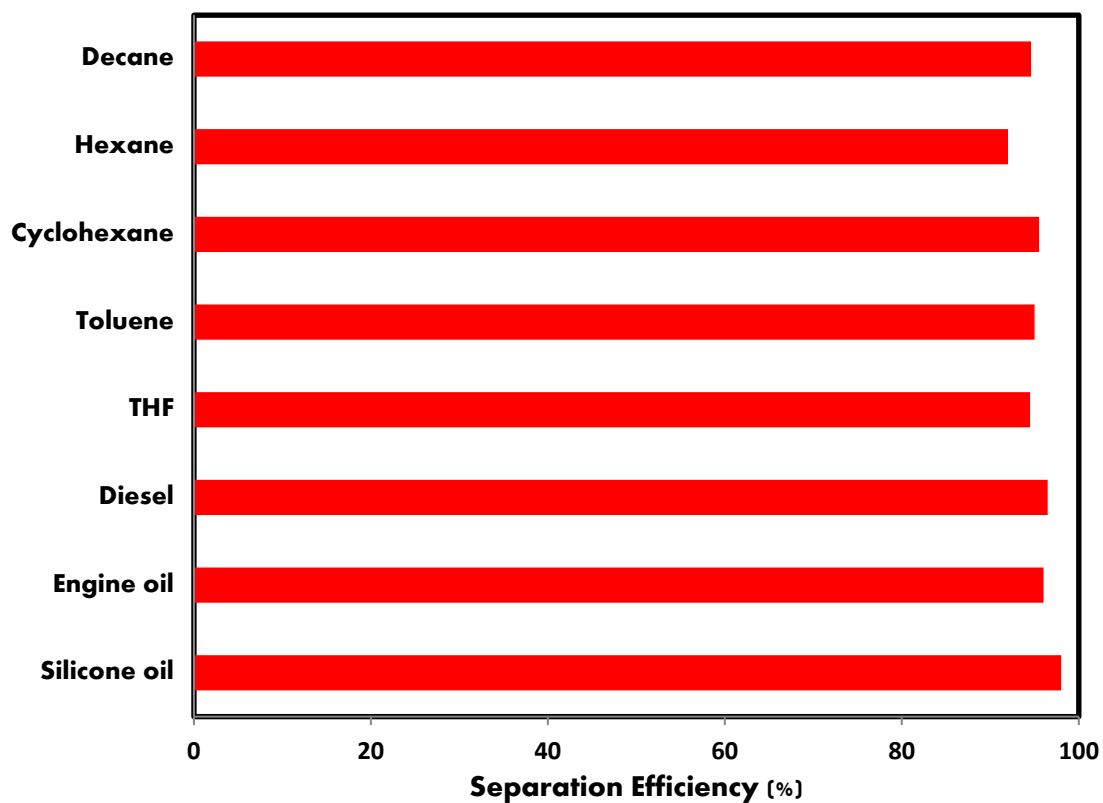


Figure 5.11: The percentage recovery of the DAA-GO/PE-2 absorbent for different types of hydrocarbons/water mixture.

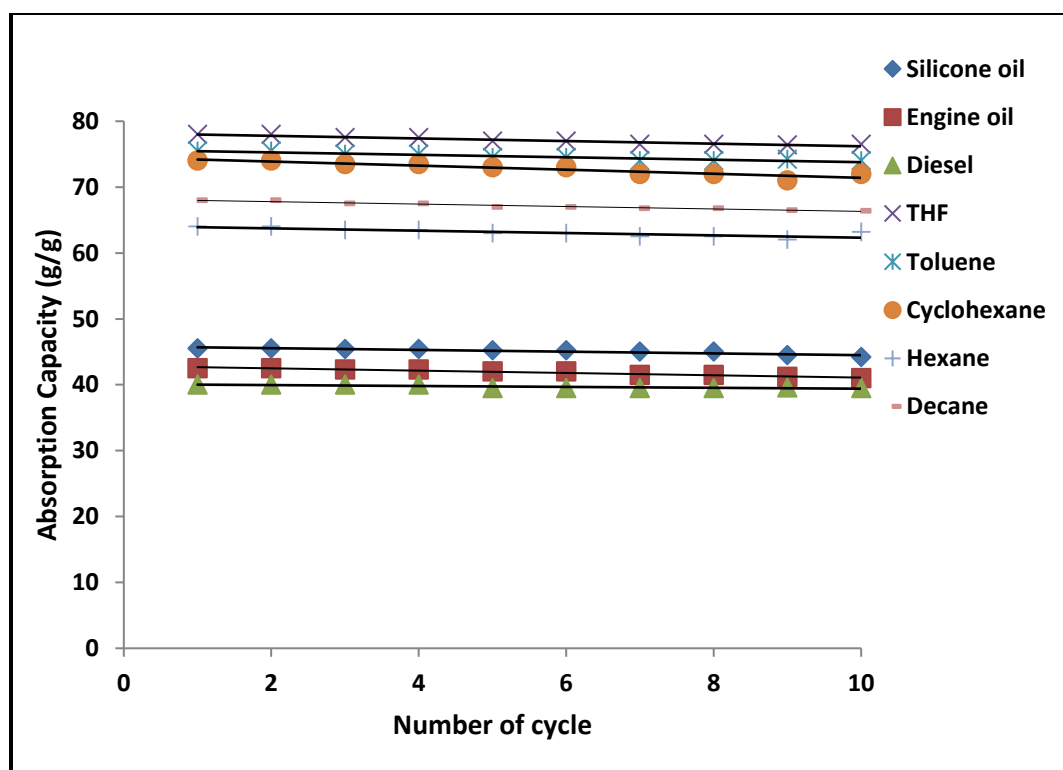


Figure 5.12: Absorption capacity of DDA-GO/PE-2 for 10 cycles of hydrocarbons-water separation.

10. CHAPTER 6

CONCLUSION

In summary, the fabrications of three sets of novel, low cost, efficient, hydrophobic and oleophilic carbon-based absorbents for effective retrieval of some selected hydrocarbons and organic solvents from the surface of water were reported. Firstly, the MWCNTs-LA was prepared by treating the pristine MWCNTs with an electrophilic reagent (NaOH) under sonication in order to attach hydroxyl groups on their surface. The LA was successfully grafted onto the surface of the MWCNTs via esterification reaction between the attached hydroxyl groups and the carboxylic acid groups on the LA chains, thereby conferring hydrophobic properties to the functionalized MWCNTs. The prepared absorbents demonstrated good hydrophobic/oleophilic property and excellent absorption capacities (20-33.5 times weight gain) for all the model hydrocarbons samples. The separation efficiency of up to 99% was recorded specifically by the best performing MWCNTs-LA2 composite. Next, two alkylamines-HA and DDA- were successfully grafted onto the surface of the GO via simple amidation reaction and subsequent chemical reduction. The prepared absorbents-FGOHA and FGODDA-demonstrated superoleophilic property and excellent absorption capacities (31.2-64 times weight gain) for the engine hydrocarbons and for the selected non polar solvents and the separation efficiency of up to 99.8% was recorded specifically by best performing FGODDA absorbent. The modified GO absorbents can separate hydrocarbons from hydrocarbons–

water mixtures with high selectivity. Lastly, for DDA-GO/PE composites, DDA was successfully grafted onto the surface of the GO via nucleophilic substitution and amidation reaction between the amino group of DDA and the GO epoxy and carboxylic acid groups. Further modification of the DDA-GO by PE through solution mixing method synergistically enhanced surface hydrophobicity and hydrocarbons/water separation efficiency. The prepared absorbents demonstrated superhydrophobic-superoleophilic property with excellent absorption capacities (38.5-78 times weight gain) for various hydrocarbons and organic solvent samples. The percentage recovery of up to 99% was recorded specifically by the best performing DDA-GO/PE-2 composite. All the three sets of the modified carbon-derived absorbents showed potential to separate model hydrocarbons samples from hydrocarbons–water mixtures with high selectivity, high separation efficiency, stable performance, and acceptable recyclability, which are promising for the applications in the recovery of hydrophobic hydrocarbons and organic solvents from water.

References

- [1] Kabiri, S.; Tran, D. N.; Altalhi, T.; Losic, D. Outstanding Adsorption Performance of Graphene–Carbon Nanotube Aerogels for Continuous Hydrocarbons Removal. *Carbon*. **2014**, 80, 523.
- [2] Aguilera F.; Mendez J.; Pasaro E.; Laffon B. Review on the effects of exposure to spilled hydrocarbons on human health. *J. Appl. Toxicol.* **2010**, 30, 291.
- [3] Gupta, R.K.; Dunderdale, G.J.; England, M.W.; Hozumi, A. Hydrocarbons/Water Separation Techniques: A Review of Recent Progresses and Future Directions, *J. Mater. Chem. A* **2017**, 5, 16025.
- [4] Saleh T.A.; Baig N.; Efficient Chemical Etching Procedure for the Generation of Superhydrophobic Surfaces for Separation of Hydrocarbons from Water. *Prog. Org. Coat.* **2019**, 133, 27.
- [5] Mullin, J. V.; Champ, M. A. Introduction/Overview to In Situ Burning of Hydrocarbons Spills. *Spill Sci. Technol. Bull.* **2003**, 8, 323.
- [6] Salanitro, J. P.; Dorn, P. B.; Huesemann, M. H.; Moore, K. O.; Rhodes, I. A.; Rice Jackson, L. M.; Vipond, T. E.; Western, M. M.; Wisniewski, H. L. Crude Hydrocarbons Hydrocarbon Bioremediation and Hydrocarbons Ecotoxicity Assessment. *Environ. Sci. Technol.* **1997**, 31, 1769.
- [7] Zhongxin, X.; Yingze, C.; Na, L.; Lin, F.; Lei, J. Special wettable materials for hydrocarbons/water separation. *J. Mater. Chem. A*. **2014**, 2, 2445.
- [8] Haiguang, Z.; Dongyun, C.; Wei, A.; Najun, L.; Qingfeng, X.; Hua, Li.; Jinghui, H.; Jianmei Lu, A. Robust and Cost-Effective Superhydrophobic Graphene Foam for Efficient Hydrocarbons and Organic Solvent Recovery. *Small*. **2015**, 11(39), 5222.
- [9] Kujawinski, E. B.; Kido Soule, M. C.; Valentine, D. L.; Boysen, A.K.; Longnecker, K.; Redmond, M. C. Fate of dispersants associated with the Deepwater Horizon hydrocarbons spill. *Environ. Sci. Technol.* **2011**, 45, 1298.
- [10] Gui, X.; Zeng, Z.; Lin, Z.; Gan, Q.; Xiang, R.; Zhu, Y.; Cao, A.; Tang, Z. Magnetic and highly recyclable macroporous carbon nanotubes for spilled hydrocarbons sorption and separation. *ACS Appl. Mater. Interfaces* **2013**, 5, 5845.
- [11] Hashim, D. P.; Narayanan, N. T.; Romo-Herrera, J. M.; Cullen, D. A.; Hahm, M. G.; Lezzi, P.; Suttle, J. R.; Kelkhoff, D.; Munoz-Sandoval, E.; Ganguli, S.; Roy, A. K.; Smith, D. J.; Vajtai, R.; Sumpter, B. G.; Meunier, V.; Terrones, H.; Terrones, M.; Ajayan, P. M. Covalently bonded three-dimensional carbon nanotube solids via boron induced nanojunctions. *Sci. Rep.* **2012**, 2, 363.
- [12] Song, J.; Li, S.; Zhao, C.; Lu, Y.; Zhao, D.; Sun, J. et al. A superhydrophilic cement-coated mesh: an acid, alkali, and organic reagent-free material for hydrocarbons/water separation. *Nanoscale* **2018**, 10, 1920–9.

- [13] Baig, N., Alghunaimi, F.I., Saleh, T.A. Hydrophobic and Oleophilic Carbon nanofiber Impregnated Styrofoam for Hydrocarbons and Water separation: A green technology. *Chem. Eng. J.* **2019**, 360, 1613.
- [14] You H, Jin Y, Chen J, Li C. Direct coating of a DKGM hydrogel on glass fabric for multifunctional hydrocarbons-water separation in harsh environments. *Chem. Eng. J.* **2018**, 334, 2273.
- [15] Baig, N., Saleh, T.A. Novel hydrophobic macroporous polypropylene monoliths for efficient separation of hydrocarbons. *Composites Part B*, **2019**, 173, 106805.
- [16] Cho,E.C.;Chang-Jian,C.W.;Hsiao,Y.S.;Lee,K.C.;Huang,J. H. Interfacial engineering of melamine sponges using hydrophobic TiO₂ nanoparticles for effective hydrocarbons/water separation. *J. Taiwan Inst. Chem. Eng.* **2016**, 67, 476–483.
- [17] Oribayo, O.; Pan, Q.; Feng, X.; Rempel, G. L. Hydrophobic Surface Modification of FMSS and Its Application as Effective Sorbents for Hydrocarbons Spill Clean-Ups and Recovery. *AIChE J.* **2017**, 63, 4090.
- [18] Zhang, J., Seeger, S. Polyester materials with superwetting silicone nanofilaments for Hydrocarbons/Water separation and selective hydrocarbons absorption, *Adv. Funct. Mater.* **2011**, 21, 4699.
- [19] Qin, Z., Xiang, H., Liu, J., Zeng, X. High-performance hydrocarbons-water separation polytetrafluoroethylene membranes prepared by picosecond laser direct ablation and drilling. *Mater. Design.* **2019**, 184, 108200.
- [20] De Gisi, S., Lofrano, G., Grassi, M., Notarnicola, M. Characteristics and adsorption capacities of low-cost sorbents for wastewater treatment: a review *Sustain. Mater. Technol.* **2016**, 9, 10.
- [21] Ahmaruzzaman, M. Industrial wastes as low-cost potential adsorbents for the treatment of wastewater laden with heavy metals *Adv. Colloid Interface Sci.* **2011**, 166, 36.
- [22] Nguyen, D. D.; Tai, N.; Lee, S.; Kuo, W. Superhydrophobic and Superoleophilic Properties of Graphene-Based Sponges Fabricated Using a Facile Dip Coat Method. *Energy Environ. Sci.* **2012**, 5, 7908.
- [23] Sayari, A., Hamoudi, S., Yang, Y. Applications of Pore-Expanded Mesoporous Silica. 1. Removal of Heavy Metal Cations and Organic Pollutants from Wastewater. *Chem. Mater.* **2005**, 17,212.
- [24] Wu, J., Wang, N., Wang, L., Dong, H., Zhao, Y., Jiang, L. Electrospun Porous Structure Fibrous Film with High Adsorption Capacity. *ACS Appl. Mater. Interfaces.* **2012**, 4, 3207.
- [25] Walcarius, A., Mercier, L. Mesoporous organosilica adsorbents: nanoengineered materials for removal of organic and inorganic pollutants. *J. Mater. Chem.* **2010**, 20, 4478.
- [26] Zhou X.-M Chuai, C.-Z. Synthesis and characterization of a novel high-hydrocarbons-absorbing resin *J. Appl. Polym. Sci.*, **2010**, 115, 3321.
- [27] Janout, V., Myers, S. B., Register R. A., Regen, S. L. Self-cleaning resins. *J. Am. Chem. Soc.* **2007**, 129, 5756.

- [28] Hayase, G.; Kanamori, K.; Fukuchi, M.; Kaji, H.; Nakanishi, K. Facile Synthesis of Marshmallow-like Macroporous Gels Usable under Harsh Conditions for the Separation of Ions and Water, *Angew. Chemie Int. Ed.* **2013**, 52, 1986.
- [29] Chu, Y., Pan, Q. Three-Dimensionally Macroporous Fe/C Nanocomposites as Highly Selective Hydrocarbons-Absorption Materials *ACS Appl. Mater. Interfaces*, **2012**, 4, 2420.
- [30] Tao, S., Wang, Y., An, Y. Superwetting monolithic SiO₂ with hierarchical structure for hydrocarbons removal. *J. Mater. Chem.* 2011, 21, 11901.
- [31] Zhang, L.; Li, H.; Lai, X.; Su, X.; Liang, T.; Zeng, X. Thiolated graphene-based Superhydrophobic Sponges for Pollutants -Water Separation, *Chem. Eng. J.* **2017**, 316, 736.
- [32] Qiang, F.; Hu, L.L.; Gong, L.X.; Zhao, L.; Li, S.N.; Tang, L.C. Facile Synthesis of Super-Hydrophobic, Electrically Conductive and Mechanically Flexible Functionalized Graphene Nanoribbon/Polyurethane Sponge For Efficient Pollutants/Water Separation At Static and Dynamic States, *Chem. Eng. J.* **2018**, 334, 2154.
- [33] Lee, C.H.; Johnson, N.; Drelich, J.; Yap, Y. K. The Performance of Superhydrophobic and Superoleophilic Carbon Nanotube Meshes in Water– Pollutants Filtration, *Carbon.* **2011**, 49, 669.
- [34] Liu, H.; Wang, Y.; Yang, M.; He, Q. Evaluation of Hydrophobic Polyurethane Foam as Sorbent Material for Hydrocarbons Spill Recovery. *J. Macromol. Sci.* **2014**, 51, 88.
- [35] Deschamps, G., Caruel, H., Borredon, M.E., Bonnin, C., Vignoles, C. Hydrocarbons removal from water by selective sorption on hydrophobic cotton fibers. 1. Study of sorption properties and comparison with other cotton fiber-based sorbents. *Environ. Sci. Technol.* **2003**, 37, 1013.
- [36] Al-Jammal, N., Juzsakova, T., Zsirka, B., Sebestyén, V., Németh, J., Cretescu, I., Halmágyi, T., Domokos, E., Rédey, A. Modified Jordanian zeolitic tuff in hydrocarbon removal from surface water. *J. Environ. Manage.* **2019**, 239, 333.
- [37] Xue, Z., Cao, Y., Liu, N., Feng, L., Jiang, L. Special wettable materials for hydrocarbons/water separation. *J. Mater. Chem.A.* **2014**, 2, 2445.
- [38] Dong, X.; Chen, J.; Ma, Y.; Wang, J.; Chan-Park, M. B.; Liu, X.; Wang, L.; Huang, W.; Chen, P. Superhydrophobic and Superoleophilic Hybrid Foam of Graphene and Carbon nanotube for Selective Removal of Hydrocarbons or Organic Solvents from the Surface of Water. *Chem. Commun.* **2012**, 48, 10660.
- [39] Zhang, X.; Liu, D.; Ma, Y.; Nie, J.; Sui, G. Super-hydrophobic graphene coated polyurethane (GN@PU) sponge with great hydrocarbons-water separation performance. *Appl. Surf. Sci.* **2017**, 422, 116.
- [40] Ge, B.; Zhang, Z.; Zhu, X.; Men, X.; Zhou, X.; Xue, Q. A graphene coated cotton for hydrocarbons/water separation. *Compos. Sci. Technol.* **2014**, 102, 100.
- [41] Ge, J.; Shi, L. A.; Wang, Y. C.; Zhao, H. Y.; Yao, H. B.; Zhu, Y. B.; Zhang, Y.; Zhu, H. W.; Wu, H. A.; Yu, S. H. Joule-heated graphene-wrapped sponge enables fast clean-up of viscous crude-hydrocarbons spill. *Nat. Nanotechnol.* **2017**, 12, 434.

- [42] Javadi, A.; Zheng, Q.; Payen, F.; Javadi, A.; Altin, Y.; Cai, Z.; Sabo, R.; Gong, S. Polyvinyl alcohol-cellulose nanofibrils-graphene oxide hybrid organic aerogels. *ACS Appl. Mater. Interfaces* **2013**, 5, 5969.
- [43] Le, V.T., Ngo, C.L. Le, Q.T., Ngo, T.T., Nguyen, D.N., Vu, M.T. Surface modification and functionalization of carbon nanotube with some organic compounds. *Adv. Nat. Sci. Nanosci. Nanotechnol.* **2013**, 4, 035017.
- [44] Meng, L., Fu, C., Lu, Q. Advanced technology for functionalization of carbon nanotubes, *Prog. Nat. Sci.* **2009**, 19, 801.
- [45] Hirsch, A. Functionalization of single-walled carbon nanotubes, *Minireview.* **2002**, 41,1853.
- [46] Liu, K.S, Yao, X., Jiang, L. Recent developments in bio-inspired special wettability. *Chem. Soc. Rev.* **2010**, 39, 3240.
- [47] Liu, K.S., Cao, M. Y., Fujishima, A., Jiang, L. Bio-Inspired Titanium Dioxide Materials with Special Wettability and Their Applications. *Chem. Rev.* **2014**, 114, 10044.
- [48] Zhang, S. N., Huang, J. Y., Chen Z., Lai, Y. K. Bioinspired Surfaces with Superwettability for Anti-Icing and Ice-Phobic Application: Concept, Mechanism, and Design *Small.* **2017**, 13, 1602992
- [49] Barthlott, W., Neinhuis, C. Purity of the sacred lotus, or escape from contamination in biological surfaces. *Planta* **1997**, 202, 1.
- [50] Pan, Z.; Cheng, F.; Zhao, B. Bio-Inspired Polymeric Structures with Special Wettability and Their Applications: An Overview. *Polymers.* **2017**, 9, 725.
- [51] Feng, X.J.; Jiang, L. Design and creation of superwetting/antiwetting surfaces. *Adv. Mater.* **2010**, 18, 3063.
- [52] Feng, L.; Li, S.; Li, Y.; Li, H.; Zhang, L.; Zhai, J.; Song, Y.; Liu, B.; Jiang, L.; Zhu, D. Super-Hydrophobic Surfaces: From Natural to Artificial. *Adv. Mater.* **2002**, 14, 1857.
- [53] Liu, M.; Wang, S.; Wei, Z.; Song, Y.; Jiang, L. Bioinspired Design of a Superoleophobic and Low Adhesive Water/Solid Interface. *Adv. Mater.* **2009**, 21, 665.
- [54] Xue, Z.; Wang, S.; Lin, L.; Chen, L.; Liu, M.; Feng, L.; Jiang, L. A novel superhydrophilic and underwater superoleophobic hydrogel-coated mesh for hydrocarbons/water separation. *Adv. Mater.* 2011, 23, 4270.
- [55] Jung, S., Tiwari, M. K., Doan N. V., Poulikakos, D. Mechanism of Supercooled Droplet Freezing on Surfaces. *Nat. Commun.*, **2012**, 3, 615.
- [56] Huang, J. Y., Lai, Y. K., Pan, F., Yang, L., Wang, H., Zhang, K. Q., Fuchs H., Chi, L. F. Multifunctional Superamphiphobic TiO₂ Nanostructure Surfaces with Facile Wettability and Adhesion Engineering. *Small*, **2014**, 10, 4865–4873.
- [57] Feng, L., Song, Y. L., Zhai, J., Liu, B.Q., Xu, J., Jiang, L., Zhu, D. B. Creation of a Superhydrophobic Surface From an Amphiphilic Polymer. *Angew. Chem., Int. Ed.* **2003**, 42, 800.
- [58] Gao, X. F., Yan, X., Yao, X., Xu, L., Zhang, K., Zhang, J. H., Yang B., Jiang, L. The dry-style antifogging properties of mosquito compound eyes and artificial analogues prepared by soft lithography. *Adv. Mater.* **2007**, 19, 2213.

- [59] Bai, H., Ju, J., Zheng, Y. M., Jiang, L. Functional Fibers with Unique Wettability Inspired by Spider Silks. *Adv. Mater.* **2012**, 24, 2786.
- [60] Bixler G.D., Bhushan, B. Rice- and butterfly-wing effect inspired self-cleaning and low drag micro/nanopatterned surfaces in water, hydrocarbons, and air flow. *Nanoscale*. **2014**, 6, 76.
- [61] Wang, S., Jiang, L. Definition of Superhydrophobic States. *Adv. Mater.* 2007, 19, 3423.
- [62] Xie, Q.D., Xu, J., Feng, L., Jiang, L., Tang, W. H., Luo X. D., Han, C. C. Facile Creation of a Super-Amphiphobic Coating Surface with Bionic Microstructure. *Adv. Mater.* **2004**, 16, 302.
- [63] Ge, M., Cao, C., Huang, J., Zhang, X., Tang, Y., Zhou, X., Zhang, K., Chen, Z., Lai, Y. Rational design of materials interface at nanoscale towards intelligent hydrocarbons–water separation. *Nanoscale Horiz.*, **2018**, 3, 235.
- [64] Gu, J. C., Xiao, P., Chen, P., Zhang, L., Wang, H. L., Dai, L.W., Song, L. P, Huang, Y. J., Zhang, J. W., and Chen, T. Functionalization of biodegradable PLA nonwoven fabric as superoleophilic and superhydrophobic material for efficient hydrocarbons absorption and hydrocarbons/water separation. *ACS Appl. Mater. Interfaces*, **2017**, 9, 5968.
- [65] Li, G. Q., Fan, H., Ren, F. F., Zhou, C., Zhang, Z., Xu, B., Wu, S. Z., Hu, Y. L., Zhu, W. L., Li, J. W., Zeng, Y. S., Li, X. H., Chua J. R., Wu, D. Multifunctional ultrathin aluminum hydrocarbons: hydrocarbons/water separation and particle filtration. *J. Mater. Chem. A*. **2016**, 4, 18832.
- [66] Gao, S., Huang, J., Li, S., Liu, H., Li, F., Chen, Y., Chen, G., Lai, Y. Facile construction of robust fluorine-free superhydrophobic TiO₂@fabrics with excellent anti-fouling, water–hydrocarbons separation and UV-protective properties. *Mater. Des.* **2017**, 128, 1
- [67] Zhang, S.N., Huang, J.Y., Cheng, Y., Yang, H., Chen, Z., Lai, Y.K. Bioinspired surfaces with superwettability for anti-icing. *Small* 2017, 13, 1701867.
- [68] Xu, Z. G., Zhao, Y., Wang, H.X., Wang X.G., Lin, T. A. Superamphiphobic Coating with an Ammonia-Triggered Transition to Superhydrophilic and Superoleophobic for Hydrocarbons-Water Separation. *Angew. Chem., Int. Ed.* **2015**, 54, 4527.
- [69] Yang, J., Song, H. J., Yan, X. H., Tang H., Li, C. S. Superhydrophilic and superoleophobic chitosan-based nanocomposite coatings for hydrocarbons/water separation. *Cellulose*, **2014**, 21, 1851.
- [70] Yang, J., Zhang, Z. Z., Xu, X. H., Zhu, X.T., Men X. H., Zhou, X. Y. Superhydrophilic–superoleophobic coatings. *J. Mater. Chem.* **2012**, 22, 2834.
- [71] Su, C., Yang, H., Song, S., Lu, B., Chen, R. A magnetic superhydrophilic/oleophobic sponge for continuous hydrocarbons–water separation. *Chem. Eng. J.* **2017**, 309, 366.
- [72] Zhang, W.B., Zhu, Y. Z., Liu, X., Wang, D., Li, J. Y., Jiang, L., Jin, J. Salt-induced Fabrication of Superhydrophilic and Underwater Superoleophobic PAA-g-PVDF Membranes for Effective Separation of Hydrocarbons-In-Water Emulsions. *Angew. Chem., Int. Ed.* **2014**, 53, 856.
- [73] Liu, X. L., Zhou, J., Xue, Z. X., Gao, J., Meng, J. X., Wang S. T., Jiang, L. Clam’s Shell Inspired High-Energy Inorganic Coatings with Underwater Low Adhesive Superoleophobicity. *Adv. Mater.* **2012**, 24, 3401.

- [74] Chaudhary, J.P.; Nataraj, S.K.; Gogda, A.; Meena, R. Bio-based superhydrophilic foam membranes for sustainable hydrocarbons–water separation. *Green Chem.* **2014**, *16*, 4552.
- [75] Zhou, T.; Yang, J.; Zhu, D.; Zheng, J.; Handschuh-Wang, S.; Zhou, X.; Zhang, J.; Liu, Y.; Liu, Z.; He, C.; et al. Hydrophilic Sponges for Leaf-Inspired Continuous Pumping of Liquids. *Adv. Sci.* **2017**, *4*, 1700028.
- [76] Dong, Y., Li, J., Shi, L., Wang, X., Guo, Z., Liu, W. Underwater superoleophobic graphene oxide coated meshes for the separation of hydrocarbons and water. *Chem. Commun.*, **2014**, *50*, 5586.
- [77] Fan, J. B., Song, Y. Y., Wang, S. T., Meng, J. X., Yang, G., Guo, X. L., Feng L., Jiang, L. Directly Coating Hydrogel on Filter Paper for Effective Hydrocarbons–Water Separation in Highly Acidic, Alkaline, and Salty Environment. *Adv. Funct. Mater.*, **2015**, *25*, 5368.
- [78] Gupta, R.K., Dunderdale, G.J., England, M.W., Hozumi, A. Hydrocarbons/water separation techniques: A review of recent progresses and future directions. *J. Mater. Chem. A* **2017**, *5*, 16025.
- [79] Lei, Z., Zhang, G., Deng, Y., Wang, C. Thermoresponsive Melamine Sponges with Switchable Wettability by Interface-Initiated Atom Transfer Radical Polymerization for Hydrocarbons/Water Separation. *ACS Appl. Mater. Interfaces.* **2017**, *9*, 8967.
- [80] Li, L., Liu, L., Lei, J., He, J., Li, N., Pan, F. Intelligent sponge with reversibly tunable super-wettability: Robust for effective hydrocarbons–water separation as both the absorber and filter tolerate fouling and harsh environments. *J. Mater. Chem. A.* **2016**, *4*, 12334.
- [81] Lei, Z., Zhang, G., Deng, Y., Wang, C. Surface modification of melamine sponges for pH-responsive hydrocarbons absorption and desorption. *Appl. Surf. Sci.* **2017**, *416*, 798.
- [82] Calcagnile, P., Fragouli, D., Bayer, I. S., Anyfantis G.C., Martiradonna, L., Cozzoli, P. D., Cingolani, R., Athanassiou, A. Magnetically driven floating foams for the removal of hydrocarbons contaminants from water. *ACS Nano*, **2012**, *6*, 5413.
- [83] Lin, X., Lu, F., Chen, Y., Liu, N., Cao, Y., Xu, L., Zhang, W., Feng, L. Electricity-induced switchable wettability and controllable water permeation based on 3D copper foam. *Chem. Commun.* **2015**, *51*, 16237.
- [84] Li, A., Sun, H.-X., Tan, D.-Z., Fan, W.-J., Wen, S.-H., Qing, X.-J., Li, G.-X., Li, S.-Y., Deng, W.-Q. Superhydrophobic conjugated microporous polymers for separation and adsorption. *Energy Environ. Sci.* **2011**, *4*, 2062.
- [85] Farag, R. K., El-Saeed, S.M. Synthesis and characterization of hydrocarbons sorbers based on docosanyl acrylate and methacrylates copolymers. *J. Appl. Polym. Sci.* **2008**, *109*, 3704.
- [86] Long-Yue M. and. Soo-Jin, P Superhydrophobic Carbon-Based Materials: A Review. *carbon Lett.* **2014**, *15*, 89–104.
- [87] Xue, Z., Cao, Y., Liu, N., Feng, L., Jiang, L. Special wettable materials for hydrocarbons/water separation. *J. Mater. Chem.A.* **2014**, *2*, 2445
- [88] Gupta, S., Tai, N.-H. Carbon materials as hydrocarbons sorbents: a review on the synthesis and performance. *J. Mater. Chem. A.* **2016**, *4*, 1550.

- [89] Noraniza, A.D., Buong, W. C., Nor, A.I., Zainal, A.T., Ernee N.M., Zurina, Z. A. Functionalizing Graphene Oxide with Alkylamine by Gamma-ray Irradiation Method. *J. Nanomater.* **2017**, 7, 135.
- [90] Zhu, Y., Murali, S., Cai, W., Li, X., Suk, J.W., Potts, J. R., Ruoff, R. S. Graphene and Graphene Oxide Synthesis. *Adv. Mater.* **2010**, 22, 3906.
- [91] Hernandez, Y.; Nicolosi, V.; Lotya, M.; Blighe, F.M.; Sun, Z.; De, S.; McGovern, I.T.; Holland, B.; Byrne, M.; Gun'Ko, Y.K.; et al. High-yield production of graphene by liquid-phase exfoliation of graphite. *Nat. Nanotechnol.* **2008**, 3, 563–568.
- [92] Dong, X., Chen, J., Ma, Y., Wang, J., Chan-Park, M. B., Liu, X., Wang, L., Huang, W., Chen, P. Superhydrophobic and Superoleophilic Hybrid Foam of Graphene and Carbon nanotube for Selective Removal of Hydrocarbons or Organic Solvents from the Surface of Water. *Chem. Commun.* 2012, 48, 10660.
- [93] Choucair, M., Thordarson, P., Stride, J.A. Gram-scale production of graphene based on solvothermal synthesis and sonication. *Nat. Nanotechnol.* **2009**, 4, 30.
- [94] Gao, W., Alemany, L. B., Ci, L. J., Ajayan, P. M. New Insights into the Structure and Reduction of Graphite Oxide. *Nat. Chem.* **2009**, 1, 403
- [95] Stankovich, S., Dikin, D. A., Piner, R. D., Kohlhaas, K. A., Kleinhammes, A., Jia, Y., Wu, Y., Nguyen, S. T., Ruoff, R. S. Synthesis of Graphene-Based Nanosheets via Chemical Reduction of Exfoliated Graphite Oxide. *Carbon* **2007**, 45, 1558.
- [96] McAllister, M. J., Li, J. L., Adamson, D. H., Schniepp, H. C., Abdala, A. A., Liu J., Herrera-Alonso, M., Milius, D. L., Car, R., Prud'homme, R. K., Aksay, I. A. Single Sheet Functionalized Graphene by Oxidation and Thermal Expansion of Graphite. *Chem. Mater.* **2007**, 19, 4396
- [97] Schniepp, H. C., Li, J. L., McAllister, M. J., Sai, H., Herrera-Alonso, M., Adamson, D. H., Prud'homme, R. K., Car, R., Saville, D. A., Aksay, I. A. Functionalized Single Graphene Sheets Derived from Splitting Graphite Oxide. *J. Phys. Chem. B* **2006**, 110, 8535.
- [98] Lerf, A., He, H. Y., Forster, M., Klinowski, J. Structure of Graphite Oxide Revisited. *J. Phys. Chem. B* **1998**, 102, 4477.
- [99] Zhang, X., Liu, D., Ma, Y., Nie, J., Sui, G. Super-hydrophobic graphene coated polyurethane (GN@PU) sponge with great hydrocarbons-water separation performance. *Appl. Surf. Sci.* **2017**, 422, 116.
- [100] Ge, B., Zhang, Z., Zhu, X., Men, X., Zhou, X., Xue, Q. A graphene coated cotton for hydrocarbons/water separation. *Compos. Sci. Technol.* **2014**, 102, 100.
- [101] Ge, J., Shi, L. A., Wang, Y. C., Zhao, H. Y., Yao, H. B., Zhu, Y. B., Zhang, Y., Zhu, H. W., Wu, H. A., Yu, S. H. Joule-heated graphene-wrapped sponge enables fast clean-up of viscous crude-hydrocarbons spill. *Nat. Nanotechnol.* **2017**, 12, 434.
- [102] Javadi, A.; Zheng, Q.; Payen, F.; Javadi, A.; Altin, Y.; Cai, Z.; Sabo, R.; Gong, S. Polyvinyl alcohol-cellulose nanofibrils-graphene oxide hybrid organic aerogels. *ACS Appl. Mater. Interfaces* **2013**, 5, 5969.

- [103] Peng, M., Chen, G., Zeng, G., Chen, A., He, K., Huang, Z., Hu, L., Shi, J., Li, H., Yuan, L., Huang, T. Superhydrophobic kaolinite modified graphene oxide-melamine sponge with excellent properties for hydrocarbons-water separation, *Appl. Clay Sci.* **2018**, 163, 63.
- [104] Ricky, T., Gregory, L., Alicia, V., Josh, B., Gordon, C., Aiping, Y. Introduction of an Enhanced Binding of Reduced Graphene Oxide to Polyurethane Sponge for Hydrocarbons Absorption. *Ind. Eng. Chem. Res.* **2015**, 54, 3657
- [105] Wang, J. L., Shi, Z. X., Fan, J. C., Ge, Y., Yin, J., Hu, G. Self-assembly of graphene into three-dimensional structures promoted by natural phenolic acids. *J. Mater. Chem.* **2012**, 22, 22459.
- [106] Li, J., Li, J.G., Meng, H., Xie, S. Y., Zhang, B. W., Li, L. F., Ma, H. J., Zhang, J.Y., Yu, M. Ultra-light, compressible and fire-resistant graphene aerogel as a highly efficient and recyclable absorbent for organic liquids. *J. Mater. Chem. A*, **2014**, 2, 2934.
- [107] Song, X.H., Lin, L.P., Rong, M.C., Wang, Y.R., Xie Z.X., Chen, X. Superhydrophobic and superoleophilic graphene aerogel for adsorption of hydrocarbons pollutants from water. *Carbon*, **2014**, 80, 174.
- [108] Zhao, Y., Hu, C.G., Hu, Y., Cheng, H.H., Shi G.Q., Qu, L. T. A versatile, ultralight, nitrogen-doped graphene framework. *Angew. Chem., Int. Ed.*, **2012**, 51, 11371.
- [109] Run, L., Caibao, C., Jing, L., Liming, X., Guyu, X., Deyue, Y. A facile approach to superhydrophobic and superoleophilic graphene/polymer aerogels *J. Mater. Chem. A*. **2014**, 2, 3057.
- [110] Jia, L.C., Jiao, Z.H., Yan, D.X., Li, Z.M. Octadecylamine Grafted Graphene Oxide Helps the Dispersion of Carbon Nanotubes in Ethylene Vinyl Acetate. *Polymers* **2017**, 9, 397.
- [111] Kuila, T., Bose, S., Mishra, A. K., Khanra, P., Kim, N. H., Lee, J. H. Effect of functionalized graphene on the physical properties of linear low density polyethylene nanocomposites. *Polym. Test.* **2012**, 31, 31.
- [112] Zhao, J., Wang, Z., White, J.C., Xing, B. Graphene in the Aquatic Environment: Adsorption, Dispersion, Toxicity and Transformation. *Environ. Sci. Technol.* **2014**, 48, 9995.
- [113] Yang, K., Xing, B. Adsorption of Organic Compounds by Carbon Nanomaterials in Aqueous Phase: Polanyi Theory and Its Application. *Chem. Rev.*, **2010**, 110, 5989.
- [114] Pei, Z., Li, L., Sun, L., Zhang, S., Shan, X., Yang, S., Wen, B. Adsorption characteristics of 1,2,4-trichlorobenzene, 2,4,6-trichlorophenol, 2-naphthol and naphthalene on graphene and graphene oxide. *Carbon*, **2013**, 51, 156.
- [115] Wang, J., Chen Z., Chen, B. Adsorption of Polycyclic Aromatic Hydrocarbons by Graphene and Graphene Oxide Nanosheets. *Environ. Sci. Technol.*, **2014**, 48, 4817.
- [116] Maphutha, S., Moothi, K., Meyyappan, M., Iyuke, S.E. A Carbon Nanotube-Infused Polysulfone Membrane with Polyvinyl Alcohol Layer for Treating Hydrocarbons-Containing Waste. *Water Sci. Rep.* **2013**, 3, 1509.
- [117] Gui, X., Li, H., Wang, K., Wei, J., Jia, Y., Li, Z., Fan, L., Cao, A., Zhu, H., Wu, D. Recyclable carbon nanotube sponges for hydrocarbons absorption. *Acta Mater.* **2011**, 59, 4798.

- [118] Al-Jammala , N., Abdullaha, T.A., Juzsakovaa, T., Zsirkaa, B., Cretescub, I., Vágvölgyic, V., Sebestyéna, V., Le Phuocd , C., Rasheede, R.T., Domokosa, E. Functionalized carbon nanotubes for hydrocarbon removal from water. *J. Environ.Chem.Eng.* **2020**, 8, 103570.
- [119] Sun, H., La, P., Zhu, Z., Liang, W., Yang, B., Zhao, X., Pei, C., Li, A. Hydrophobic carbon nanotubes for removal of hydrocarbons and organics from water. *J. Mater. Sci.*, **2014**, 49, 6855.
- [120] Wang, H., Wang, E., Liu, Z., Gao, D., Yuan, R., Sun, L., Zhu, Y. A novel carbon nanotubes reinforced superhydrophobic and superoleophilic polyurethane sponge for selective hydrocarbons–water separation through a chemical fabrication. *J. Mater. Chem. A*, **2015**, 3, 266.
- [121] Le, V.T., Ngo, C.L. Le, Q.T., Ngo, T.T., Nguyen, D.N., Vu, M.T. Surface modification and functionalization of carbon nanotube with some organic compounds. *Adv. Nat. Sci. Nanosci. Nanotechnol.* **2013**, 4, 035017.
- [122] Meng, L., Fu, C., Lu, Q. Advanced technology for functionalization of carbon nanotubes. *Prog. Nat. Sci.* **2009**, 19, 801.
- [123] Hirsch, A. Functionalization of single-walled carbon nanotubes, *Minireview*. 2002, 41, 1853.
- [124] Chang, S.E., Stone, J., Demes, K., Piscitelli M. Synthesis, part of a special feature on vulnerability and adaptation to hydrocarbons spills consequences of hydrocarbons spills: a review and framework for informing planning. *Ecol. Soc.* **2014**, 19, 26.
- [125] Toyoda, M., Inagaki, M. Heavy hydrocarbons sorption using exfoliated graphite new application of exfoliated graphite to protect heavy hydrocarbons pollution. *Carbon N. Y.* **2000**, 38, 199.
- [126] Allan, S. E., Smith, B. W., Anderson, K. A. Impact of the Deepwater Horizon Hydrocarbons Spill on Bioavailable Polycyclic Aromatic Hydrocarbons in Gulf of Mexico Coastal Waters. *Environ. Sci. Technol.* **2012**, 46, 2033.
- [127] Prendergast, D. P.; Gschwend, P. M. Assessing the Performance and Cost of Hydrocarbons Spill Remediation Technologies. *J. Cleaner Prod.* **2014**, 78, 233.
- [128] Jiang, Z., Tijing, L. D., Amarjargal, A., Park, C. H., An, K. J., Shon, H. K., Kim, C. S. Removal of hydrocarbons from water using magnetic bicomponent composite nanofibers fabricated by electrospinning. *Composites, Part B.* **2015**, 77, 311.
- [129] Wu, Z. Y., Li, C., Liang, H. W., Zhang, Y. N., Wang, X., Chen, J. F., Yu, S. H. Carbon nanofiber aerogels for emergent cleanup of hydrocarbons spillage and chemical leakage under harsh conditions. *Sci. Rep.* **2015**, 4, 4079.
- [130] Ajayan, P. M. Covalently bonded three-dimensional carbon nanotube solids via boron induced nanojunctions. *Sci. Rep.* **2012**, 2, 363.
- [131] Shen, J., Liu, A., Tu, Y., Foo, G., Yeo, C., Chan-Park, M. B., Jiang, R., Chen, Y. How carboxylic groups improve the performance of single-walled carbon nanotube electrochemical capacitors? *Energy Environ. Sci.* **2011**, 4, 4220.

- [132] Kang, S.Z., Yin, D.E., Li, X.Q., Mu, J. A facile preparation of multiwalled carbon nanotubes modified with hydroxyl groups and their high dispersibility in ethanol. *Colloids Surf. A.*, **2011**, 384, 363.
- [133] Yaghoubi, A., Alavi Nikje, M.M. Silanization of multi-walled carbon nanotubes and the study of its effects on the properties of polyurethane rigid foam nanocomposites. *Composites Part A*. **2018**, 109, 338.
- [134] Farbod, M., Khajepour Tadavani, S. Electrical properties and glass transition temperature of multiwalled carbon nanotube/polyaniline composites. *J. Non-Cryst. Solids*. **2012**, 358, 1339.
- [135] Edwards, E.R., Antunes, E.F., Botelho, E.C., Baldan, M.R., Corat, E.J. Evaluation of residual iron in carbon nanotubes purified by acid treatments. *Appl. Surf. Sci.* **2011**, 258, 641.
- [136] Feng, Y., Wei, R., Huang, Z., Zhang, X., Wang, G. Thermal properties of lauric acid filled in carbon nanotubes as shape-stabilized phase change materials. *Phys. Chem. Chem. Phys.* **2018**, 20, 7772.
- [137] Nguyen, P.Q.P., Hoang, A.T., Al-Tawaha, A.R.M.S. A Study of Hydrocarbons Absorbing Capacity of Cellulose-implemented Polyurethane for the Recovery of Hydrocarbons Spills. *International Journal of e-Navigation and Maritime Economy* .**2018**, 9, 025.
- [138] Peterson, C. H.; Rice, S. D.; Short, J. W.; Esler, D.; Bodkin, J. L.; Ballachey, B. E.; Irons, D. B. Long-term ecosystem response to the Exxon Valdez hydrocarbons spill. *Science*. **2003**, 302 (5653), 2082.
- [139] Aurell, J., Gullett, B. K. Aerostat Sampling of PCDD/PCDF Emissions from the Gulf Hydrocarbons Spill In Situ Burns. *Environ. Sci. Technol.* **2010**, 44 (24), 9431.
- [140] Zhu, Q., Pan, Q., Liu, F. Facile Removal and Collection of Hydrocarbons from Water Surfaces through Superhydrophobic and Superoleophilic Sponges. *J. Phys. Chem. C*. **2011**, 115, 17464
- [141] Sun, X.-F., Sun, R., Sun, J.-X. Acetylation of rice straw with or without catalysts and its characterization as a natural sorbent in hydrocarbons spill cleanup. *J. Agric. Food Chem.* **2002**, 50, 6428.
- [142] Sakthivel, T., Reid, D.L., Goldstein, I., Hench, L., Seal, S. Hydrophobic high surface area zeolites derived from fly ash for hydrocarbons spill remediation. *Environ. Sci. Technol.* **2013**, 47, 5843.
- [143] Reynolds, J.G., Coronado, P.R., Hrubesh, L.W. Hydrophobic aerogels for hydrocarbons-spill clean up—synthesis and characterization. *J. Non-Cryst. Solids*. **2001**, 292, 127.
- [144] Adebajo, M.O., Frost, R.L., Klopogge, J.T., Carmody, O., Kokot, S. Porous materials for hydrocarbons spill cleanup: a review of synthesis and absorbing properties. *J. Porous. Mater.* **2003**, 10, 159.
- [145] Ahmad, A., Sumathi, S., Hameed, B. Residual hydrocarbons and suspended solid removal using natural adsorbents chitosan, bentonite and activated carbon: a comparative study. *Chem. Eng. J.* **2005**, 108, 179.
- [146] Sun, H. Y., Xu, Z., Gao, C. Multifunctional, Ultra-Flyweight, Synergistically Assembled Carbon Aerogels. *Adv. Mater.* **2013**, 25 (18), 2554.

- [147] Daniel, R.; Sungjin, P., Christopher, W.; Rodney, S. The chemistry of graphene oxide. *Chem Soc Rev.* 2010, 39, 228.
- [148] Paulchamy, B., Arthi, G., Lignesh, B. D. A Simple Approach to Stepwise Synthesis of Graphene Oxide Nanomaterial. *J Nanomed. Nanotechnol.* **2015**, 6 (1), 1.
- [149] Peng-Gang, R., Hao, W.; Hua-Dong, H.; Ding-Xiang, Y.; Zhong-Ming, L. Characterization and performance of dodecyl amine functionalized graphene oxide and dodecyl amine functionalized graphene/high-density polyethylene nanocomposites: A comparative study. *J. Appl. Polym. Sci.* 2014, 131, 39803.
- [150] Compton, O.C., Dikin D. A., Putz K.W., Brinson L.C., Nguyen, S.T. Electrically conductive “alkylated” graphene paper via chemical reduction of amine-functionalized graphene oxide paper. *Adv Mater.* **2010**, 22, 892.
- [151] Diagboya, P. N., Olu-Owolabi, B. I., Adebowale, K. O. Synthesis of covalently bonded graphene oxide–iron magnetic nanoparticles and the kinetics of mercury removal. *RSC Adv.* **2015**, 5, 2536.
- [152] Xuezhong, G., Guozhen, L., Yingshun, Li., Denis, Y.W.Y., Wey, Y. T. Functionalized-Graphene Composites: Fabrication and Applications in Sustainable Energy and Environment *Chem. Mater.* **2016**, 28, 8082.
- [153] Lai , L.F., Chen, L.W., Zhan, D. et al. One-step synthesis of NH₂-graphene from in situ graphene-oxide reduction and its improved electrochemical properties. *Carbon.* **2011**, 49, 3250.
- [154] Gokhale, A. A., Lu, J., Lee, I. Immobilization of cellulase on magnetoresponsive graphene nano-supports. *J. Mol. Catal. B Enzym.* **2013**, 90, 76.
- [155] Zhu, C., Guo, S., Fang, Y., Dong, S. Reducing Sugar: New Functional Molecules for the Green Synthesis of Graphene Nanosheets. *ACS Nano.* **2010**, 4, 2429
- [156] Carreira, L., Mendes, L., Ribeiro, M., Sebastião, P. Organically-Expanded Graphite/Octadecylamine: Structural, Thermal and Relaxation Evaluation. *Mater. Sci. Appl.* **2013**, 4, 281.
- [157] Sonmez, H.B., Wudl, F. Cross-Linked Poly(orthocarbonate)s as Organic Solvent Sorbents. *Macromolecules.* **2005**, 38, 1623.
- [158] Choi, S. J., Kwon, T. H., Im , H., Moon , D. I., Baek, D. J., Seol, M. L., Duarte, J. P., Choi, Y. K. A polydimethylsiloxane (PDMS) sponge for the selective absorption of hydrocarbons from water. *ACS Appl. Mater. Interfaces.* **2011**, 3, 4552.
- [159] Niu, Z., Chen, J., Hng, H.H., Ma, J., Chen, X. A leavening strategy to prepare reduced graphene oxide foams. *Adv. Mater.* **2012**, 24, 4144 .
- [160] Duan, B., Gao, H., He, M., Zhang, L. Hydrophobic modification on surface of chitin sponges for highly effective separation of hydrocarbons. *ACS Appl. Mater. Interfaces.* **2014**, 6, 19933.
- [161] Wu, Z. Y., Li, C., Liang, H. W., Chen, J. F., Yu, S. H. Ultralight, flexible, and fire-resistant carbon nanofiber aerogels from bacterial cellulose. *Angew. Chem. Int.Ed.* **2013**, 52, 2925.

- [162] Li, J.J., Zhou, Y. N., Jiang, Z.D., Luo, Z. H. Electrospun fibrous mat with pH switchable superwettability that can separate layered hydrocarbons/water mixtures. *Langmuir*. **2016**, 32 13358
- [163] Li, H., Zheng, M., Ma, L., Zhu, C., Lu, S. Two-dimensional ZnO nanoflakes coated mesh for the separation of water and hydrocarbons. *Mater. Res. Bull.* **2013**, 48, 25.
- [164] Huang, L., Lau, S. P., Yang, H.Y., Leong, E.S.P., Yu, S.F., Prawer, S. Stable superhydrophobic surface via carbon nanotubes coated with a ZnO thin film, *J. Phys. Chem. B*, 109, 7746.
- [165] Yu, S., Tan, H., Wang, J., Liu, X., Zhou, K. High, porosity supermacroporous poly-styrene materials with excellent hydrocarbons–water separation and gas permeability properties. *ACS Appl.Mater.Interfaces*. **2015**, 7(12), 6745.
- [166] Lee, J. H., Tan, J. Y., Toh, C. T., Koenig, S. P., Fedorov, V. E., Castro Neto, A. H., Ozyilmaz, B. Nanometer thick elastic graphene engine. *Nano Lett.* **2014**, 14, 2677.
- [167] Withers, F., Bointon, T. H., Craciun, M. F., Russo, S. All Graphene Photodetectors. *ACS Nano*. **2013**, 7, 5052.
- [168] Yoo, J. J., Balakrishnan, K., Huang, J., Meunier, V., Sumpter, B. G., Srivastava, A., Conway, M., Reddy, A. L., Yu, J., Vajtai, R., Ajayan, P. M. Ultrathin planar graphene supercapacitors. *Nano Lett.* **2011**, 11, 1423.
- [169] Bi, H.; Xie, X.; Yin, K.; Zhou, Y.; Wan, S.; He, L.; Xu, F.; Banhart, F.; Sun, L.; Ruoff, R. S. Spongy Graphene as a Highly Efficient and Recyclable Sorbent for Hydrocarbons and Organic Solvents. *Adv. Funct. Mater.* 2012, 22, 4421.
- [170] Compton, O.C., Nguyen, S.T. Graphene oxide, highly reduced graphene oxide, and graphene: versatile building blocks for carbon-based materials. *Small*, **2010**, 6, 711.
- [171] Huang, H. D., Ren, P.-G., Chen, J., Zhang, W.-Q., Ji, X., Li, Z.M. High Barrier Graphene Oxide Nanosheet/Poly(vinyl alcohol) Nanocomposite Films. *J. Mater. Sci.* **2012**, 409, 156.
- [172] Niyogi, S., Bekyarova, E., Itkis, M. E., McWilliams, J. L., Hamon, M. A., Haddon, R. C. Solution properties of graphite and graphene. *J. Am. Chem. Soc.* **2006**, 128, 7720.
- [173] Gulmine, J.V., Janissek, P.R., Heise, H.M., Akcelrud, L. Polyethylene characterization by FTIR. *Polymer Testing*. **2002**, 21, 557.
- [174] Nethravathi, C., Rajamathi M. Chemically modified graphene sheets produced by the solvothermal reduction of colloidal dispersions of graphite oxide. *Carbon*. **2008**, 46 (14), 1994.
- [175] Sabet, M., Soleimani, H. The research design of graphene inclusion on LDPE characterization. *IJMME*. **2019**, 14, 9.
- [176] Tuinstra, F., Koenig J. L. Raman Spectrum of Graphite. *J. Chem. Phys.* **1970**, 53, 1126.
- [177] Paredes, J., Burghard, M., Martínez-Alonso, A. et al. Graphitization of carbon nanofibers: visualizing the structural evolution on the nanometer and atomic scales by scanning tunneling microscopy. *Appl. Phys. A*. **2005**, 80, 675.

- [178] Palomba, M., Longo, A., Carotenuto, G. Optical and electrical characterizations of graphene nanoplatelet coatings on low density polyethylene. *J. Vac. Sci. Technol. B.* **2018**, 36(1), 01A104.
- [179] Zhou, S., Jiang, W., Wang, T., Lu, Y. Highly Hydrophobic, Compressible, and Magnetic Polystyrene/Fe₃O₄/Graphene Aerogel Composite for Hydrocarbons–Water Separation. *Ind. Eng. Chem. Res.* **2015**, 54 (20), 5460.
- [180] Zhang, T., Xiao, C., Zhao, J., Cheng, J., Chen, K., Huang, Y. Graphene-Coated Poly(ethylene terephthalate) Nonwoven Hollow Tube for Continuous and Highly Effective Hydrocarbons Collection from the Water Surface. *ACS Omega.* **2019** 4 (4), 7237.
- [181] Parangusan, H., Ponnammma, D., Hassan, M.K., Adham, S., Al-Madeed, M.A. Designing Carbon Nanotube-Based Hydrocarbons Absorbing Membranes from Gamma Irradiated and Electrospun Polystyrene Nanocomposites. *Materials*, **2019**, 12, 709.
- [182] Lu, Y., Yuan, W. Superhydrophobic/Superoleophilic and Reinforced Ethyl Cellulose Sponges for Hydrocarbons/Water Separation: Synergistic Strategies of Crosslinking, Carbon Nanotube Composite, and Nanosilica Modification *ACS Appl. Mater. Interfaces*, **2017**, 9, 29167.
- [183] Gui, X., Zeng, Z., Lin, Z., Gan, Q., Xiang, R., Zhu, Y., Cao, A., Tang, Z. Magnetic and Highly Recyclable Macroporous Carbon Nanotubes for Spilled Hydrocarbons Sorption and Separation. *ACS Appl. Mater. Interfaces* **2013**, 5, 5845.
- [184] Huang, H., Wang, X., Liu, X., Li, Y., Sun, H., Li, Q. One-Step Solution-Immersion Process of Hydrophobic Octyl Graphene Oxide-Modified Nickel Foam for Highly Efficient Hydrocarbons–Water Separation. *ACS Omega* **2020**, 5, 766.
- [185] Mi, H-Y., Jing, X., Huang, H-X., Peng, X-F., Turng, L-S. Superhydrophobic Graphene/Cellulose/Silica Aerogel with Hierarchical Structure as Superabsorbents for High Efficiency Selective Hydrocarbons Absorption and Recovery. *Ind. Eng. Chem. Res.* **2018**, 57, 1745.
- [186] Periasamy, A.P., Wu, W-P., Ravindranath, R., Roy, P., Lin, G-L., Chang, H-T. Polymer/reduced Graphene Oxide Functionalized Sponges as superabsorbents for Hydrocarbons Removal and Recovery. *Mar. Pollut. Bull.* **2017**, 114, 888.
- [187] Chen, Y.; Tao, J.; Ezzeddine, A.; Mahfouz, R.; Al-Shahrani, A.; Alabedi, G.; Khashab, N. Superior Performance Nanocomposites from Uniformly Dispersed Octadecylamine Functionalized Multi-Walled Carbon Nanotubes. *C J. Carbon Res.* **2015**, 1, 58.
- [188] Shanmugharaj, A.M.; Yoon, J.H.; Yang, W.J.; Ryu, S.H. Synthesis, characterization, and surface wettability properties of amine functionalized graphene oxide films with varying amine chain lengths. *J. Colloid Interface Sci.* **2013**, 401, 148.

Vitae

Name : Abdullahi Biodun Olabintan |

Nationality : Nigerian |

Date of Birth : 6/9/1986 |

Email : deeunikchm@yahoo.com |

Address : 16, Olayinka street, Aboru, Alimosho, Lagos State, 100275 |

Academic Background :

2020: King Fahd University of Petroleum and Minerals (KFUPM). Dhahran, KSA.

M.Sc. Chemistry; CGPA: 3.821/4.0.

2019: Ladoke Akintola University of Technology (LAUTECH), Ogbomoso, Nigeria.

M.Tech. Physical Chemistry; Distinction.

2012: Ladoke Akintola University of Technology (LAUTECH), Ogbomoso, Nigeria.

B.Tech. Pure and Applied Chemistry; CGPA: 4.65/5.0.

Personal Skills

- self-confidence and drive to investigate and solve complex problems
- excellent communication skills
- an effective team player
- project planning and coordination.
- can cope with heavy work pressure without losing focus, under little or no supervision.
- presentation skills and the ability to convey technical information to non-technical people
- a good standard of numeracy and skills in data analysis
 - IT and technology skills to work with advanced techniques
 - creativity and the ability to use initiative for independent work
 - a flexible and methodical approach to work.

Technical Skills

HyperChem, ChemDraw, OMNIC spectra software, avatange software, Gaussian 08, dye synthesis, wastewater remediation, hydrocarbons-waterseparation, water purification, water treatment for power generation, nanomaterial development and characterization, FTIR, Raman, XRD, optical tensiometer (Biolin scientific), SEM-EDS, NMR, MS Office, etc.

Certification

Course: Online Safety Course for Laboratory Instructors. "Certifacate of Achievement"

Award Body: Environment, Health, and Safety Department, KFUPM.

Work Experience

Chemistry Department, King Fahd University Petroleum and Minerals

Dhahran 31261, Saudi Arabia

Research Assistant, May, 2018 – Present

Duties / Responsibilities:

- Using various methods in samples and nanomaterials analyses.
- Preparing experimental reagents and standards.
- Collaborative work with others.
- Using several characterization tools for nanomaterials elucidation including FTIR, Raman, XRD, BET, SEM, Optical tensiometer among others.
- Analysis and interpretation of data from experiment as well as reporting and documentation of findings.
- Performing analysis of samples from diverse source to disclose their compositions qualitatively and quantitatively.
- Fabrication of functionalized nanomaterials and conduct their characterization for various applications.

Department of Pure & Applied Chemistry, LAUTECH, Ogbomoso, Nigeria.

Teaching Assistant, January, 2017 - January, 2018

Duties / Responsibilities: Taking undergraduate Chemistry labs, lab grading, course grading, tutorial session, coordinating undergraduate research, analysis and interpretation of data from experiments.

National Youth Service Corps (NYSC)- Community Secondary School,

Nkim, Ikom, Cross River State, Nigeria

Chemistry and Basic Science Teacher, February, 2013 - March, 2014

Egbin Electric Power Plc, Egbin Ikorodu, Lagos State, Nigeria.

Student Industrial Work Experience Scheme, June, 2011- February, 2012.

Duties / Responsibilities: Analysis of hydrocarbonser's feed water for power generation, demineralization plant operation, sewage treatment, potable water treatment, chemical dosage, Lub hydrocarbons and transformer hydrocarbons analysis, resin capacity test.

Publications

- Hydrophobic and Oleophilic Lauric Acid Grafted Multiwalled Carbon Nanotubes for Efficient and Recyclable Hydrocarbons Absorption. (Under Review)
- Polyethylene/Amine Functionalized Reduced Graphene Oxide Composite Materials: Morphological and Hydrocarbons Absorption Properties for Remediation of Hydrocarbons Spills.(Under Review)
- Hydrophobic and Oleophilic amine functionalized graphene oxide nanocomposite for efficient hydrocarbons and organic solvent recovery. (Under Review)
- **Abdullahi Biodun Olabintan**, Isah Adewale Bello, Abdu-rahim Adebisi Giwa, Olugbenga Solomon Bello, Tawfik Abdo Saleh . Fenton Oxidative Degradation of Methylene Blue Dye in Aqueous Solution, *Applied Water Science*, 2019. (Under Review)
- Bello Isah Adewale, Abdul-rahim Adebisi Giwa, Aderinto Stephen, **Olabintan Abdullahi**.(2013). Effect of Position of Substituents on the Exhaustion and Thermodynamic Parameters of 6 Monoazo Acid and Disperse Dyes on Nylon 6, *Chemistry and Materials Research*, **Volume 3** No.9, pages 6-11.

Conference Proceedings

- **Abdullahi B. Olabintan** and Tawfik A. Saleh. Green Chemistry for Decomposition of Dye Pollutants : Kinetic Studies. Presented at 11th International Conference and Exhibition on Chemistry in Industry, October **2019**, Manama, Kingdom of Bahrain.

Honor and Award

- King Fahd University of Petroleum and Minerals, KSA Full M.S. Scholarship Award, 2018.
- **Tugbiyele Prize** for the Best Graduating Student in the Department of Pure and Applied Chemistry for 2011/2012 Academic Session.