

**CO₂ CAPTURE AT AMBIENT CONDITION USING AMINE-
FUNCTIONALIZED MAGNESIUM OXIDE AND GRAPHENE
DERIVATIVES NANO-COMPOSITES**

BY

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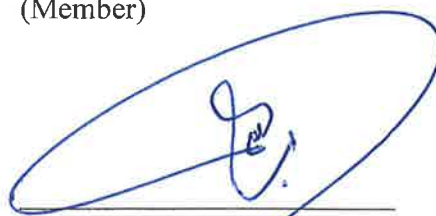
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Dedicated to my parents, my wife, and family brothers and sisters whom this thesis
would not have been completed without them

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LIST OF ABBREVIATIONS

AFM	:	Atomic Force Microscopy
APTES	:	3-aminopropyl-triethoxysilane
APTES/GO	:	ratio of APTES to GO in the solution
BET	:	(Brunauer–Emmett– Teller) surface area
CN	:	Cyano group
DEA	:	Diethanolamine
DETA	:	Diethylenetriamine
EDX	:	Energy-Dispersive X-ray
FTIR	:	Fourier-transform infrared spectroscopy
GO	:	Graphite Oxide
Hexamine	:	Hexamethylenetetramine
MDEA	:	Methyldiethanolamine
MEA	:	Monoethanolamine
MgO	:	Magnesium Oxide
MgO-A	:	Magnesium Oxide obtained by ammonia precipitant
MgO-N	:	Magnesium Oxide obtained by sodium hydroxide precipitant
MgO-O	:	Magnesium Oxide obtained by oxalic acid precipitant

NH	:	Amine Functional
OH	:	hydroxyl group
OMS	:	Ordered mesoporous silicas
PEI	:	polyethylenimine
PSA	:	Pressure-Swing Adsorption
RGO	:	Reduced graphite oxide
SEM	:	Scanning Electron Microscopy
TEM	:	Transmission Electron Microscopy
TGA	:	Thermogravimetric Analysis
TSA	:	Temperature Swing Adsorption
XPS	:	X-ray Photoelectron Spectroscopy
XRD	:	X-Ray Diffraction

ABSTRACT

Full Name : Ali Mahfouz Ali Al Kadhem
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Since the begun of the large-scale industrialization, carbon dioxide capture has obtained great attention due to the rapid increase of CO₂ concentration in the atmosphere. Moreover, the carbon dioxide (CO₂) outflow is considered a key factor of abnormal climate change. Therefore, the capture of CO₂ with minimal energy consumption is very attractive approach. Accordingly, we report in this work, the capture of CO₂ at ambient conditions using magnesium oxide (MgO) and graphene derivatives as base adsorbents respectively. First of all, a series of MgO-based adsorbents were prepared through different facile synthesizing methods using sol-gel technique. The results demonstrate that the MgO synthesis route play a significant role in altering its crystallinity, morphology, surface area, and pore size which resulted in a variety in its CO₂ uptake capacity, with MgO-A being the most effective one. The modification of MgO-A with 3-aminopropyl-triethoxysilane (APTES) and diethylenetriamine (DETA) has resulted in CO₂ adsorption enhancement with capacity of 65 and 47.6 mg/g, respectively. However, the functionalization with a poly amine caused a severe reduction in the adsorbent surface area, leading to a decrease in CO₂ adsorption. Regeneration, stability and fully restore of APTES-MgO-A original capacity suggest the potential commercial use of APTES-MgO-A for CO₂ capture with a minimal energy requirement. In the second part, graphene derivatives were prepared through oxidization of graphite and chemical reduction of graphite oxide. As a result, GO attained a considerable adsorption capacity of 45 mg/g comparing to RGO of 13.1 mg/g. The functionalization of GO with APTES and DETA have shown enhancement with capacity of 63 and 56 mg/g, respectively. However, the impregnation of PEI and Hexamine resulted in 30% reduction of adsorption capacity of GO. Finally, variants ratios of APTES/GO were prepared to specify the optimal ratio.

ملخص الرسالة

الاسم الكامل: علي محفوظ علي الكاظم

عنوان الرسالة: امتزاز ثاني أكسيد الكربون في الظروف الطبيعية باستخدام أكسيد المغنيسيوم و مشتقات الجرافين المحسنه بالأمين.

التخصص: هندسة كيميائية

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منذ بدء التصنيع على نطاق واسع ، حظي التخلص من ثاني أكسيد الكربون باهتمام كبير بسبب الزيادة السريعة في تركيز ثاني أكسيد الكربون في الغلاف الجوي. علاوة على ذلك ، يعتبر تدفق ثاني أكسيد الكربون إلى الخارج عاملاً رئيسياً في تغير المناخ الجوي . لذلك ، فإن التخلص من ثاني أكسيد الكربون بأقل الطرق استهلاكاً للطاقة هو أمر مهم للغاية. وفقاً لذلك أقمنا دراسة لإزالة ثاني أكسيد الكربون في الظروف المحيطة باستخدام أكسيد المغنيسيوم (MgO) و مشتقات الجرافين كمادة ماصة أساسية. أولاً، تم إعداد سلسلة من المواد الماصة المستندة إلى MgO من خلال طرق تحضيرية مختلفة باستخدام تقنية sol-gel. توضح النتائج أن طرق التحضير لمادة MgO يلعب دوراً مهماً في تحديد درجة البلورة ، التشكل ، مساحة السطح ، وحجم المسام مما أدى في الحصول على مجموعة متنوعة من MgO ذات قدرات مختلفة على امتزاز ثاني أكسيد الكربون ، مع كون MgO-A هو الأكثر فعالية. أسفر تعديل MgO-A مع 3-أمينوبريل-ترايثوكسيسيلان (APTES) وثنائي إيثيلينيتريامين (DETA) في زيادة امتزاز ثاني أكسيد الكربون بأكثر من 2 و 1.5 مرة على التوالي. ومن جهة أخرى ، تسبب التعديل باستخدام بولي أمين (بولي إيثيلين أمين) في انخفاض شديد في مساحة السطح الممتصة ، مما أدى إلى انخفاض في امتزاز ثاني أكسيد الكربون. والأهم من ذلك، يشير الاستقرار و الاستعادة الكاملة لقدرة APTES-MgO-A الأصلية إلى إمكانية الاستخدام التجاري المحتمل لـ APTES-MgO-A في امتزاز ثاني أكسيد الكربون مع مراعاة الحد الأدنى من الطاقة المستهلكة. في الجزء الثاني من البحث ، تم تحضير مشتقات الجرافين من خلال أكسدة الجرافيت والاختزال الكيميائي لأكسيد الجرافيت. ونتيجة لذلك ، حصل ال GO على قدرة امتزاز كبيرة تبلغ 45 مجم / جم مقارنة بـ RGO البالغة 13.1 مجم / جم. أظهر تحسين ال GO باستخدام APTES و DETA تعزيزاً على قدرة الامتزاز بمقدار أعلى 1.4 و 1.24 مرة على التوالي . ومن جهة أخرى ، أدى التعديل باستخدام PEI و Hexamine إلى انخفاض بنسبة 30 ٪ من قدرة الامتزاز GO الغير معدل . وأخيراً ، تم إعداد نسب مختلفة من - APTES / GO لتحديد النسبة المثلى.

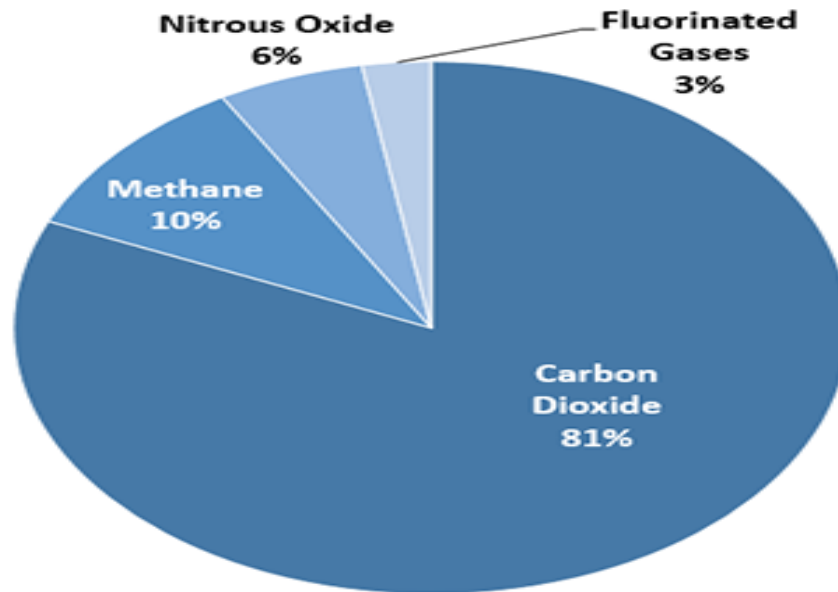
CHAPTER 1

INTRODUCTION

1.1 Carbon Dioxide and Environment

Since the last five decades , the carbon dioxide removal and emission control have become one of the foremost essential environmental subjects due to its rapidly increased concentration in the atmosphere compared to the pre-industrial level [1]. Moreover, carbon dioxide is considered as the most significant produced gas among the greenhouse gases due to the current human activities and the continuous use of fossil fuel and natural gas as energy sources as shown in Fig. 1 [2-4]. Also, the carbon dioxide (CO₂) outflow addressed as the main driver of the abnormal climate change [2, 5]. As a result, the atmospheric temperature of the world is anticipated to still increase to an extra 1.5 °C throughout the twenty-first century with the current massive CO₂ emission [2, 6]. For those reasons, the CO₂ concentration has to be reduced to satisfy the ecological guideline and to meet the global need for CO₂ reduction.

Overview of Greenhouse Gas Emissions in 2016



U.S. Environmental Protection Agency (2018). Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-2016

Figure 1-1 United States Environmental Protection Agency/ based on global emissions from 1990-2016[7]

1.2 Existing technology for CO₂ capture

In the effort of CO₂ capture a several technologies have been applied so far to reduce the CO₂ emission including, chemical and physical solvent absorption processes by using liquid amine solution [2, 3, 8-10], cryogenic processes [11], adsorption processes [12, 13], membrane and biological separation technics [14, 15]. Briefly, let's review those technologies and discovered their advantages and disadvantages.

1.2.1 Chemical absorption

The chemical adsorption is a process mostly consists of two parts absorber and stripper. First of all, the absorption process is generally conducted in a gas/liquid contactor in which the alkanolamine solution often be applied as an absorption liquid of acid gas through an exothermic and reversible reaction. Secondly, the regeneration process is taking place in a regenerator in which the acidic components are eliminated from the solvent at typical low pressure and high temperature [8, 9]. In fact, the alkanolamines solutions such as Monoethanolamine (MEA) a primary amine, Diethanolamine (DEA) secondary amine, and Methyldiethanolamine (MDEA) tertiary amine are the most commonly applied absorbents for CO₂. Although the cost of regenerating primary and secondary amines is expensive because of high heat of absorption associated with the formation of carbamate ions, the carbamates formation through the fast reaction of amines with CO₂ is widely used [5, 10]. Due to the energy penalty of using alkanolamines, a widely research is currently conducted to find an alternative solvents for CO₂ capture[5, 16].

1.2.2 Physical absorption

process based on thermodynamics equilibrium in according to henry law constant, in which CO₂ is captured by the means of applying high pressure and low temperature. In usual practice, physical absorption uses organic solvents to physically capture CO₂ that presents in the inlet flue gas stream instead of reacting chemically. Therefore, physical absorption unlike chemical absorption, it has no absorption limitation. The amount of CO₂ absorbed by the solvent is specified according to the vapor-liquid equilibrium of the mixture, which is governed by the pressure and temperature. Higher partial pressure of CO₂ and lower temperature favor the solubility of CO₂ in the solvents (Absorbent). On the other

hand, lowering the pressure and increasing the temperature will regenerate the solvent, then the solvent can be reused again after cooling [2, 3]. Currently, a variant of advanced and fully developed physical absorption processes have been implemented in industry such as Selexol Process, Purisol Process, Rectisol Process and Fluor process. Selexol Process used Dimethyl Ethers of Polyethylene Glycol that can physically absorb acid gas such as CO₂ [2, 3, 17].

1.2.3 Hybrid solvent processes

In this process, a mixture of chemical solvent and physical solvent are mixed at once to obtain the advantages of both processes [18].

1.2.4 Membrane separation process

It is an alternative technology wherein semi-permeable barriers of organic or inorganic material are applied to selectively sieve definite components such as acid gases and diffuses them through its pores while preventing other components to invade by deferent means (solution diffusion, Knudsen diffusion, molecular sieve and ionic transport). In general, membrane selectivity of the CO₂ is regarded to appropriate fitting between membrane pore size and molecule size, as well to the chemical solubility of a component into membrane's material [3, 19, 20].

In the last decade's, a membrane separation has acquired huge attention therefore, a massive quantity of membrane materials category have been manufactured and examined in order to evaluate their possibility to be used in gas separation process mainly polymeric, inorganic, hybrid organic-inorganic membrane. Polymeric membrane is an organic material which exhibits astonishing gas separation. It is widely used membrane due to its

unique properties of light weight and easy processing. However, the polymeric membrane has limitation in its performance due to some major problems such as plasticization and swelling. Inorganic membrane is sorted into porous and nonporous membrane classification such as Zeolite membrane which is a porous membrane. Zeolite membrane exhibited an excellent outcome in gas treatment because of its chemical resistance ability and hydrophobic behavior. However, usage of commercial inorganic membrane is very rare due to its high purchasing price and weak resistance to poisoning. Hybrid or mixed membrane is made of inorganic Nano-scale particles inserted on polymeric membrane to compromise the properties of both and overcome the permeability and selectivity trade-off problem of polymer and the high cost of inorganic fabrication [14, 15, 21].

1.2.5 Adsorption process

Adsorption is a process that depends on the thermodynamic properties of a substance to transfer from the gas phase and diffuse inside a solid material (adsorption) followed by regeneration (desorption), that can be completed either by lowering the pressure in comply with Pressure-Swing Adsorption approach (PSA), or via elevating the temperature by applying (Temperature Swing Adsorption, or TSA). The adsorption process can be either through a physical attachment (physisorption) or chemical attachment (chemisorption). In short term, physical adsorption is a process where the acid gas will diffuse through solid adsorbents such as activated carbon, MOFs and zeolite. On the other hand, the chemical adsorption is just a physical adsorption process enhanced by impregnated and grafted adsorbent by amino group or metal oxides which can react with acid gas efficiently. Also, the rate determining step which is the diffusivity is three orders higher than the mass transfer in absorption process which reflects the feasibility of adsorption process especially

on low concentration of contaminate [2, 3] .

In a number of excellent reviews that discussed the CO₂ capture by adsorption, it has been agreed that in order to improve an outstanding CO₂ removal, a adsorbent material must satisfy the following criteria (1) inexpensive based material, (2) has a low heat capacity, (3) expresses a rapid adsorption and desorption kinetics, (4) shows a high CO₂ adsorption capability, (5) deliberate excellent CO₂ selectivity (6) durable mechanical and stable chemical properties and (7) infinite regeneration through a proper path way [2, 22, 23] .Moreover, the decision of selection the correct adsorbent, is also depends on the type of adsorption process because the adsorption could be run at a variant range of temperatures. In the case of low temperature like room temperature, carbon-based adsorbents can be used while in the case of high temperature process such as the treatment of gas formed after the fuel conversion then heat-resistant adsorbents must be used such as metal oxide and activated carbon [13, 18] .

1.3 Objectives

The key objectives of this thesis are:

1. Developing of new adsorbents of CO₂ by using simple synthesizing techniques such as sol-gel precipitation and reflux.
2. Tuning the properties of the adsorbents to make them effective at ambient conditions.

The scope of the thesis:

1. Synthesizing of new adsorbents based on magnesium oxide and graphene derivatives using variants facile synthesizing techniques and different calcination temperature.
2. Modifying of adsorbents surface by Amine functionalization
3. Characterizing of the prepared adsorbents to get insights into the physical, morphological and chemical characteristics of adsorbents using different techniques such as FTIR, XRD, SEM, EDX (elemental composition) and BET.
4. Studying the application of CO₂ capture by the prepared adsorbents at ambient conditions using TGA
5. Studying the regeneration process for the spent adsorbents and evaluate their stability and feasibility.

CHAPTER 2

LITERATURE REVIEW

Over the last two decades, different kinds of adsorbents have been developed and improved through metals impregnation or amine modification to capture carbon dioxide. Those designed adsorbents are microporous and mesoporous silica [24, 25], carbon-based adsorbents [26, 27], metal oxides [28, 29] and metal-organic frameworks MOFs [30, 31]. During the last decades, graphene has appealed considerable attention among the scientific research and has been implanted in a wide range of technological applications such as energy storage (super-capacitors) [32] and adsorbents material including water purification [33], gas sensing, [34] and selective chemical aqueous adsorption [35]. In the subsequent sections will be discussed each group separately in brief.

2.1 Common adsorbents for CO₂ Capture

2.1.1 Silica based adsorbents

Silica gel based adsorbents have been widely and commercially used to achieve an efficient elimination of carbon dioxide and cleaning natural gas since World War I. The silica has extensive range of surface area varies from 200 up to 800 m²/g. The silica based adsorbents can be sorted into two main categories: (1) Micro porous silica named as zeolite which has pore with diameter less than 2 nm and (2) Meso porous silica named as ordered meso porous silica which has pore diameter varies between 2 and 50 nm [12, 23].

2.1.1.1 Zeolite

Zeolites are micro porous class of a widespread group of natural and man-made hydrated crystalline aluminosilicates. Zeolites are often described based on the three complex dimensional structures of silicon, aluminum ions which are bounded in a tetrahedral configuration with four oxygen ions and have a huge cage like cavities. Those cavities can host sodium, calcium and other cations which have positive clouds atoms and even small organic molecules. The aluminum atoms contained in the silica based adsorbents material works in defining the magnitude of charge-balancing cations of the structure and specify the nature of those moieties that influenced the zeolite characterization surface. It has been proposed that the strength of zeolites base could be improved as result of increasing the aluminum content due to the inferior electronegativity of aluminum in contrast to silicon electronegativity. The characteristics of zeolites mechanical structure can lead to capture a wide-ranging of gas contaminate molecules, containing the undesired acidic gas compounds such as CO₂. Moreover, the ions and particles existed in the cavities can be extracted or substituted without deforming the aluminosilicate structure. Also, the zeolites have been widely utilized in industrial processes as an ion-exchange agents, molecular filters, and catalysts for catalytic reforming [22] .

The development of adsorptive process technologies have noticed prominent role of commercial synthetic zeolites in gas separation comparing to the natural zeolites such as clinoptilolite, mordenite, erionite, chabazite, ferrierite and phillipsite which had observed limited records of potential use in gas separation and CO₂ removal. Although the natural zeolites have great abundance and cost-effective, they express a small purity and inconstant

compositions as well they could display a low removal performance in comparing with synthetic zeolites [36]. Zeolites offer a great selectivity for CO₂ with 5 to 10 times higher than carbonaceous materials but the capacity is 2 to 3 times lower and the effectiveness reduced as well with the presence of water vapor. However, the chemical composition, charge density and size of zeolites are mainly the major factors that play role in adsorption efficiency. On the other hand, the zeolites adsorption efficiency can be enhanced by the impregnated and grafted with amino group [2, 13] .

A vast numbers of research which have been published in literature have revealed the potential and feasibility of using zeolites as promising and efficient capture of CO₂. A study of natural chabazite zeolite which was synthesized and blended with alkaline-earth cations including Ca, Ba, Mg, and alkali cations like Na, K, Li has been conducted via performing vacuum swing adsorption for a diverse range of temperatures below 120 °C to evaluate its potential and capacity in CO₂ elimination from flue gas. As result, it has been observed that the adsorption is better with the higher charge density of chabazite zeolite. Therefore, Li – chabazite and Na-chabazite showed the higher adsorption capacity 135 mg/g and 171mg/g respectively. This great result can be attributed to the strong interaction between chabazite electrostatic field and quadrupole moment of CO₂ molecular as well to the large pore volume of Li – chabazite and Na-chabazite [37].

In further study of CO₂ capture, a Zeolite13X was employed to investigate its potential in CO₂ removal including the study of the adsorbent capacity, capture ratio, recovery efficiency and service life of Zeolite13X. A single-bed temperature swing TSA process was applied in which described as adsorption at ambient temperature and desorption at elevated temperature. The first run capacity was 78 g CO₂/kg zeolite with 63% capture

ratio and 88% recovery efficiency of 13X zeolite. Then, 13 X zeolite capacities have decreased with each consecutive cycle ending up with 23% drop and 60 g CO₂/kg zeolite 13X after 5 cycles [38]. Also, in a study of biogas upgrading a two man-made adsorbents (zeolites 13X and 5A) along with one natural zeolite (Clinoptilolite) were tested and compared to investigate their potential in eliminating CO₂ via a pressure swing adsorption process at 25 °C and 7 atm operating condition. It was observed that the natural zeolite (Clinoptilolite) has excellent CO₂ removal ability of 173.9 mg CO₂/g clinoptilolite which makes Clinoptilolite a very promising adsorbent [39]. Moreover, commercial zeolite was improved by coating with Mg–Al hydrotalcite that has been prepared by co-precipitate with ratio 3:1 respectively. This coated zeolite has been studied under different adsorption conditions of 1 atm pressure and temperature of 30, 100, 200 and 300 °C to understand the possibility of enhancing zeolite performance in CO₂ capture through this coating. As result, it has shown that the adsorption of CO₂ on the coated zeolites increased with the decrease in temperature and achieved 176 g CO₂/ kg coated zeolite at 30 °C [40].

2.1.1.2 Ordered meso porous silica

Ordered mesoporous silicas (OMSs) are significantly appealing to be employed in gas adsorbent application due to their distinctive features including large pore volume, huge surface area, flexible pore size (2–50 nm), narrow distribution of pore size, and extraordinary thermal stability [25]. OMSs are synthesized based on micelle-process, either by electrostatically mean or by the nonionic pathway in the existence of surfactant as directional structure agent. In General, surfactants are commonly utilized as micelle model to develop a well-organized meso porous material while the meso phase can be achieved using hydrothermal preparation, microwave assisted hydrothermal synthesis and

sol gel synthesis [1]. The surface chemistry of OMS is mainly controlled by silanols (Si-O-H), or surface hydroxyl groups in which those functional groups contribute in enhancing adsorption as well as in enabling the chemical modification of OMS surfaces [41].

OMSs are an excellent solid adsorption for CO₂ removal in which there have been a different number of studies were conducted on various types of OMS such as SBA-15, MCM-48 and MCM-41 to evaluate their prospective capability in CO₂ capture [1]. A synthesized SBA-15 silica under acidic media by using nonionic surfactant as structure directing agent at different conditions had specific surface areas between 530 and 880 m²/g. The potential application of this material was discovered in relation to the CO₂ capture. It has been shown that SBA-15 is promising adsorbent for the CO₂ capture with attainable capacity of 22 mg CO₂/g SBA-15 at ambient temperature and normal atmospheric pressure [42].

In further study of CO₂ adsorption, five diverse samples of SBA-15 were also, prepared under acidic condition and crystallized at alternate temperature and different aged times. Consequently, the attained SBA-15 samples were of variant textural properties and have specific surface area with the range in between of 500 and 900 m²/g. The sample which was synthesized at 393 K has a comparatively greater specific surface area and extended pore volume. As result, the one with higher surface area has been chosen for further measurements study of adsorption in which it has achieved a similar result as found in literature of 22 mg CO₂/ g SBA-15 at 298 K and 1atm [24]. Moreover, MCM-41 a type of ordered meso-porous molecular sieve has been synthesized hydrothermally and tested to evaluate its potential in CO₂ adsorption. The CO₂ capture/releasing performance was studied by using a microbalance in a flow system mode to detect the change of adsorbent

weight. The attained adsorption capacity was 14.3 mg CO₂/g MCM-41 at 50 °C and 1 atm [43].

However, the unmodified surfaces of ordered meso-porous silica offer a weak adsorption interaction with CO₂ because the residual hydroxyl groups that are available on the adsorbent surface are ineffective to integrate strong interactions with CO₂. Therefore, the adsorption properties of ordered meso-porous silica can be simply adjusted by surface modification with variant sorts of silanes and polymer which contains amino group such as 3-Aminopropyltrimethoxysilane using direct co-condensation or post-synthesis grafting methods and polyethyleneimine polymer [1]. In a remarkable study, MCM-41 has been also, prepared hydrothermally and modified with PEI to evaluate its efficiency on CO₂ capture. Again, the ultimate peak of CO₂ adsorption 215 mg/g was obtained for the 50 wt % loading of PEI at 75 °C and 1 atm. This result is 24 times greater than the adsorption achieved by MCM-41 alone and it is greater by more than two times of pure PEI solution which is used in absorption process as well it has a constant and complete 7 cycles of capturing and releasing efficiency [43].

In addition, MCM-48 has been also, modified with four different amine groups and it was investigated to discover their potential in CO₂ separation from N₂. The CO₂ adsorption was carried out by utilizing microelectronic recording balance system at 1 atm and 298 K. The study has shown that the power of interactions and accessibility of amino groups with CO₂, have essential role in CO₂ adsorption rate and capacity despite the low concentration of amine surface loading. APTES - MCM-48 has lower loading but higher rate of adsorption with 35 mg/g while the pyrrolidinepropyl group in PyrPS-MCM-48 has hindered the structure of a tertiary amine to interact with CO₂ [44].

Moreover, the preparation method effect was also, investigated using meso cellular silica foams (MSFs) modified with Tetraethylenepentamine (TEPA) as physical adsorbent using two different preparation approaches (1) physical impregnation method and (2) chemical grafting method. The CO₂ elimination capacity of those MSFs modified with TEPA were conducted by utilizing microbalances at 348 K and ambient pressure. The study had shown that (MSFs), prepared by physical impregnation (MSF-Tx) and chemical grafting (MSF -CTy) methods, have achieved CO₂ removal capacities in between of two ranges 57.2–193.6 and 26.3–58.0 mg CO₂/g-sorbent, respectively [45]. Table 2-1 illustrates a selected studies result on silica based adsorbent for CO₂.

Table 2-1 Summary of selected study based silica adsorbent

adsorbent	system	capacity	condition	ref
Li – chabazite	CO ₂	135 mg/g	below 120°C	[37]
Na-chabazite	CO ₂	171.2 mg/g	below 120°C	[37]
Zeolite13X	CO ₂	78 mg/g	25 °C, 1 bar	[38]
Mg–Al hydrotalcite –zeolite	CO ₂	176 mg/g	25 °C, 1 bar	[40]
MCM-41	CO ₂	14.3mg/g	50 °C, 1 bar	[43]
SBA-15	CO ₂	22mg/g	25 °C, 1 bar	[24, 42]
50 % PEI/MCM-41	CO ₂	215mg/g	75 °C, 1 bar	[43]

2.1.2 Metal oxide based adsorbent (MgO)

The oxide metal based adsorbent is one of the most commercial adsorbent for CO₂ capture. Previously, Metal oxides have widely been considered as based adsorbents to remove CO₂ at high temperature range processes of industrial gas streams. On the meanwhile, the reduction of CO₂ observed an advanced adsorption approach at low temperatures to meet the terms of environment regulations and act in accordance with economic preference [12, 46]. However, among these metal oxides adsorbent, MgO is appalling great attention and consider as one of the strong candidate sorbents for post-combustion capture. Briefly, in the next sub section MgO will be discussed.

2.1.2.1 Magnesium oxide

As a possible candidate for CO₂ capture at ambient temperature, MgO based material is an auspicious material for CO₂ removal in a wide temperature range and recently has obtained a significant research interest. Also, Magnesia (MgO) is the most important product of the magnesium compound industry. [47]. Moreover, MgO has favorable thermodynamics reaction properties with CO₂ since the exothermic reaction of the product requires only low regeneration temperature and it has decent CO₂ adsorption capacity comparing to the other metal oxides and theoretically to capture 1 ton of CO₂, about 0.92 ton of MgO is required [48]. MgO will react with CO₂ to form MgCO₃ as illustrated below with presence and absence of vapor.

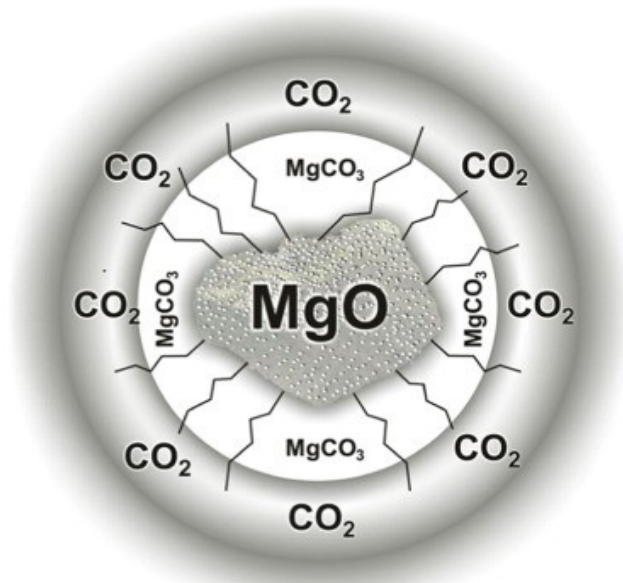
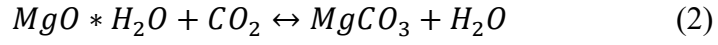
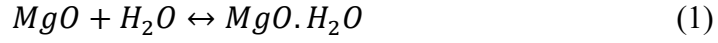


Figure 2-1 CO₂ chemisorption mechanism on MgO-based adsorbent. [49]

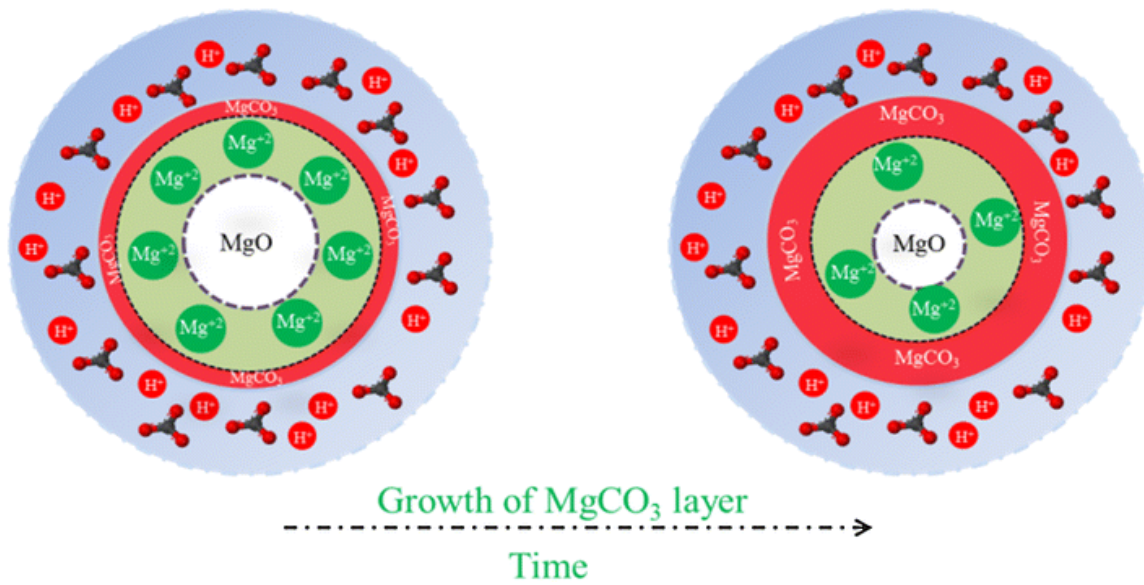


Figure 2-2 Adsorption model for MgO–CO₂–H₂O reaction [48]

In general, the metal compound (MgO) has an extensive use and several industrial applications such as remedy of toxic discarded product, additive in refractory [50, 51], adsorbent for several pollutants [52], and it is very well known as suitable catalyst support materials for a number of reactions [53, 54]. MgO is a white solid mineral adsorbent that occurs naturally and prepared under different synthetic conditions, the fabricated MgO materials might exhibit different structural characteristics, such as different physical, chemical, and surface properties [55], and it can be formed through variants techniques such as salt magnesium calcination [56], dehydration of magnesium hydroxide [57, 58] and thermal decomposition of magnesium chloride [59, 60]. Many efforts have been applied so far to enhance the MgO capability for carbon dioxide capture. The ordinarily used methods involve enhancement for the porous area using template [61, 62], varying the dynamic operation conditions and incorporating promoters [63, 64]. Among those suggested enhancement techniques, the employment of suitable promoters has been reported as the best method. Furthermore, Mg-based minerals are widely available in nature so that MgO adsorbents can be prepared in a large amount with low cost. Therefore, extensive works have been devoted to synthesize MgO-based adsorbents for CO₂ adsorption.

Recently, MgO sorbents for CO₂ sorption at ambient temperature were prepared by a thermal decomposition, and they had a high surface area of 161- 252 m²/g [65]. Moreover, a kinetic model was applied to interpret the sorption behavior of CO₂ in porous MgO at ambient temperatures and in MgO composite at intermediate temperatures [66]. However, the typical adsorption capacity of MgO for the CO₂ at ambient condition is 28mg/g [22]. Nevertheless, the CO₂ capture by alkali earth metal oxides were developed recently

following with the utilization of solid adsorbents of high surface area which include alkali earth metal and alkali metal over their surface such as Na_2CO_3 and K_2CO_3 to enhance the CO_2 capture at low temperature[67]. However, the water vapor plays an important role in enhancing CO_2 sorption capacities at ambient temperatures on MgO for example the synthesized regenerable MgO-based sorbent promoted with K_2CO_3 for CO_2 capture at low temperatures has a significant adsorption up to 197.6 mg CO_2 /g at 50°C and 11% v water vapor while in the absence of water vapor, no CO_2 was absorbed at the same low temperature range. Nevertheless, CO_2 was absorbed at the temperature range between 200 and 320 °C and above 600 °C [68].

Moreover, MgO was also, utilized to enhance the adsorption capacity for different metal oxide. A novel study of alkali metal MgO/ Al_2O_3 with variant MgO loading wt % was performed to investigate the CO_2 removal potential of alkali metal at low temperature. The study revealed that the adsorbent loading by 10 wt % of MgO exhibited a better performance in CO_2 removal at low temperature. The potency of adsorption is referred to the governing balance of physical and chemical adsorption of alkali metal. Moreover, the physical and chemical adsorption processes over metal oxide surface are based on an exothermic reaction that prefers low temperature condition. Therefore, the CO_2 capture capacity is directly affected by the surrounding temperature in which the temperature raise caused a capacity decrease. However, 42.7 mg/g was the highest adsorption capacity reported by MgO/ Al_2O_3 at 60 °C and 1 atmospheric pressure in dry condition for a gas stream consisting of 8% CO_2 and N_2 balance. It was also, noticed that water vapor up to a certain extent 13% can enhance the adsorption efficiency till 60 mg/g [28]. In addition, MgO-modified MCM-41 materials were applied to study the adsorption of CO_2 . As a result

the synthesized sample of MgO-MCM-41 with 20% loading of MgO demonstrated the highest adsorption capacity of 42 mg/g at ambient condition of 25°C and 1 bar. Table 2-2 illustrates the summary of selected study based on metal oxide adsorbent.

Table 2-2 summary of selected study based metal oxide adsorbent

adsorbent	system	capacity	condition	ref
MgO	CO ₂	28 mg/g	25°C, 1 bar	[22]
MgO/Al₂O₃	CO ₂	42.7 mg/g	60 °C, 1 bar	[28]
MgO-MCM-41	CO ₂	42mg/g	25°C, 1 bar	[69]
K₂CO₃/MgO	CO ₂	0-196.7 mg/g	50 °C, 1 bar 0- %11 H ₂ O	[68]

2.1.3 Carbon based adsorbent

The carbon based adsorbents are broadly used in CO₂ removal. In general, they are well-known as activated carbon which is extremely contains an advanced porosity mainly micro and meso-pores. Activated carbon is widely applied in industrial and scientific applications, including gas adsorption. Activated carbon derived from different precursors, including coals (bituminous coal), industrial by-products (waste of polymeric material) and lignocellulose materials (saw dust and coconut shells). In usual, activated carbon either used as a virgin or impregnated activated carbon because of its high specific surface area and ordered porous structure [12, 26]. Nevertheless, the porous structure, surface area, pore size scattering in conjunction with the surface chemistry play essential role in determining the performance of CO₂ removal using activated carbon. Accordingly, the chemistry of

activated carbon surface has been confirmed to have very prominent role in controlling the adsorption properties due to its strong interaction to the acidic nature of CO₂. Therefore, the introduction of Lewis base interaction on those activated carbons is significantly improves the CO₂ removal of activated carbons. In general, the acidic surface is mainly characterized by the availability of oxygen functional group that exists on the outer surface such as carboxylic, lactone, phenol and carbonyl group. The basic surface is identified by nitrogen containing group that can be prepared by the introduction of nitrogen functional groups or by heat treatment of activated carbon at high temperature around 800 °C.

Several approaches have been applied to increase the basicity of activated carbon such as removing or neutralization of the acidic groups that are attached on activated carbon surface or substitute them with basic group like nitric acid, and amines [70]. The effect of surface chemistry clearly was found in the study performed at room temperature using three activated carbons made by Westvaco (wood based, H₃PO₄ activation) which had different Ph surface. The study has showed that the carbon with highest Ph value attained the higher CO₂ adsorption capacity of 295 mg/g. This result supported the improvement obtained by the introduction of Lewis base interaction [71]. Enormous numbers of research were conducted to evaluate the activated carbon performance toward CO₂ capture along with comparative studies between virgin and impregnated activated carbon to deeply understand the modification effect. Recently, a high and efficient adsorbent based on carbon of a well-constructed meso-porous structure and large pore volume was prepared by loading polyethylenimine (PEI) on meso porous carbon to study the CO₂ removal and define the main elements that affected the adsorption capability of impregnated carbon and identify the optimal loading percentage of PEI. The CO₂ elimination was achieved by a fixed-bed

flow adsorber worked at atmospheric pressure and temperature was varied in range of 30 to 100 °C. The study revealed that the adsorbent with 65% loading of PEI exhibited the optimal adsorption capacity of 212 mg/g at 75 °C. The result is significantly higher than unmodified (MC) 2.2 mg/g adsorption and similar to the obtained capacity (215mg/g) by PEI (50%)-impregnated MCM-41 at 75 °C [43, 72].

The enhancement obtained in the adsorbent performance of CO₂ capture by PEI impregnation is further investigated with the low production cost (fly ash). Wet impregnation method was used to synthesis PEI/FA adsorbent and thermo gravimetric analyzer (TGA) was employed to measure the adsorption capacity and regeneration limit. The study point out that at 90 °C and normal pressure a high adsorption mass 145mg/g was achieved. The result indicated that PEI/FA is promising cost effective adsorbent because it maintained 90% adsorption efficiency after 100 regeneration cycle [73].

Table 2-3 Summary of selected study based activated carbon adsorbent

adsorbent	system	capacity	condition	ref
AC	CO ₂	8.8 mg/g	25 °C, 1bar	[74]
PEI/MC	CO ₂	212 mg/g	75 °C	[72]
PEI/FA	CO ₂	145mg/g	90 °C, 1 bar	[73]

2.1.4 Metal organic framework based adsorbent

During the past decade, the area of selective gas removal has noticed nonstop evolution for the newly discovered branch of adsorbents called metal-organic frameworks. Those new invented materials are assembled by joining metal-containing units or cluster which is called a secondary building units such as Zn₄O (CO₂)₆, M₃O (CO₂)₆, and

$\text{Zr}_6\text{O}_8 (\text{CO}_2)_8$ with organic linkers such as cyanide, pyridyl, phosphate or carboxylate. Strong bonds are formed and build up open crystalline frameworks which have a permanent porosity in harmony with reticular synthesis [75, 76]. In short words, chemistry of reticular synthesis can be defined as strong bonds (networks) linked molecular building blocks into predetermined ordered periodic structures. As a result, reticular synthesis has directed to the development of new porous materials in which compositions, metrics, structure and functionality can be thoroughly diverse [77].

MOFs is considered as new branch of crystalline micro-porous materials that demonstrate distinguish properties including astonishingly high surface area extended beyond $6000 \text{ m}^2/\text{g}$, modifiable internal surface properties, adjustable pore size, framework flexibility, catalytic activities and gas separation ability among others. The synergistic combining between organic and inorganic constituents to obtain a variant physical properties play an important role to afford amended features of MOFs. Topological diverse of MOFs is very promising sign because tetrahedral building blocks can be linked together into structures to form more than 100 different topologies at one kind of vertex.

According to those marvelous properties, along with flexible changeability to the structure of both organic and inorganic constituents, MOFs are so attractive and obtained great interest in different prospective applications such as the clean energy, significant storage media for gases including hydrogen and methane, and used as a high-capacity adsorbents to the acid gas in which could meet various separation needs [75, 78]. The metal organic framework application of acid gas removal was investigated for Cu-BTC that prepared through the reaction of dissolved copper nitrite with trimesic acid to evaluate its selective potential of CO_2 adsorption. The study demonstrated that the capacity of selective

CO₂ uptake at ambient temperature of 25 °C has increased rapidly in line with pressure elevation till 5 atm. This behavior is attributed to the quadrupolar CO₂ molecules interactions with partial positive charges of metal sites in Cu-BTC surface which lead to the maximum adsorption amount 12.7 mol/kg at 15 bar. In addition, water vapor up to certain limit is preferable conditions for the Cu-BTC adsorbent in PSA technique [79].

Moreover, Mg-MOF-74 metal organic framework was prepared to study the MOF potential in CO₂ removal at ambient operating environment. The investigation of breakthrough capacity of Mg-MOF-74 was performed in a packed bed for the gas mixture of CO₂ and methane at operating condition of 303K and 1 bar. MOF-74 has been compared to the adsorption capacity achieved by 13X powder in which the study showed a higher adsorption of CO₂ 391.6 mg/g compared to 378.8 mg/g obtained by 13X at 298 K. Also, it was observed that at lower temperature 30 °C, the Mg-MOF-74 had better capacity in contrast to a higher temperature of 45 °C and above [30]. Table 4 demonstrates summary of selected study based MOFs adsorbent.

Table 2-4 Summary of selected study based MOFs adsorbent

adsorbent	system	capacity	condition	ref
Cu-BTC	CO ₂	726 mg/g	25 °C, 15 bar	[79]
Mg-MOF-74	CO ₂	391.6 mg/g	30 °C, 1 bar	[30]
amino-MIL-53	CO ₂	36.5 mg/g	30 °C, 1bar	[31]

2.2 Graphene

There are no doubts that the 21st century is the age of flourishing the carbon nanomaterial opening with graphite and ending up by carbon nanotubes and currently with high focus and directed research on graphene. Graphene is an expression given to the commonly isolated horizontal monolayer carbon atoms from graphite. The monolayer comprises a densely packed sp^2 hybridized carbon which bonded together in a hexagonal honeycomb lattice to provide a two-dimensional (2D) of atomically thin layer. The isolated or fabricated monolayer is considered as basic construction element of all other dimensionalities of graphitic formation. Graphene can be covered up into a zero dimensions such as fullerenes and balled into one-D like nanotube or piled into three-D as graphite [80]. In general, graphene can be sorted into three different categories starting with graphene of a single-layer (SG), graphene of bilayer (BG), and graphene of few-layer those not exceeding 10 layers. Although, 100 layers are considered as a thin film of a three-D material, the situation in graphene has recently turned out to be a little different in which the graphene of a 10 layers could approach the 3D limit of graphite [80, 81]. Graphene has become one of the most important and excited topic of research during the last decades due to the marvelous physical and mechanical properties observed on graphene surface.

Typically, graphene is stable and exhibits excellent electronic and mechanical features. First of all, graphene is a two-dimensional plane regarded as a semiconductor of zero-band gap in which the valence and conduction bands raised a tiny overlap. Secondly, graphene exhibits a robust effect of am-bipolar electric field which leads the concentrations of charge carrier to reach up to 10^{13} cm^{-2} and the mobility of charge-carrier can reach up to $250\,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at ambient temperature. Moreover, $5000 \text{ Wm}^{-1} \text{ K}^{-1}$ thermal

conductivity and 6000 S cm^{-1} electrical conductivity were reported along with $2630 \text{ m}^2 \text{ g}^{-1}$ theoretical specific surface area. In addition, graphene is considered as transparent material that displays 97.7 % optical transmittance towards the visible light. While the single layer of graphene is considered as the robust material ever measured using atomic force microscopy (AFM) in which the attained result is 1 TPa Young's modulus and 130 GPa ultimate strength [82-84]. Indeed, graphene has appealed a huge attention among the scientific research and according to the reported literatures, the newly found material (graphene) seems to be a very promising base adsorbent and can be further utilized for acid gas separation. Therefore, in the remaining subsections we will review the synthesized method of graphene, techniques of graphene characterization, reduction methods and finally the applications of graphene as based adsorbent of acid gas.

2.2.1 Graphene preparation approach

Currently, there are variant techniques to prepare graphene that can be mainly classified into two different approaches, the bottom up and top-down approach. However, those two methods are evaluated on the bases of different parameters (quality) that defines the lack of defect from the produced graphene, (size) of the formed layers, (amounts) of the produced graphene and the synthesis controllability as well as the complexity of graphene [82, 85]. In bottom-up method, the graphene is produced by variant approaches including epitaxial graphene, and mechanical cleavage [82, 83]. The epitaxial graphene demonstrates the formation of crystalline layer over the crystalline substrate in which the growth follows the structure of the underlying substrate [86]. The epitaxial graphene method involves the chemical vapor deposition (CVD) process in which the substrate is stand as catalyst surface for the converted hydrocarbon gas such as the adsorbed CH_4 on

Cu and Ni surface. Followed by the partial dehydrogenation of normal methane and resulting on deposition of carbon at 1000 °C and 900 °C respectively. Large-size and high-quality graphene is the advantage of CVD synthesis process [86-88]. Moreover, the epitaxial growth of graphene could take place by directly heating and cooling down of a SiC crystal whereas the growth mechanism is simply described through the instant Si sublimation at high temperatures. Si sublimation has a faster rate than C because the vapor pressure of Si is higher than carbon. The sublimation has the advantages of possible production for large amounts of graphene, controllability to reproduce the same quality and comparatively low complexity [89].

In mechanical exfoliation, the graphene is obtained via repeated peeling process of graphite crystal by means of scotch tape and deposited on to silicon substrate. A single layer can be obtained by mechanical cleavage with variant sizes range from nanometers to several tens of micron. This technique has the advantage of producing large size and high quality sheet with very low complexity but it has a lack of controllability and limited quantity of produced graphene in which it is only suitable for preliminary laboratory research and is not adequate for achieving industrial targets [82, 86, 90]. In top-down approach, graphene is produced by chemical method that can be categorized into liquid direct exfoliation or graphite oxide reduction into graphene [91]. Liquid direct exfoliation performed by intercalating graphite in the organic aromatic solvents such as hexafluorobenzene, octafluorotoluene and pentafluoronitrobenzene by means of sonication bath [92] or by dispersing graphite powder in to Ionic-Liquid [93]. Liquid exfoliation approach is affording high volume production and low complexity but has a low size range and lack of controllability [91]. However, graphene produced by the graphite oxide

production following by reduction has a similar performance of liquid-phase exfoliation of pristine graphene. The only difference is the higher complexity, because graphite oxide is produced in the beginning which includes the use of oxidizing agents. Then, the attained graphene oxide is reduced subsequently, using thermal treatments or chemicals reducing agent [94].

2.2.2 Graphite oxide

The graphene oxide or the GO bulk form is commonly known as graphite oxide. It has obtained great concern since it has been produced in 1855 by Brodie due to the abundance of oxygen functionalities, which permits a relaxed manipulation and configuration [95]. Graphene oxide is a product chemically synthesized and results in a non-stoichiometric “molecule”. In general, graphene oxide is well-introduced as carbon sheet with graphitic sp^2 island that is occupied by oxygen functionalities, such as carbonyl ($C=O$), alkoxy ($C-O-C$) and hydroxyl (OH) groups [96]. Three primary methods for the preparation of graphite oxides have been reported in the literature: Brodie method, Staudenmaier’s (ST) and method Hummers’ (HU) method [95]. In Brodie method, graphite is blended with potassium chlorate ($KClO_3$). Then, the blend is mixed with fuming nitric acid to oxidize the graphite. The elemental analysis shows 38% oxidation in which the obtained product is a combination of graphite oxide and graphene [96, 97]. In Staudenmaier Method, the reaction between graphite and oxidizing agent was enhanced through increasing mixture acidity by adding sulfuric acid. Those amendments resulted in a wealthy oxidized graphitic compound [95].

In hummer method, graphite is first blended with half quantity of sodium nitrate ($NaNO_3$). Then, the blend is dispersed in a concentrated sulfuric acid (H_2SO_4), followed

by the addition of potassium permanganate (KMnO_4) to achieve a brownish grey paste. The reported degree of oxidization was similar to Staudenmaier Method [96, 98]. However, the resulted GO produced by bulk graphite is a discrete of graphene layers that line up tightly and piled together. In order to accomplish the oxidization of those layers, the penetration and dispersion of oxidizing agent between those layers is required. As a result, the development of GO includes three discrete and independent mechanisms. The first stage is started by graphite conversion into graphite intercalation compound (GIC) stage-1 which takes place instantaneously during the graphite dispersion in the acidic oxidizing medium such as sulfuric acid in hummer method. The central stage is the second mechanism that includes the conversion of GIC stage-1 into oxidized graphite by the utilization of oxidizing agent such as KMnO_4 in Hummer methods. The last stage includes the conversion of pristine graphite oxide into GO graphene oxide via water flooded [99]. Moreover, the oxidization temperature and time of reaction playing effective role in defining the oxidization degree in which using relatively lower reaction temperature and short oxidation time is only sufficient for the partially oxidization of the graphite [100].

2.2.3 Characterization

Graphene and graphene oxide have been extensively investigated using different microscopic analyzers along with several physical and chemical methods such as Transmission Electron Microscopy (TEM), Atomic Force Microscopy (AFM), Scanning Electron Microscopy (SEM), X-ray Diffraction (XRD), Thermo Gravimetric Analyzer (TGA), infra-red (FTIR), X-ray Photoelectron Spectroscopy (XPS) and Raman Spectroscopy [81, 86]. Raman spectroscopy is one of the most informative and attractive practices used for the characterization of graphene and graphene oxide. The easiest of

spectral interpretation makes the Raman measurements so attracted techniques. The Raman spectra of graphene has two main peaks known as G and D peaks in which they fall at 1560 and 1360 cm^{-1} visible excitation length respectively [101]. The G peak is an interpretation to the stretching motion between sp^2 carbon atoms of the plane. The D band is attributed to the disorder in sp^3 hybridization that causes structural defects and edge effects. Therefore, Raman spectroscopy is very useful technique to identify graphene's edges, atomic structure and in counting number of layers that exist in graphene's piles. As shown in figure 3, graphene has three main peaks called D, G, and 2D [102]. Moreover, the sites of D, G peak and the intensity ratios of D/G are very informative to study the layer expanding of graphite. Accordingly, a raise in D peak intensity and widen in G peak is corresponding to graphite conversion to GO in which it confirms the surface modification with oxygen functional group [103]. The atomic force microscope (AFM) is widely used technique to study the surface structure of both insulators and conductors. Also, it gives a rapid characterization of the surfaces and thickness for both graphene and graphene oxide [104].

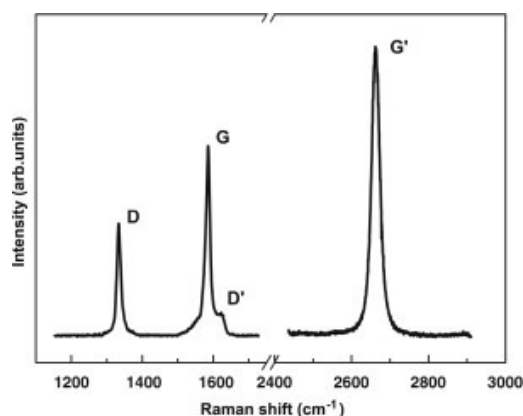


Figure 2-3 Main Raman peaks: D, G and 2D bands of graphene layer [102].

Transmission Electron Microscope (TEM) is based on transmitted electrons and it is widely used technique to study the Nano-carbon materials. In details, the electron-beam energy is reduced to 80 kV to stimulate a smaller extent of defects in graphene. TEM is a high resolution technique able to analyze at high resolution for Nano level and provides the details about internal composition [86, 105]. Scanning Electron Microscopy (SEM) is based on scattered electrons. SEM gives information about surface morphology and crystalline structure as well it is very beneficial technique to characterize the number of layers at graphene growth on SiC [106]. X-ray diffraction (XRD) is commonly used technique to recognize the crystallite arrangement of unknown material as well to measure the average spacing between layers or rows of atoms. XRD exhibited a sharp peak for the crystal material and it is used to evaluate the distance between layers in graphene and graphene oxide (GO). Accordingly, RGO has wide peak at 23.76° with 0.4 nm distance between layers while GO has a sharp peak at 9.98° and 0.9 nm distance between layers [107]. Thermo Gravimetric Analysis (TGA) is a tool employed to study the decomposition behaviors of GO and RGO based on the evaluation of thermal stability for GO and RGO with respect to the rise in temperature [108]. X-ray Photoelectron Spectroscopy (XPS) is a common performance usually utilized to analyze graphite oxide and reduced graphite oxide composition. Peak intensities that founded in XPS for C1s spectrum of graphene oxide and reduced graphene give clear information about the oxidation degree with four components functional group including the non-oxygenated carbon ring at (284.8 eV), the carbon with hydroxyl group at (286.2 eV), the carbon with carbonyl group at (287.8 eV), and the carboxylate carbon group at (289.0 eV) [109]. Infra-red (FTIR) characteristic is applied to confirm the existing of oxygen functional group in the synthesized GO. For example, the stretching vibration of O-

H group is found to be at 3340 cm^{-1} absorption band. Also, the stretching vibration of carboxylic C=O and/or carbonyl moiety functional groups are found between 1730 cm^{-1} and 1630 cm^{-1} absorption peak. While the C–O stretching vibrations is found at two absorption peaks about 1226 cm^{-1} and 1044 cm^{-1} . Those peaks intensity are reduced when reduced GO is desired [110].

2.2.4 Reduction methods

In fact, GO reduction to rGO can be achieved via several approaches in which those methods are mainly categorized into two sorts. First approach is chemical reduction [111, 112] which includes hydrothermal [113], Solvothermal [114, 115] and electrochemical reduction [116, 117]. Second approach is thermal reduction that includes thermal annealing [118-120], microwave and photo reduction [121]. Graphene oxide's reduction methods are conducted by means of oxygen functional groups removal. Those two different approaches would end up into graphene of unconventional features in physical structural, surface morphological properties and electronic capacity. However, the graphene oxide reduction to graphene can be observed by the color change of brown GO to black (RGO) and through hydrophobicity increase of material due to oxygen functional groups removal. The removal of elemental oxygen and the reduction efficiency can be analyzed in details through the measurement of C/O ratio and calculating of graphene materials' conductivity. In general, the reduction of GO is performed to achieve two main goals, the first is to remove the functional groups and the second to emendate the structural defects [82, 94, 122].

The chemical reduction approach is based on the chemical reaction between GO and reducing agent and it is considered as a promising approach toward high production of graphene. The chemical reduction usually conducted at room or moderate temperature

therefore, it is more preferable and less critical than thermal reduction [94]. However, the chemical reduction of graphite oxide is usually achieved through the utilization of variant reducing agents such as hydrazine monohydrate [111], sodium borohydride [112] and Hydroxylamine [123]. Hydrazine monohydrate is considered as the most common and widely used reducing agent in which 12.5 is the highest reported C/O ratio of hydrazine [124]. Sodium borohydride has been reported to provide 8.6 C/O ratio of graphene sheet which exhibits a lower resistance than the sheet provided by hydrazine [112]. Also, Hydroxylamine has been found to be an efficient reducing agent that could attain 10.3 C/O ratio within 24 h reducing time [123]. As regards of harmful effects that caused to the environment by using the traditional chemical reduction agents, a number of environmental friendly, cost-effective and large-scale production methodologies of RGO have been invented. Those methods have been proven to be more profoundly and efficiently than the traditional reducing agents. Recently, it has been reported that under acidic condition using of Zn powder (Zn/HCl) can have a substantial ultrafast sonication reduction of GO and achieve as high as 33.5 C/O ratio[125]. Zn powder reduction ability was also, tested in alkaline condition such as using of ammonia or KOH which significantly reduce GO and obtain as high as 8.09 and 8.58 C/O ratio within 10 min and 60 min of ultra-sonication, respectively[126].

Aluminum powder has been, also proved to be an efficient method and environmental friendly approach in reducing graphene oxide as high as 18.5 C/O ratio within 30 min of vigorous stirring under acidic condition and RT [127]. Tin powder was reported to have a similar potential as Zn powder in reducing graphene oxide and demonstrated a facile approach of reduction [128]. On the other hand, thermal reduction of

GO to RGO has been widely applied in fabrication for the most of electronic applications in which graphene is prepared by thermal annealing which took place in rapid heating greater than 2000 °C/min heating rate up to 1050 °C under inert gas flow. As result, the oxygen containing groups will be released as CO or CO₂ gas due to rapid heating [118]. Also, it has been observed that the GO reduction is highly affected by heating temperature in which C/O ratio could be higher for the higher heating temperature [119, 120]. As alternative to the thermal annealing the thermal reduction usually performed by thermal irradiation (microwave reduction) in which graphite oxide could be reduced within 1 min by using commercial microwave oven [121].

2.2.5 Graphene based adsorbent

Huge research interest has been observed during last decade in graphene based (Nano-composites) synthesis because of their excellent properties such as thermal stability, mechanical strength, and good conductivity. In general, graphene and its perspective derivatives are regarded as very important materials that have broad range of technological applications such as energy storage (super capacitors) [32] and adsorbents material including water purification [33], gas sensing, [34] and selective chemical aqueous adsorption [35]. Apart from the applications stated of graphene based nano-composites, one of the main goals of this review is to highlight the significance of graphene as CO₂ removal based adsorbent.

Recently, the studies of the potential graphene based adsorbent for the CO₂ removal have gained tremendous attention. As result, new novel nano-structured graphene based adsorbents have been synthesized and tested. In recent work, a successful combination of Graphene-silica sheet was synthesized and impregnated with PEI. The adsorbent has

shown a very high surface area and high loading content of PEI. The obtained PEI/G-silica sheets have displayed excellent adsorption capacity of 190 mg/g at 75 °C and average cycle stability of CO₂ capture. This result can be attributed to the favorable diffusion of CO₂ due to high thermal conductivity and fast heat transfer of graphene as well to the high loading of PEI. This upright result has emphasized the potential of graphene as promising adsorbent [129]. In continues study of CO₂ capture by graphene based adsorbent, 3-aminopropyl-triethoxysilane (APTES) modified graphite oxide was developed via GO functionalization with amine group. In fact, graphite itself has virtually no adsorption ability toward CO₂ while GO has a very low adsorption capacity of CO₂. However, Gr-APTS has shown a significant adsorption increase up to 75 mg/g at a temperature of 30 °C and 1 atmospheric pressure [130]. APTES functionalization on GO was also, investigated on further study in which they had better adsorption capacity as high as 88 mg/g at wet condition of 30 °C and 1 bar. As result, the amine functionalization using APTES was found to be more efficient at wet condition which represents the real situation of CO₂ removal application in extracted natural gas [131].

GO was also, modified with other amine such as tetraethylenepentamine (TEPA). According to the conducted study, the GO with 3% and 5% TEPA called AGO have demonstrated a better adsorption performance than unmodified GO. The development of AGO with 5% and 3% have achieved 85.77 mg/g and 91.46mg/g adsorption at 25°C respectively which is greater than 78.43 mg/g of pristine GO [132]. Moreover, Graphene-manganese oxide (Graphene-Mn₃O₄) hybrid porous material that has been fabricated via hydrothermal method in which the reduction of GO and the formation of Mn₃O₄ are conducted simultaneously was also investigated to evaluate its performance in carbon

dioxide adsorption. The study have shown that Graphene-Mn₃O₄ exhibited a decent adsorption capacity 110 mg/g of CO₂ at 25 °C and 1 atm which is comparable with other carbon materials [133]. Table 5 illustrates the summary of some selected study based graphene adsorbent.

Table 2-5 Summary of selected study based Graphene adsorbent.

adsorbent	system	capacity	Condition	ref
PEI/G-silica	CO ₂	190 mg/g	75 °C, 1 bar	[129]
Gr-APTS	CO ₂	65 mg/g	30 °C, 1 bar	[130]
		75 mg/g	30 °C, 1 bar, wet	[131]
Graphene-Mn₃O₄	CO ₂	110 mg/g	25 °C, 1bar	[133]
TEPA/ GO	CO ₂	91.46 mg/g	24 °C, 3 bar	[132]

CHAPTER 3

CO₂ Capture at Ambient Conditions using Fully Regenerable

Amine-Functionalized Magnesium Oxide Adsorbents

This chapter presents novel magnesium oxide-based nano-porous adsorbents which were developed for carbon dioxide capture at ambient condition. The new adsorbents were produced through variants simple synthesizing approach using the sol-gel technique. As a result, the synthesized MgO using ammonia precipitation method attained the highest CO₂ uptake capacity in contrast to the other used methods. Different morphology structures were obtained through thermal treatment for the magnesium hydroxide precipitate at variants curing temperature. The sample thermally treated at 400°C has demonstrated the highest adsorption capacity of 30 mg/g at ambient condition. In this study, three types of amine were employed to enhance the CO₂ uptake capacity of MgO. Those amines are 3-aminopropyl-triethoxysilane (APTES), diethylenetriamine (DETA), and polyethylenimine (PEI). APTS and DETA both have offered a remarkable enhancement on the CO₂ uptake capacity of MgO at ambient condition up to 65 mg/g and 47.6 mg/g, respectively. On the other hand, PEI has shown only a slight improvement with increased operating temperature. Characterizations of the synthesized samples were accomplished using various analytical techniques including N₂ adsorption/desorption measurements (BET), X-ray diffraction (XRD), SEM combined with energy dispersive X-ray analysis (EDX) and

Fourier transform infrared spectroscopy (FTIR). Thermo-gravimetric analysis (TGA) was used to evaluate the CO₂ adsorption capacity of the produced catalysts.

3.1 Introduction

Global warming is one of the most serious problems, threatening the continuous development of human civilization. It has been predicted that an increase in the average earth temperature by a few degrees might lead to disastrous consequences such as the melting of the polar ice caps, a significant increase in the water level of oceans and seas and, thus, the submerging of some islands and coastal cities, in addition to other undesirable consequences. The predicted increase in the average earth temperature in this century is about 1.5 °C [6] if the emissions of greenhouse gases continue at their current rates. However, the emission of carbon dioxide (CO₂), a key greenhouse gas, has been steadily increasing since the beginning of the industrial revolution, bringing the atmospheric concentration of CO₂ from about 300 ppm in the fifties of the twentieth century to more than 413 ppm in June 2019 with an annual growth rate of 2 ppm [134, 135].

With this alarming level of atmospheric CO₂, reduction of its emissions becomes an inevitable task. Thus, CO₂ capture and sequestration have been (and are still) a focal point of research in academia and industry in the past few decades. A number of processes have been developed and utilized for CO₂ capture; the most common one is CO₂ absorption into an aqueous solution of a suitable amine(s) [2, 3, 8-10]. However, this process is corrosive, energy-intensive, and utilizes environment-unfriendly organic solvents (i.e., amines). Accordingly, several alternatives, such as cryogenic distillation [11], adsorption [12, 13], membrane separation, and microbial treatment [14, 15] have been sought. Among these

processes, adsorption is the most attractive one due to its simplicity, possibly low energy requirement, and potentially ease of regeneration and reuse of the utilized adsorbents [22].

Despite the above attractive characteristics of adsorption, most of the known adsorbents have low CO₂ adsorption capacity, making the adsorption process less appealing to industry. In an effort to resolve this issue, several researchers have developed different adsorbents and utilized them for CO₂ capture in the past decades. Generally, most of the developed adsorbents are microporous/mesoporous silica [24, 25], carbon-based adsorbents [26, 27], metal oxides [28, 29] and metal-organic frameworks (MOFs) [30, 31]. Although these adsorbents showed promising results, most of them require high pressure or temperature to function effectively [22]. Moreover, some of these adsorbents might be non-regenerable or require prohibitively high regeneration energy [136].

As alternatives to the above-mentioned adsorbents, metal oxide/salts such as CaO [137, 138], Li₄SiO₄ [139], and MgO [140] have also been used for CO₂ adsorption. Although these metallic adsorbents can function well at atmospheric pressure, they are only effective at relatively high temperatures [137, 139]. The high operating temperatures might cause a severe structural deformation of these adsorbents, deteriorating their adsorption capability with extended use [137, 141]. In addition to the above limitations, metal oxides adsorbents require high regeneration temperatures, increasing energy consumption and, thus, the operational cost of the adsorption process [136]. Moreover, the formation of metal carbides through the reaction between CO₂ and the metal oxides at high regeneration temperatures might make the regeneration process a very challenging task [138].

Therefore, the development of CO₂ adsorbents that are effective at ambient conditions is a very attractive goal, addressing (at least partially) the above issues. The modification of metal oxides with amines has the potential to yield adsorbents that are effective at ambient conditions. Among the many available metal oxides, magnesium oxide (MgO) is the most appealing one since it has been shown that alkali metal salts supported on MgO are the most effective CO₂ adsorbents at elevated temperatures [142, 143]. Besides its use as a support for alkali metal salts in CO₂ capture, MgO has also been used extensively in several industrial applications such as the remediation of toxic pollutants [52] and as a catalyst support in a number of reactions [53, 54]. The effectiveness of MgO as support for adsorption and catalytic applications depends on its porosity (i.e., surface area), which might be enhanced through the use of templates [61, 62] or via the incorporation of promoters during the synthesis of MgO [63, 64]; the latter is more effective.

In this study, MgO is synthesized using three different facile methods. In the first method, magnesium nitrate and ammonium hydroxide were used as the starting materials. The produced precipitate was dried and then calcinated at 400 °C for 10 h to yield magnesium oxide. In the second method, ammonium hydroxide was replaced with oxalic acid while in the third method, sodium hydroxide was used instead. These different agents have resulted in an MgO with different characteristics according to the different characterization results. The synthesized MgO adsorbents were used to adsorb CO₂ at ambient conditions and the one synthesized using the ammonium hydroxide route displayed the highest CO₂ adsorption capacity. This adsorbent was functionalized with three different amines (APTES, DETA, and PEI) in order to enhance its CO₂ adsorption

efficiency; the first two amines enhanced CO₂ adsorption at ambient conditions while the last one compromised the CO₂ uptake capacity of the parent MgO. The amine modification was conducted in water solvent to pertain the textural properties and morphology of the based adsorbent because it has been reported that MgO has a very poor reactivity with water below 90 °C comparing to the other solvents with maximum hydration conversion and surface area reduction of 5% and 15%, respectively at room temperature [144, 145]. Repetitive use without a loss in the CO₂ adsorption capacity of these MgO based adsorbents has been demonstrated using APTES-functionalized MgO (prepared via the ammonium hydroxide route) as an example.

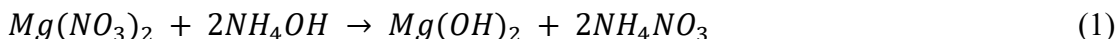
3.2 Materials and methods

3.2.1 Materials

In this study, magnesium nitrate $\geq 99\%$, ammonium hydroxide (30%), oxalic acid $\geq 99\%$, sodium hydroxide $\geq 99\%$, distilled water, ethanol $\geq 99\%$, 3-aminopropyltriethoxysilane (APTES) $\geq 99\%$, diethylenetriamine (DETA) $\geq 99\%$ and polyethylenimine (PEI) with 10000 MW $\geq 99\%$ were used to prepare MgO-based adsorbents with different characteristics. All chemicals used in this work were of analytical grade or above; the chemicals were obtained from Sigma-Aldrich and used as received.

3.2.2 Preparation of porous MgO using ammonium hydroxide route

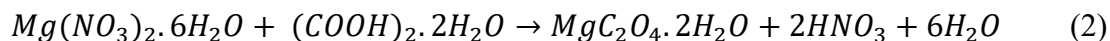
In this approach, MgO was synthesized first by dissolving 7 g of magnesium nitrate hexahydrate ($Mg(NO_3)_2 \cdot 6H_2O$) in 100 mL distilled water. After that, the mixture was stirred at room temperature until a homogenous magnesium nitrate solution was formed (~ 5 min). Then, a certain amount of ammonium hydroxide (NH_4OH) solution was added to the magnesium nitrate solution to make the molar ratio of NH_4OH : Mg as 5:1. The addition of NH_4OH was followed by stirring for 5 min at room temperature. Then, the flask was tightly closed (to prevent ammonium hydroxide evaporation) and slowly heated in a water bath until the temperature reached 60 °C. The mixture was maintained at this temperature under continuous stirring for 6 h. Then, the solution was removed from the water bath and kept at room temperature while stirring for 24 h. The flask was kept open during this 24-h stirring process. The continuous stirring resulted in the formation of a thick paste (consists of $Mg(OH)_2$ and NH_4NO_3) according to the following reaction [140]:



The paste was, then, washed with distilled water several times to remove NH_4NO_3 ; the dissolved NH_4NO_3 in water was removed through repeated 5-min centrifugation at 4500 rpm. This extensive wash would also remove any unreacted $Mg(NO_3)_2 \cdot 6H_2O$. The produced $Mg(OH)_2$ was dried overnight in an oven at 60 °C. The obtained solid was ground and, then, it was calcinated for 10 h at 400 °C under air atmosphere to yield MgO. The produced MgO using this preparation method was designated as MgO-A. Calcination at 300 and 500 °C was also conducted to probe the effect of the calcination temperature on the morphology, crystallinity, and porosity of MgO, in addition to its CO_2 adsorption capacity.

3.2.3 Preparation of porous MgO using an oxalic acid route

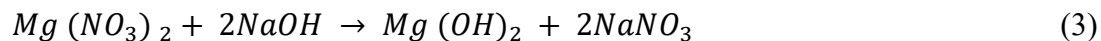
A 5.6 g of $Mg(NO_3)_2 \cdot 6H_2O$ and 2 g of oxalic acid ($C_2H_2O_4$) were dissolved separately in 25 mL ethanol. Then, a mixture of equimolar concentrations of $Mg(NO_3)_2 \cdot 6H_2O$ and $C_2H_2O_4$ was prepared by mixing the above two solutions. The resultant mixture was stirred vigorously at room temperature for 12 h to ensure the completion of the reaction. The result of the reaction between $Mg(NO_3)_2 \cdot 6H_2O$ and $C_2H_2O_4$ is a white gel consists of magnesium oxalate ($MgC_2O_4 \cdot 2H_2O$), nitric acid (HNO_3) and water according to the following reaction [146]:



At this stage, the obtained white gel was first dried at 100 °C for 24 h to evaporate the formed nitric acid and water. Finally, the obtained white solid was ground and, then, it was calcinated at 400 °C for 10 h under air atmosphere, and the obtained magnesium oxide was labeled as MgO-O.

3.2.4 Preparation of porous MgO using sodium hydroxide route

In this MgO preparation method, about 5.13 g of $Mg(NO_3)_2 \cdot 6H_2O$ was dissolved in 100 mL distilled water to yield 0.2 M solution. To this solution, 0.5 M sodium hydroxide (NaOH) was added drop-wise, while stirring, until the pH of the solution reached 12.5. Then, the mixture was stirred at room temperature for 30 min. The reaction between $Mg(NO_3)_2 \cdot 6H_2O$ and NaOH produces a white precipitate of $Mg(OH)_2$ and sodium nitrate ($NaNO_3$) according to the following reaction [147]:



The sodium nitrate salt was removed through an extensive wash with ethanol and distilled water; $\text{Mg}(\text{OH})_2$ was removed from the sodium nitrate solution via centrifugation at 4500 rpm for 5 min after every wash with ethanol or distilled water. After the last wash, $\text{Mg}(\text{OH})_2$ was dried at 60 °C overnight. The obtained solid was ground before subjecting it to 10-h calcination at 400 °C under air atmosphere. The obtained magnesium oxide was designated as MgO-N.

3.2.5 Functionalization of MgO with APTES

In a typical synthesis procedure, 500 mg of the synthesized MgO-A was first dispersed in 600 mL distilled water by subjecting the MgO-A suspension to a 5-min stirring. Then, 1 g of APTES was added to the MgO-A suspension, followed by heating at 65 °C for 24 h while stirring and refluxing. After the completion of this solvent-assisted grafting of APTES to MgO, the sample was rinsed three times with distilled water, and the amine-modified MgO was obtained through centrifugation at 4500 rpm for 15 min after each rinse with distilled water. The collected precipitate was dried at 60 °C overnight; the dried sample was labeled as APTES-MgO-A.

3.2.6 Functionalization of MgO with DETA and PEI

The functionalization of MgO with DETA and PEI was achieved using the wet impregnation method, described elsewhere [148], with some modifications. The first step in such a functionalization protocol was the preparation of an ethanolic solution of each amine by mixing 0.25 g of either DETA or PEI with 25 mL ethanol, followed by stirring at room temperature for 15 min. Then, 500 mg of the synthesized MgO-A was added to each amine solution, and the resultant slurries were stirred continuously for 2 h. After that,

the formed pastes (some ethanol evaporates during mixing) were dried at 60 °C overnight. The obtained samples were labeled as DETA-MgO-A and PEI-MgO-A.

3.3 Characterization of the synthesized adsorbents

The synthesized MgO-based adsorbents were characterized using different techniques. The BET (Brunauer–Emmett– Teller) surface area of MgO-based adsorbents (including amine-functionalized MgO) was obtained through the measurements of nitrogen adsorption/desorption isotherms at -195°C using an ASAP 2020 system (Micromeritics Instruments, Inc.). The morphologies of the synthesized MgO-based adsorbents and their elemental compositions were determined using a scanning electron microscopy (SEM) coupled with an energy-dispersive X-ray spectroscopy (EDX) technique. The crystallinity of the synthesized MgO-based adsorbents was studied using XRD pattern by XRD-6000 X-ray diffractometer (Shimadzu) with Curadiation 40 kV and 30 mA. Functional groups in the synthesized adsorbents were identified using Fourier Transform Infrared (FTIR) spectra (NICOLET 6700 spectrometer, Thermo Scientific) and recorded at room temperature in a wavenumber ranging from 400 to 4000 cm^{-1} using KBr pellets.

3.4 Evaluation of CO₂ adsorption capacity

The measurements of CO₂ uptake capacity by the synthesized MgO-based adsorbents were carried out using the thermogravimetric analysis technique (TGA Q600 SDT). In each run, about 10 mg of the synthesized adsorbent was placed on an alumina oxide pan. Then, the adsorbent was degassed at 100°C using a stream of pure N₂ gas flowing at 100 mL/min. Once the weight of the sample reached a steady value (i.e., all water is removed), the temperature was dropped to 30 °C and left to equilibrate. After the stabilization of the adsorption temperature at 30 °C, the valve of the carbon dioxide (99.9% pure) gas cylinder was opened, and the flow rate of CO₂ was kept constant at 100 mL/min. The adsorption of CO₂ was monitored in time until the adsorption approached equilibrium (within 90 min contact between CO₂ and each adsorbent).

To assess the stability and regenerability of the most promising adsorbent (i.e., APTES-MgO-A), this adsorbent was regenerated by conducting 6 cycles of consecutive adsorption and regeneration. Regeneration was performed using pure N₂ gas flowing at 100 mL/min. The regeneration temperature and time were at 120 °C and 30 min. The regeneration experiments of the spent adsorbent were also carried out at atmospheric pressure.

3.5 Results and discussion

3.5.1 Characterization of the synthesized adsorbents

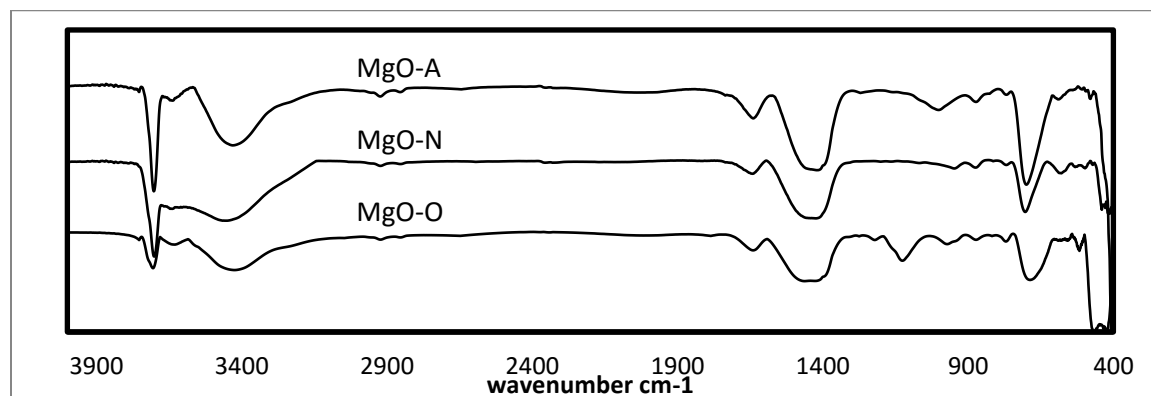
The synthesized MgO-based adsorbents were characterized using FTIR in order to confirm the formation of MgO and to get insights into the effects of different preparation methods, the calcination temperature and the functionalization with different amines on the chemical properties of MgO. Fig. 1 (a) presents the FTIR spectra of the parent (unmodified) MgO prepared using ammonium hydroxide, oxalic acid, and sodium hydroxide in the wavenumber range from 400 to 4000 cm^{-1} . As revealed by fig. 1 (a), the spectral patterns of MgO-A, MgO-O, and MgO-N are comparable. The strong peaks appearing between 400 and 700 cm^{-1} correspond to the metal-oxygen bending vibration [149, 150], confirming the formation of magnesium oxide. The sharp and intense peaks at 3700 and 1650 cm^{-1} and the broad peaks centered around 3400 and 1450 cm^{-1} are associated with the presence of water moisture and/or the presence of some residual surface hydroxyl groups ($-\text{OH}$) [150, 151]. The minor peak appearing at 1100 cm^{-1} in MgO-O might be attributed to C–O stretching vibration. The reason for detecting this band is likely due to the presence of some impurities remained from the starting materials [151, 152].

Despite the comparable spectral patterns of MgO-A, MgO-O, and MgO-N, their CO_2 adsorption capacities were reasonably different, to be presented and discussed later, with MgO-A adsorbs more CO_2 than the other two. Thus, the effect of the calcination temperature and amine-functionalization are only reported for MgO-A. Fig. 1(b) shows the spectral patterns of MgO-A, calcinated at 300 (MgO-A-300), 400 (MgO-A-400) and 500 $^{\circ}\text{C}$ (MgO-A-500). As it is the case with the different MgO synthesis routes, different

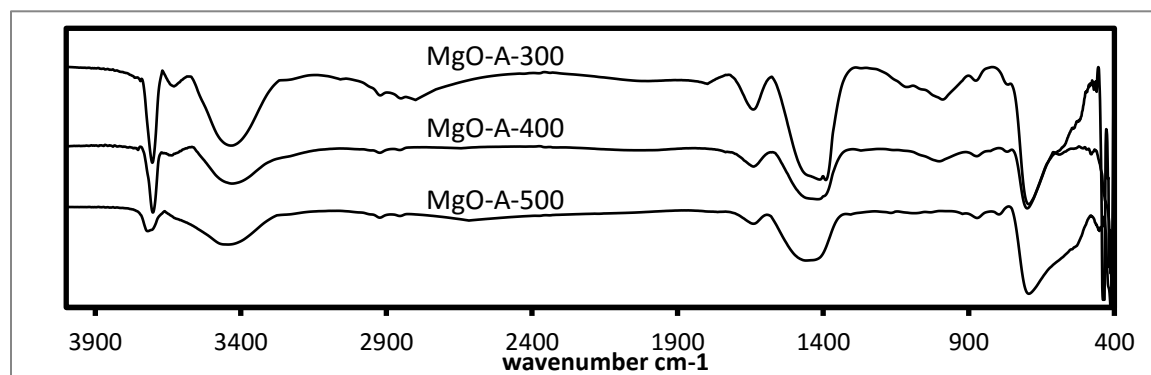
calcination temperatures did not significantly alter the FTIR spectral pattern of the metal oxide, with the exception for the minor change in the peak intensity at 3700 cm^{-1} , related to water moisture and/or the presence of some residual surface hydroxyl groups ($-\text{OH}$), which becomes more intense at the lower calcination temperature. This peak disappears at the higher calcination temperature of $500\text{ }^{\circ}\text{C}$, likely due to the removal of some hydroxyl groups ($-\text{OH}$).

Fig. 1(c) shows the FTIR spectra of MgO-A (calcinated at $400\text{ }^{\circ}\text{C}$, which provides the highest CO_2 adsorption capacity as will be presented and discussed later) after functionalization with the three different amines (APTES, DETA, and PEI). The functionalization of MgO-A with these amines has resulted in the appurtenance of new peaks at 2960 and 2840 cm^{-1} , which are attributed to the C-H bonds of the amine molecules. The bands which appeared between 1560 and 1300 cm^{-1} are associated with the NH and NH_2 deformation [72, 73, 130, 131, 153]. The sharp peak at 1020 cm^{-1} in the case of APTES-MgO-A corresponds to the asymmetric stretching vibration of the Si-O bond, which confirms the APTES attachment to MgO-A [131, 154].

(a)



(b)



(c)

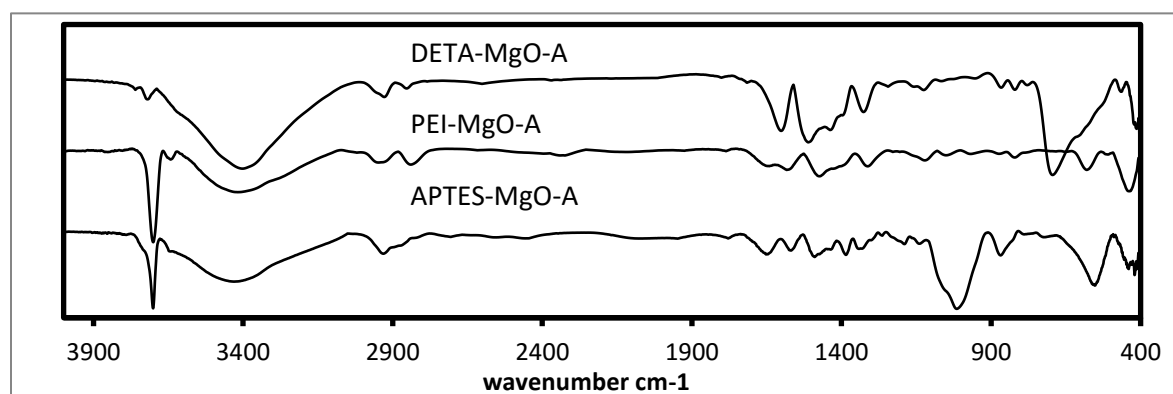
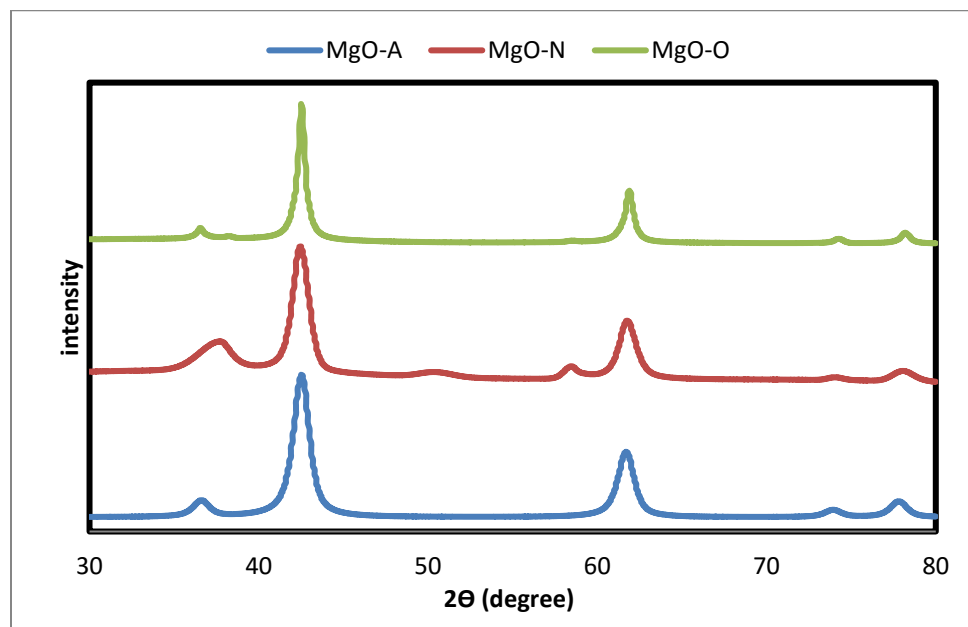


Figure 3-1 (a) FTIR patterns of MgO-A, MgO-N and MgO-O, (b) FTIR patterns of MgO-A calcinated at 300 (MgO-A-300), 400 (MgO-A-400) and 500°C (MgO-A-500), (c) FTIR patterns of MgO-A functionalized with APTES, DETA and PEI.

In order to assess the crystallinity of the synthesized MgO samples, XRD analysis was performed, and the results are shown in Fig. 2. The unmodified MgO samples (MgO-A, MgO-O, and MgO-N) have comparable patterns (see Fig. 2(a)). Each sample exhibits 5 diffraction peaks at 36.8° , 42.2° , 61.2° , 74.1° , and 77.9° that can be, respectively, assigned to the planes (111), (200), (220), (311) and (222) of cubic MgO, confirming its crystalline nature. These results are in a good agreement with the reported observations in the related literature [65, 155, 156]. The peaks intensity of the prepared MgO series at 42.2° decreased in the order of MgO-O > MgO-A > MgO-N. These results demonstrate that the magnesium oxide synthesized using the oxalic acid route has higher crystallinity than those prepared using ammonium hydroxide and sodium hydroxide [140]. Upon the functionalization of MgO-A with APTES, DETA and PEI, new peaks appeared at $\sim 50.2^\circ$, $\sim 62.4^\circ$ and $\sim 72.2^\circ$ as shown in Fig. 2(b). Moreover, the intensity of the originally small peak of MgO-A at around 36.8° has significantly increased upon amine-functionalization. Furthermore, the main MgO-A peak at 42.2° has been shifted to lower angle (for the case of APTES and PEI), and its intensity dropped quite significantly. This is also the case for the original MgO-A peak at 61.2° . The other minor peaks of MgO-A at 74.1° and 77.9° have also vanished upon its functionalization with each of the three amines. The appearance of new peaks at other diffraction angles as well as the shifting to lower diffraction angle and decrease in the intensity of the MgO-A peaks at 42.2° and 61.2° confirm the attachments of the amine molecules between the MgO layers [130, 148].

(a)



(b)

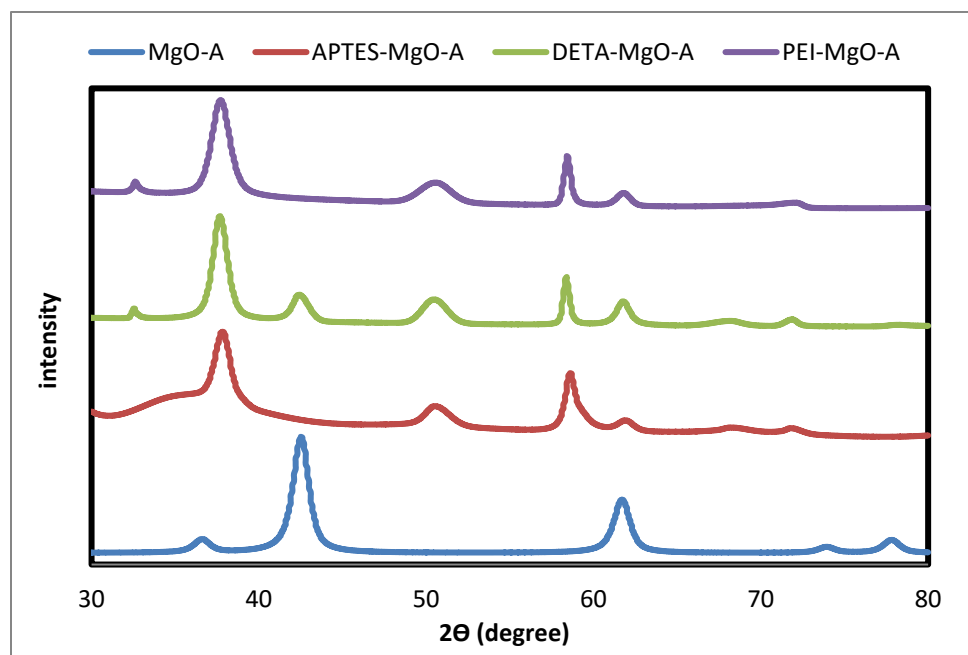


Figure 3-2 (a) XRD patterns of MgO-A, MgO-N and MgO-O, (b) XRD patterns of MgO-A functionalized with APTES, DETA and PEI.

In addition to studying the crystallinity of the MgO-based adsorbents, their textural properties (i.e., BET surface area, pore size, and pore volume) have also been investigated using the N₂-physisorption at 77 K. Table 1 summarizes the textural properties of the synthesized MgO-based adsorbents. The International Union of Pure and Applied Chemistry (IUPAC) has classified nanoporous adsorbents, based on pore size, into three main categories: macroporous (pore diameter > 50 nm), mesoporous (2 nm < pore diameter < 50 nm) and microporous (pore diameter < 2 nm) [157]. Accordingly, all the MgO-based adsorbents synthesized in this work (see Table 1) fall into mesoporous category. Nonetheless, the pore size of MgO-O is the highest, followed by MgO-N and then MgO-A, revealing the effect of the chemistry of the MgO synthesis solution on its pore size. Despite having the smallest pore size amongst the unmodified magnesium oxides, MgO-A possesses the highest surface area.

Unlike the order of the pore size, BET surface area showed the opposite trend where MgO-A has a surface area that is 58 and 65% higher than those of MgO-N and MgO-O, respectively. More importantly, the three unmodified MgO displayed higher surface areas than those of MgO produced using templates [65, 151]. Furthermore, the three unmodified MgO adsorbents possess much higher surface areas than the commercial MgO. For instance, MgO-A possesses a surface area of 350 m²/g, which is almost ten times higher than the reported value for the commercial MgO, which is 32 m²/g [65]. Benchmarking the surface areas of the three unmodified MgO with their crystallinity obtained from the XRD analysis reveals the usual inverse relationship between the surface area of an adsorbent and its crystallinity [158].

In order to investigate the effect of the functionalization of MgO with amines on its textural properties, the pore size, BET surface area, and pore volume of the amine-modified MgO-A have been measured. As shown in Table 1, both the surface area and pore volume have decreased upon the attachment and intercalation of the amine molecules on the MgO surface and inside the pores. Such a reduction in surface area, and pore volume upon the attachment of the amine molecules to magnesium oxide are expected since the amine molecules are likely to fill some pores [43, 45]. Accordingly, the surface area of the parent MgO-A has dropped by a factor of more than 2.6, 3.8, and 4.9 upon the functionalization with APTES, DETA, and PEI, respectively. The huge reduction in the surface area and pore volume of PEI-MgO-A can be attributed to the bulky size of this polymeric amine. On the other hand, APTES and DETA are simple monomeric amines that cause a less reduction in the surface area of the parent MgO-A upon their attachment to the adsorbent surface comparing to PEI. It is interesting to note that the pore size of the original MgO-A has been further expanded due to amine attachments and intercalation inside the pores. Such an outcome induces the fast adsorption of CO₂ in the initial adsorption stages and postpones the intra- particle diffusion effect, to be presented and discussed later [66].

Table 3-1 BET surface area, average pore size and average pore volume of the synthesized MgO-based adsorbents.

Samples	Surface area (BET) (m ² /g)	Pore volume (cm ³ /g)	Pore size (nm)
MgO-A	350	0.414	4.73
MgO-N	149	0.598	16.03
MgO-O	124	0.546	17.59
APTES-MgO-A	134	0.301	8.95
DETA-MgO-A	91.4	0.203	8.87
PEI-MgO-A	72.5	0.178	9.81

Insights into the morphologies of the synthesized MgO-based adsorbents have been obtained using SEM imaging. The results of such analysis are presented in Fig.3. It is clear from Fig. 3(a) that the particles of MgO-A are small in size with irregular platelet-like morphology. Contrarily, MgO-N particles are bigger in size than MgO-A, with an irregular sphere-like morphology, as shown in Fig. 3 (b). The irregular shape is also evident from Fig. 3 (c) for the MgO-O particles. These particles resemble grains with a cubic-like morphology, and they are bigger in size than MgO-N and MgO-A. Such observations clearly demonstrate the impact of the chemistry of the MgO synthesis solution on its morphological properties even when the same magnesium salt (i.e., MgO precursor) is used. A similar observation has been reported in the literature on the effect of catalyst preparation protocol on its morphological properties [56]. The results of SEM analysis are in line with the confirmed phase crystal using XRD that displayed MgO-O as high crystal adsorbent with larger particles size.

As stated above, the chemistry of MgO synthesis solution has significantly altered its morphology. Thus, it is worthwhile to probe the effect of the amine chemistry on the morphological properties of the amine-functionalized MgO. Fig. 3(d), (e), and (f) show the SEM images of APTES-MgO-A, DETA-MgO-A, and PEI-MgO-A, respectively. These images reveal that the morphology of the parent MgO-A has dramatically altered upon amine-functionalization, probably due to the coverage of the metal oxide surface with the amine molecules. Another observation that can be extracted from these images is the huge reduction in the porosity of the original MgO-A due to the filling of its pores with the amine molecules. Furthermore, the reduction in porosity revealed in these images matches, at least qualitatively, the reduction trend obtained from the BET analysis, reported above. These observations have a similar trend with the reported results of similar work as the surface area, and pore volume was reduced for the graphite oxide material modified with 3-aminopropyltriethoxysilane and tetraethylenepentamine [130, 132].

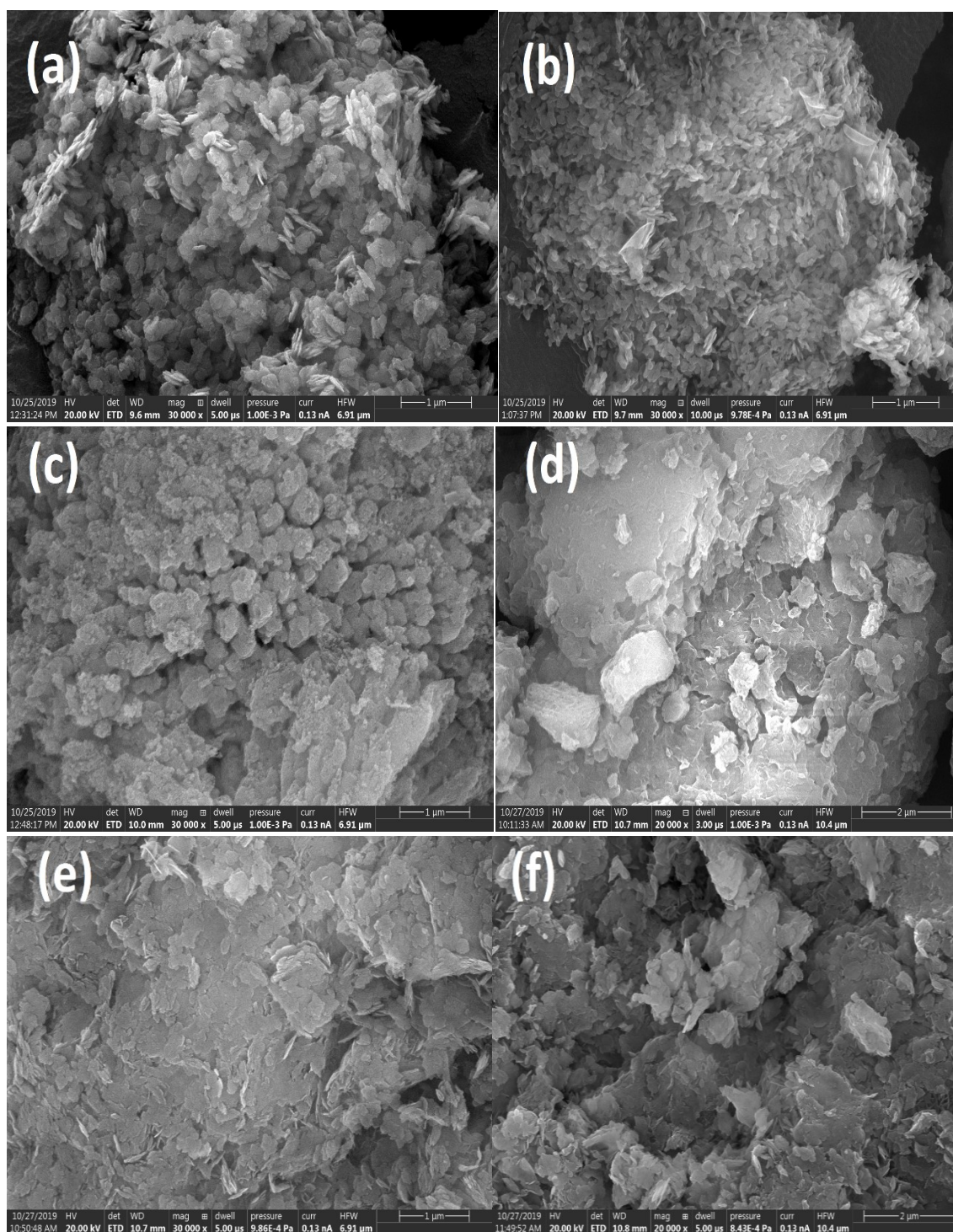


Figure 3-3 SEM images of the synthesized MgO-based adsorbents: (a) MgO-A, (b) MgO-N, (c) MgO-O, (d) APTES-MgO-A, (e) DETA-MgO-A and (f) PEI-MgO-A.

The above characterization results have revealed useful information on the synthesized MgO-based adsorbents. Particularly, the FTIR results suggested the formation of magnesium oxide and its subsequent modification with amines. To support these results, elemental compositions of the synthesized MgO-based adsorbents have been analyzed using EDX, and the results are summarized in Table 2. The EDX results of high contents of Mg and O has confirmed the formation of crystal MgO for the three different approaches. With respect to the EDX result, it can be seen that MgO-A has higher Mg content comparing to MgO-N and MgO-O, which confirm the effect of procures material in the final composition distribution of the obtained catalyst. Moreover, MgO-O has contained carbon as impurity due to incomplete burning of the residual carbon resulted from the oxalic acid preparation route. This result demonstrates the advantage of using clean precipitant in having pure catalyst as the case for MgO-A and MgO-N. It can also, be observed from the elemental analysis that after amine modification, the carbon and nitrogen were detected in the catalyst composition which represents the alkyl chain and amino groups associated with APTES, DETA, and PEI [131]. As a result, the carbon and nitrogen content has further confirmed the proper attachments of amines group, which have been already proven by FTIR analysis. Moreover, PEI-MgO-A has shown the highest content of nitrogen and carbon comparing to APTES-MgO-A and DETA-MgO-A as expected due to the higher molecular weight of PEI. It is interesting to note that despite having a high content of nitrogen and carbon, the adsorption capacity of the modified MgO was further reduced instead of being improved as a result of pores filling and pathway blockage which will be further discussed and presented in the adsorption section.

Table 3-2 Elemental compositions of the synthesized samples.

Samples	Mg % w/w	O % w/w	C % w/w	N % w/w	Si % w/w
MgO-A	47.2	52.8	—	—	—
MgO-N	56.9	43.1	—	—	—
MgO-O	44.6	48.76	6.64	—	—
APTES-MgO-A	23.3	43.3	23.1	2.55	7.75
DETA-MgO-A	29.5	46.2	20.27	4.03	—
PEI-MgO-A	17.4	42.2	27.2	13.2	—

3.5.2 CO₂ adsorption on the synthesized MgO-based adsorbents

The adsorption of CO₂ on the synthesized MgO-based adsorbents was carried out at ambient conditions (i.e., 30 °C and atmospheric pressure) using TGA. After the complete degassing of each adsorbent, CO₂ gas was pumped at a flow rate of 100 mL/min and the total mass of the system (CO₂ plus adsorbent) was followed in time until a steady value is approached. We first investigated the adsorption of CO₂ on the unmodified MgO, prepared using the three different synthesis routes, to probe the effect of the chemistry of the MgO synthesis solution on its CO₂ adsorption capacity. The result of such an investigation is shown in Fig. 4, which demonstrates the superiority of the magnesium oxide synthesized via the ammonium hydroxide route (i.e., MgO-A). For instance, the adsorbed amount of CO₂ on MgO-A when the adsorption process approached equilibrium is about 30 mg/g. In contrast, the adsorption capacity of CO₂ on MgO-N and MgO-O are about 25 and 24 mg/g, respectively. The CO₂ uptake capacities by the three MgO adsorbents are in a good agreement with the results of the textural analysis shown in Table 1. For example, MgO-A displays the highest porosity (i.e., the highest surface area and the smallest particle size.

This high porosity is likely to result in higher adsorption, according to some published reports [65, 159]. Moreover, it is interesting to note the close CO₂ adsorption capacity of MgO-N and MgO-O, such a result can also, be attributed to the comparable textural properties of MgO-N and MgO-O, whereas MgO-N is slightly have a higher surface and smaller pore size which induced the slight higher adsorption of CO₂.

It is well-known that calcination temperature is one of the key factors that might significantly alter the characteristics (e.g., crystallinity, morphology, porosity, compositions) of adsorbents and, accordingly, their adsorption capability. Thus, MgO-A was calcinated at 300, 400, and 500 °C for 10 h; the effect of the calcination temperature of MgO-A on its CO₂ adsorption capacity is shown in Fig. 5. The results clearly demonstrate that calcination at 400 °C produces MgO adsorbent with the highest CO₂ adsorption capacity relative to the other two calcination temperatures. Increasing the calcination temperature to 500 °C causes a slight reduction in the adsorption capacity, most likely due to a certain level of MgO agglomeration at this temperature [160]. A more significant reduction (nearly 30%) in CO₂ adsorption capacity is encountered when MgO-A was calcinated at 300 °C. Such a reduction in CO₂ adsorption capacity might be attributed to the incomplete conversion of magnesium hydroxide to MgO at this calcination temperature. The presence of some magnesium hydroxide in the MgO sample is likely to impact its CO₂ adsorption capacity negatively. The very low CO₂ adsorption capacity of the as-prepared sample, which was not subjected to calcination, supports this assertion, as shown in Fig. 5. Accordingly, the above results suggest that the optimal calcination temperature of MgO-A is about 400 °C. This optimal calcination temperature is in line with that reported by other researchers [161].

Although MgO-A, calcinated at 400 °C, provides the highest CO₂ uptake capacity among all unmodified MgO adsorbents, the adsorbed amount of CO₂ is still unsatisfactory. To enhance CO₂ adsorption, MgO-A was functionalized with three amines (APTES, DETA, and PEI) having different features. The adsorption of CO₂ on the amine-functionalized MgO-A is shown in Fig. 6, which reveals the enhancement of CO₂ adsorption upon the functionalization of MgO-A with the amines, with the exception of PEI. For instance, the CO₂ adsorption capacity increased by more than 2 and 1.5-fold when MgO-A was functionalized with APTES and DETA, respectively. Contrarily, the functionalization of MgO-A with PEI resulted in a 20% decrease in its adsorption capacity. Contrasting these results to the textural properties of these adsorbents suggest that the enhancement of CO₂ adsorption upon the attachment of APTES and DETA to MgO-A compensate for the huge loss in the porosity of the support (i.e., MgO-A) whereas, on the other side PEI did not completely compensate. Moreover, the higher CO₂ affinity of APTES relative to DETA might have also contributed towards the higher CO₂ adsorption on APTES-MgO-A. This finding is supported by the observation that the enhancement of CO₂ adsorption on graphene oxide functionalized with APTES was the highest amongst other amines, including DETA [130, 131]. On the other hand, the functionalization of graphene oxide with PEI resulted in a lower adsorption capacity as a result of a significant pore blockage by the bulky molecules of PEI [131], in line with our observations.

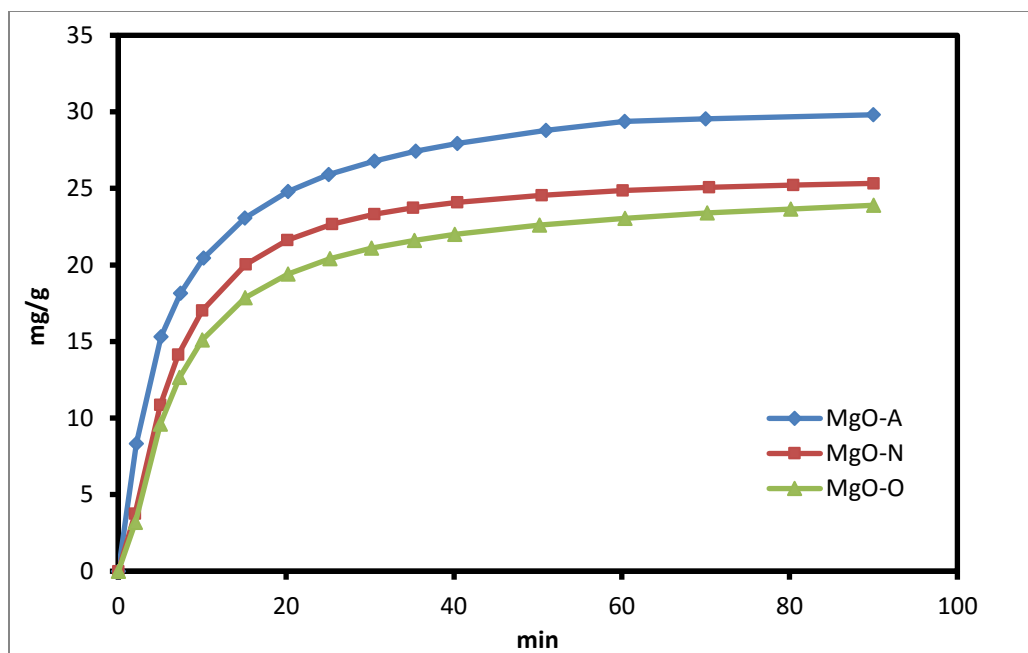


Figure 3-4 Effect of the synthesis route of MgO on its CO₂ adsorption capacity. The adsorption took place at 30 °C and atmospheric pressure. The flow rate of pure CO₂ was kept constant at 100 mL/min.

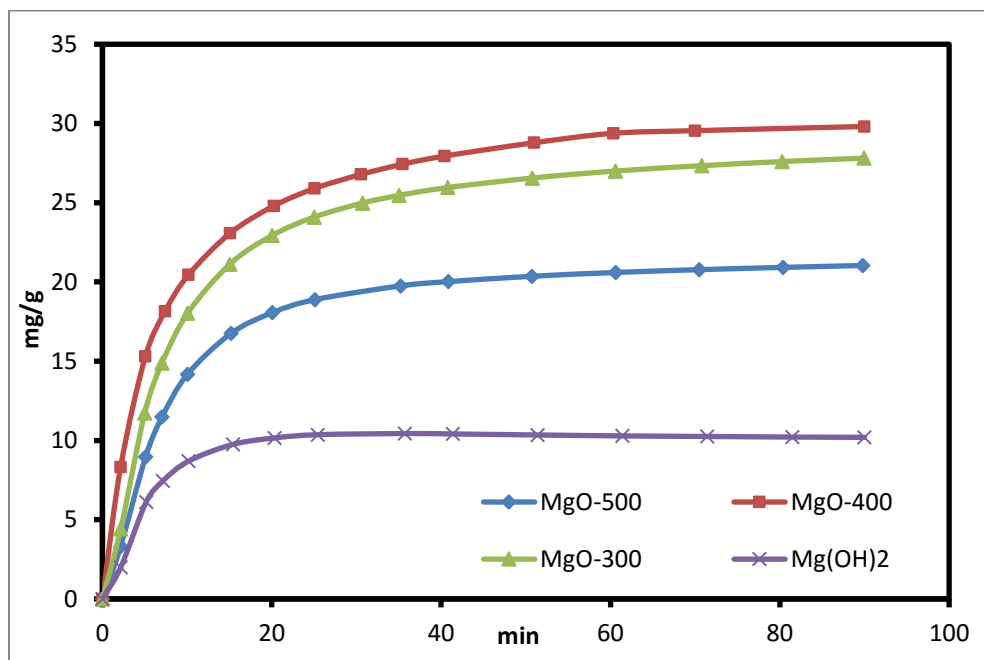


Figure 3-5 Effect of calcination temperature of MgO-A on its CO₂ adsorption capacity. The adsorption took place at 30 °C and atmospheric pressure. The flow rate of pure CO₂ was kept constant at 100 mL/min.

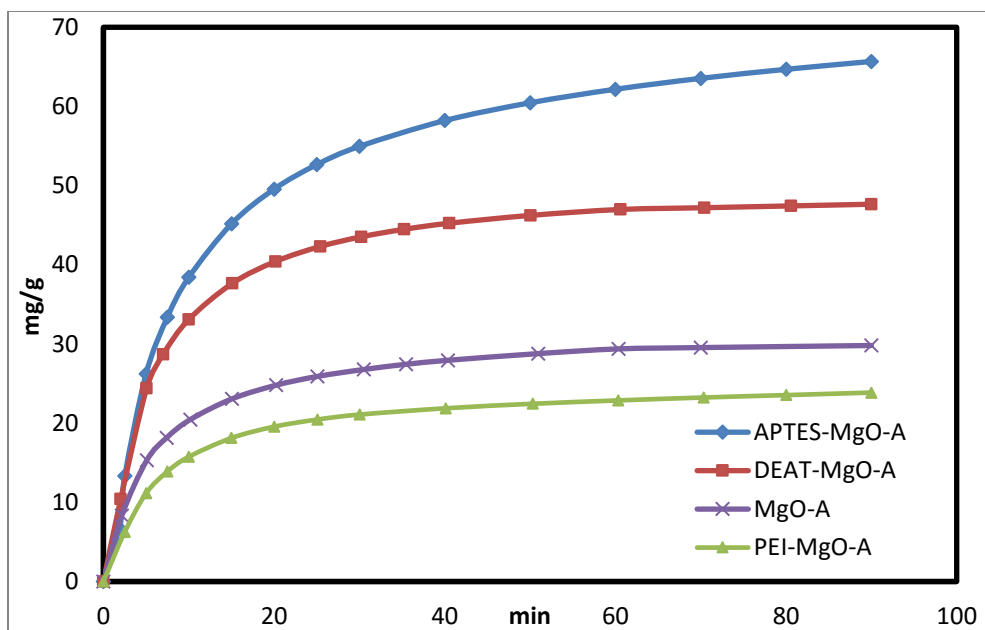


Figure 3-6 Effect of the functionalization of MgO-A with APTES, DETA and PEI on its CO₂ adsorption capacity. The adsorption took place at 30 °C and atmospheric pressure. The flow rate of pure CO₂ was kept constant at 100 mL/min.

3.6 Regeneration of APTES-MgO-A adsorbent

Regenerability and stability of CO₂ adsorbents are extremely important economic factors. Accordingly, we have conducted a study to assess the regenerability and the stability, under the regeneration conditions, of the most effective adsorbent (i.e., APTES-MgO-A), and the result is shown in Fig. 7. The regeneration was carried out at 120°C and atmospheric pressure using 100 mL/min of pure N₂. It was observed that a 30-min regeneration time is sufficient to fully restore the adsorption capacity of the spent APTES-MgO-A. Six cycles of CO₂ adsorption followed APTES-MgO-A regeneration were performed without any noticeable reduction in the adsorbent capacity. This finding suggests that this adsorbent is highly stable with an excellent regenerability at a relatively

low temperature compared to other adsorbents [142, 143] . These characteristics of APTES-MgO-A, in addition to its reasonably good adsorption capacity at ambient conditions, make it a very promising candidate for commercial CO₂ capture with a minimal regeneration energy requirement.

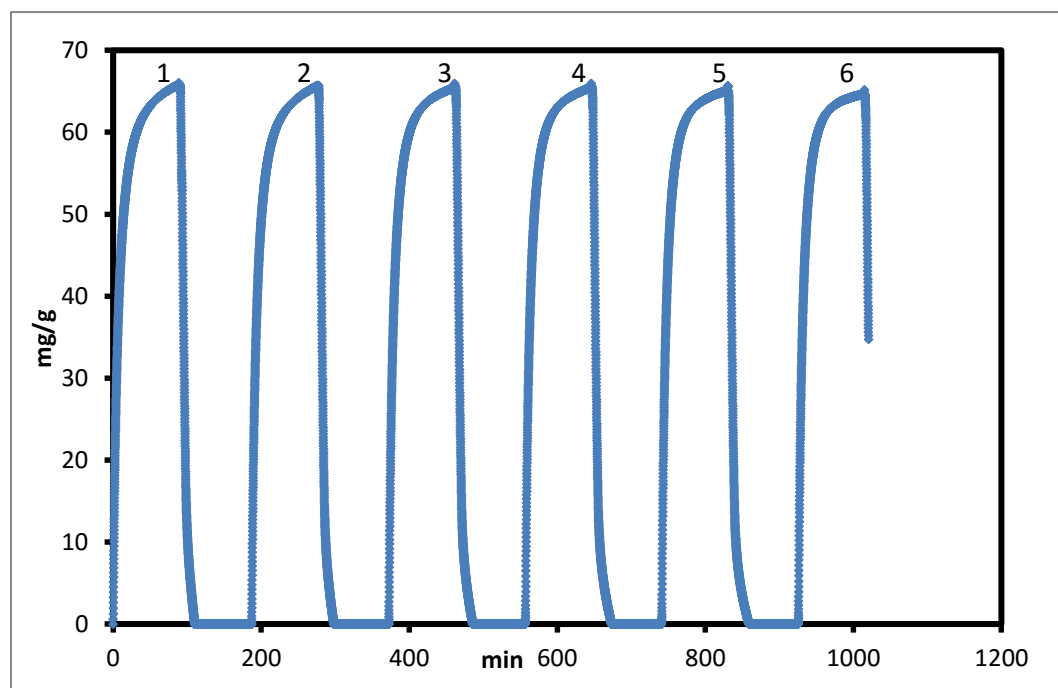


Figure 3-7 Regeneration cycles of APTES-MgO-A using pure N₂ gas, flowing at 100 mL/min. The regeneration temperature and pressure were 120 °C and 1 atm, respectively.

3.7 Conclusions

MgO-based adsorbents are promising materials for CO₂ capture at ambient conditions. MgO can be produced via different synthesis routes; however, the utilized route (i.e., the chemistry of the MgO synthesis solution) has altered the characteristics of the obtained MgO and, accordingly, its CO₂ adsorption capability. Among the three MgO synthesis routes utilized in this work, the ammonium hydroxide route is the best. MgO synthesized using this route displayed the highest surface area and the highest CO₂ adsorption capacity. In addition to the chemistry of the MgO synthesis solution, the calcination temperature of the as-prepared material is also a key factor. Calcination at 400 °C results in higher CO₂ adsorption. A higher calcination temperature (i.e., 500 °C) has caused a certain level of agglomeration while a low calcination temperature (i.e., 300 °C) has resulted in incomplete oxidation of the as-prepared adsorbent. Functionalization of MgO with amines results in an enhancement of CO₂ adsorption unless the surface area of the adsorbent is severely not compromised as it was the case for the functionalization of MgO with PEI. Although the surface area is a key factor, it is not the only one. Porosity, amine-CO₂ interaction (i.e., amine affinity for CO₂) and adsorbent morphology are also important factors as evident from the higher CO₂ adsorption on APTES-MgO-A relative to DETA-MgO-A. In addition to the relatively high affinity for CO₂ in the case of APTES-MgO-A, this adsorbent is completely and repeatedly regenerable, making it a good candidate for the commercial CO₂ capture applications, with low-energy consumption during the mild regeneration process.

CHAPTER 4

CO₂ Capture at Ambient Conditions using Amine-

Functionalized Graphene Derivatives Nano-Composites

During the last decade, considerable research work in graphene-based (nano-composites) synthesis has been conducted because of their excellent properties such as thermal stability, mechanical strength, and good conductivity. Thus, the work presented over here is aimed to emphasize the efficient use of graphene derivatives (nano-composites) as based adsorbent for CO₂ capture at ambient condition using Thermo-gravimetric analysis (TGA). First of all, the graphite was used as a precursor material for the graphite oxide (GO) preparation. The oxidization of graphite was carried out by utilizing KMnO₄ as an oxidizing agent using strong acid in an ice bath. Reduction of GO was performed by following the chemical reagent reduction using Zn and Al foil as reducing agents. GO achieved a considerable adsorption capacity of 45 mg/g comparing to RGO uptake capacity of 13.1 mg/g. In this study, four types of amine were employed to enhance the CO₂ uptake capacity of graphite oxide at ambient condition. Those amines are 3-aminopropyl-triethoxysilane (APTES), Diethylenetriamine (DETA), polytheylenimine (PEI) and hexamine. Moreover, variants APTES/GO mass ratios were prepared to study the effect of APTES grafting amounts in adsorption capacity. As a result, a ratio of 1:1 for 3-aminopropyl-triethoxysilane/GO has revealed the optimal ratio in compromising the loss of surface area and oxygen functional group in which case attained the highest uptake

capacity of 63 mg/g. Characterizations of the synthesized samples were accomplished using various analytical techniques including N₂ adsorption/desorption measurements, X-Ray diffraction (XRD), SEM with (energy dispersive X-ray analysis) EDX, and Fourier transform infrared spectroscopy (FTIR).

4.1 Introduction

Since the industrial revolution, the CO₂ emission has been rapidly built up in the atmosphere due to human activities and significant consumption of fossil fuels such as petroleum and natural gas [29, 62, 162]. Also, the atmospheric temperature of the earth is expected to continue to increase to an additional 1.5 °C during the 21st century with current CO₂ emission and human activities [6]. Since carbon dioxide (CO₂) outflows are viewed as the primary driver of an earth-wide temperature boost and have an immediate effect on the abnormal environmental change, thus, the release of CO₂ emission must be minimized to comply with the ecological guideline and to save our planet [130, 162]. In the effort of CO₂ capture a several technologies have been applied so far to reduce the CO₂ emission including, chemical and physical solvent absorption processes by using liquid amine solution [2, 3, 8-10], cryogenic processes [11], adsorption processes [12, 13], membrane and biological separation technics [14, 15]. Among those different technologies, adsorption is the most commonly used approach due to simple regeneration design and low energy consumption [22].

Over the last two decades, different kinds of adsorbents have been developed and improved through metals impregnation or amine modification to capture carbon dioxide. Those designed adsorbents are microporous and mesoporous silica [24, 25], carbon-based

adsorbents [26, 27], metal oxides [28, 29] and metal-organic frameworks MOFs [30, 31]. During the last decades, Graphene has appealed considerable attention among the scientific research and has been implanted in a wide range of technological applications such as energy storage (super-capacitors) [32] and adsorbents material including water purification [33], gas sensing, [34] and selective chemical aqueous adsorption [35].

In general, Graphene is a new founded material that has fabulous physical and mechanical properties. Typically, graphene is stable and exhibits excellent electronic and mechanical features [80]. Nevertheless, the analog oxidized form of graphene (graphite oxide) equivalently has obtained great research appreciation as well since it has been produced in 1855 by Brodie. This extraordinary attention in graphite oxide (GO) is attributed to the abundance of oxygen functionalities such as carbonyl (C=O), alkoxy (C–O–C) and hydroxyl (OH) groups, which permit a relaxed manipulation and configuration [95]. Three commonly approaches for the preparation of graphite oxides have been reported in the literature, Brodie method, Staudenmaier's (ST) and method Hummers' (HU) method [96, 97]. In addition to the interest that given to GO, reduced graphite oxide (RGO) as well takes a roll in research attention. Overall, RGO has several preparation approaches; the first approach is chemical reduction [111, 112] which includes hydrothermal [113], Solvothermal [114, 115] and electrochemical reduction [116, 117]. The second approach is a thermal reduction that includes thermal annealing [118-120], microwave, and photo reduction [121]. In general, Graphene oxide's reduction methods are conducted using oxygen functional groups removal. Apart from the applications stated of Graphene-based Nano-composites, the main goals of this study are to highlight the significance of graphene derivative's (GO & RGO) as based adsorbent for carbon dioxide.

In this study, graphite oxide was synthesized using graphite as starting material and KMnO_4 as an oxidizing agent. The produced graphite oxide was converted to reduced GO by chemical reduction means using two reducing agents. Both GO, and RGO was grafted by APTES to enhance the CO_2 removal capacity. Accordingly, the highest adsorbent capability was further considered to be a base adsorbent and has been further modified using variants types of amine molecules, including PEI, DETA, and Hexamine. Finally, a different mass ratio of APTES/GO was prepared and examined to identify the influence of amine amounts in uptake capacity of the synthesized adsorbent.

4.2 Materials and methods

4.2.1 Chemicals and materials

The required chemicals are Graphite powder, H_2SO_4 (98%), $\text{NaNO}_3 \geq 99$, H_2O_2 (30%), $\text{KMnO}_4 \geq 99$, HCl (37%), 3-aminopropyl-triethoxysilane (APTES) ≥ 99 , Diethylenetriamine (DETA) ≥ 99 , Hexamethylenetetramine (Hexamine) ≥ 99 , polyethylenimine (PEI) 10000MW ≥ 99 , Zn powder, Al foil, NaOH pellets ≥ 99 , and deionized water. All the chemicals are lab-grade purchased from Sigma-Aldrich and used without further modification.

4.2.2 Synthesis of graphene oxide (GO)

The synthesis of graphene oxide (GO) was achieved by the oxidization of graphite powder using the procedure of modified Hummer's method [163]. In concise, first of all, 2.0 g of graphite powder was blended with 1.0 g of potassium nitrate. Subsequently, 46 ml of concentrated sulphuric acid 98% was poured over the blend, and the obtained mixture was kept under continuous stirring in an ice bath for one hour. Then, 6.0g of KMnO_4 was added slowly in small quantity to the mixture while the temperature was maintained below 20°C to avoid overheating and outburst. After that, the mixture temperature was kept at 35°C under continuous stirring for four hours. Then, 92 ml of deionized water was added gradually followed by stirring at 98°C for 15 minutes. After that, the suspension was treated with 2 ml of 30% H_2O_2 solution in 280 ml of deionized water to assure the end of reaction with KMnO_4 . Then, the mixture was stirred at room temperature overnight. For refinement, the mixture is centrifuged at 4500 rpm for 5 minutes and washed with 10% HCl two times and then washed with deionized water three times to eliminate the residual metal ions and acid. Finally, the precipitate was dried at 60°C overnight.

4.2.3 Synthesis of amine-modified graphite oxides

In brief, one gram of the synthesized GO was first dispersed in 600 ml of deionized water. Then, one gram of amine molecule was added to the GO solution. In this study, GO was functionalized by APTES, DETA, PEI, and hexamine separately in different batches. For APTES-GO with variants APTES/GO mass ratios, different APTES quantities were added to GO dispersion in different batches to attain various APTES/GO ratios. After the addition of the required amine quantity, the mixture was stirred for 5 minutes, followed by bath sonication in ultrasonicator for one hour. Next, the mixture was refluxed for 45 h at

65 °C with continuous stirring. After the end of solvent-assisted amine modification; the sample was rinsed three times with deionized water and obtained using a centrifuge at 4500 rpm for 5 minutes [164]. The past was left in the dry oven at 60 °C overnight. Those, the modified GO samples were coded as APTES-GO, PEI-GO, DETA-GO, and Hexamine-GO following the attached amine compound.

4.2.4 Chemical reduction using Zn/HCl

First, the synthesized GO or APTES-GO was dissolved in deionized water with a concentration of 1mg/ml. Then, it was stirred for 5 minutes at room temperature, followed by sonication for 10 minutes. After that, the Ph of the mixture was adapted to 2 by a small addition of 37% HCl. Then, the Zn powder was added to the mixture in a ratio of 2:1 to the GO or APTS-GO. After that, the mixture was immediately sonicated for another 20 minutes. Then, an additional amount of 37% HCl was added, about 20 ml for each gram of Zn to ensure the dissolving of the excessive Zn powder and stirred for an extra 5 minutes [125]. Finally, the reduced adsorbent was collected with centrifugation and washed with deionized water three times. Then, it was dried at 60 °C overnight, and the obtained adsorbents were coded as RGO-1 and APTES-RGO-1, respectively.

4.2.5 Chemical reduction using Al / HCl (1N)

In concise, one gram of the synthesized GO was diluted first with 918.3 ml deionized water. Then, the solution is sonicated for 10 minutes to obtain a homogenous mixture. After that, 81.7 ml of 37% HCl was added to the GO dispersions to get 1 mol /l HCl concentration mixture. Then, the mixture was left for an additional 10 minutes of mixing and sonication to get a proper homogenization. Subsequently, 3 g of Al foil was added to the GO solution with 1mg/ml dilution. The reduction was completed by continuous stirring for two hours

[165]. RGO recovered by centrifugation, and the paste was washed with 0.1N HCl and deionized water several times. Finally, the paste was dried at 60 °C overnight and coded as RGO-2.

4.2.6 Chemical reduction using (Al foil & Zn)/ NaOH (1N)

In this experiment, the synthesized GO was diluted with deionized water up to 1.0 mg /ml. Then, the solution was sonicated for 10 minutes to obtain a homogenous mixture. After that, 40 g of NaOH ballets were added gradually to the graphene oxide dispersions until 1N NaOH achieved. Then, an additional 10 minutes of mixing and sonication was applied for dispersing the formed aggregate. Subsequently, 2 g of Zn powder & Al foil were added to the GO solution. The reduction was completed by continuous stirring for one hour. The RGO was obtained by centrifugation and washed with 0.1N HCl and deionized water several times. Finally, the paste was dried at 60 °C overnight and named as RGO-3.

4.3 Sample characterization

The surface area BET (Brunauer–Emmett– Teller) of Graphene derivative-based adsorbents & modified GO were measured using nitrogen adsorption isotherms at 77 K using an ASAP 2020 system (Micromeritics Instruments, Inc.). The morphologies structures of prepared adsorbents were studied using scanning electron microscopy (SEM). The adsorbents crystal structures were studied using XRD pattern by Shimadzu XRD-6000 X-ray diffractometer with Curadiation 40 kV and 30 mA. The elemental analysis was carried out using Energy-dispersive X-ray spectroscopy (EDX) equipped with SEM. Functional groups were identified using Fourier Transform Infrared (FTIR) spectra and

recorded at room temperature on range 400 to 4000 cm^{-1} by NICOLET 6700 spectrometer from Thermo Scientific using KBr pellets.

4.4 Evaluation of CO₂ adsorption capacity

The measurement of CO₂ uptakes capacity for the synthesized samples was carried out by using a TA Q600 SDT. About, 10 mg of the sample was weighed by TGA using alumina oxide pan. After that, the sample was outgassed at 100°C under the flow of pure N₂ gas at 100 mL/min for 30 minutes. Then, the temperature equilibrated to 30 °C. As a final point, the gas was switched to pure carbon dioxide (99.9%) with a flow rate of 100 ml/min for 90 minutes to compute the uptake capacity of the synthesized sample.

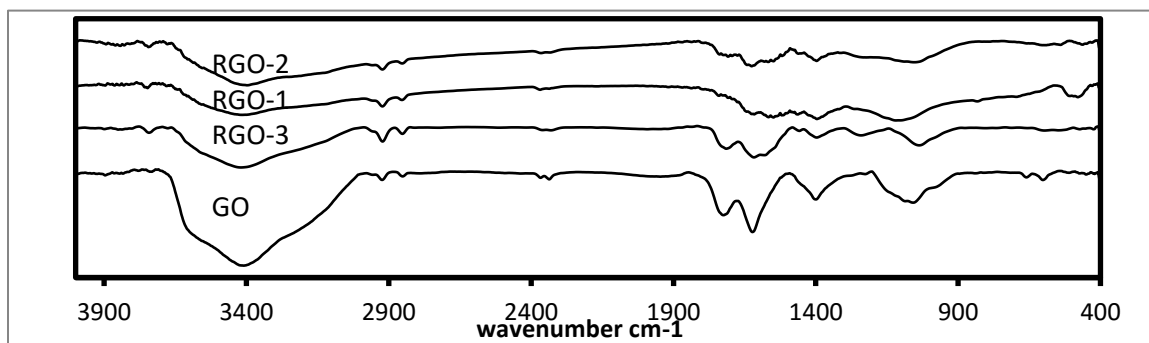
4.5 Result and discussion

4.5.1 Characterization of samples

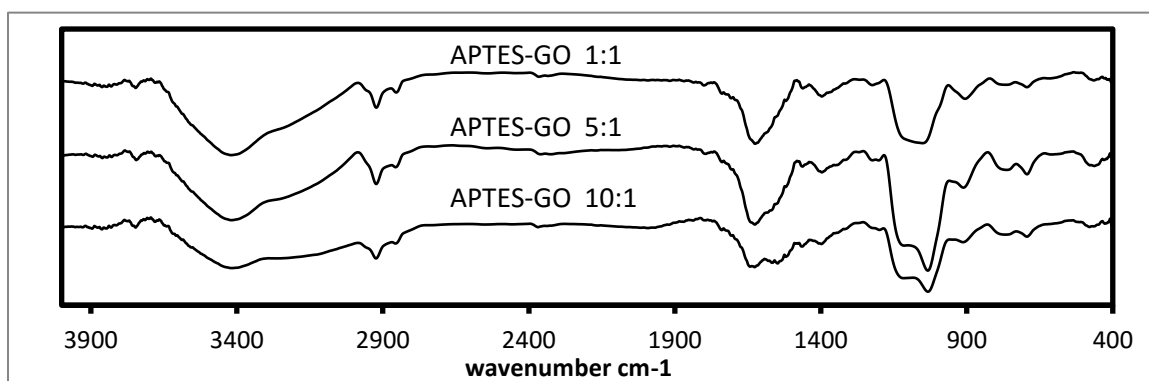
Fig. 1 shows the FTIR spectra of the synthesized samples in the range of 400 to 4000 cm^{-1} wavenumber. Accordingly, Fig. 1(a) presents the FTIR spectra manner of graphite oxide and the reduced graphite oxides. As a result, both GO, and RGOs have the same FTIR pattern, but the peaks band intensity of the functional groups which were identified in GO have decreased or disappeared in RGOs samples. The wide-ranging peak centered at 3400 cm^{-1} stands for O–H stretching vibration while the minor peaks at 2920 and 2850 cm^{-1} are corresponding to C–H bending vibration [96, 110, 157]. The band peak at 1750 cm^{-1} stands for –C=O stretching vibration of the carboxyl group and the band at 1615 cm^{-1} could be attributed to the skeletal vibrations of un-oxidized sp² hybridized carbons from the graphitic structure [96, 110, 125, 157]. The peak at 1400 cm^{-1} corresponds to C–OH

stretching vibrations of carboxyl group while the band at 1220 cm^{-1} is corresponding to C–O–C stretching vibration. The bands at 1040 and 970 cm^{-1} stand for C–O stretching of epoxide groups [96, 157]. Fig. 1(b) depicts the FTIR spectra of APTES-GO prepared at variants APTES / GO ratio. After APTES grafting, the peaks at 3395 and 694 cm^{-1} are attributed to the N–H stretching vibration and the peaks at $2920 - 2850\text{ cm}^{-1}$, which were assigned to the bending vibration of CH_2 now are associated with the CH_2 bending vibration of the APTES chain molecules [131, 154]. The peak at 1750 cm^{-1} has reduced or disappeared that corresponding to $\text{C}=\text{O}$ stretching vibration while the intensity of the peak at 1615 cm^{-1} has increased which might be attributed to the presence of C–N groups. The vibrational band at 1050 cm^{-1} can be assigned to Si–O stretching vibration [154, 166]. Fig. 1(c) displays the FTIR spectra of GO, DETA-GO, APTES-GO, and PEI-GO. Concerning PEI functionalization, the new peak at 3200 cm^{-1} is corresponding to νNH stretching vibration. The peaks at 2920 and 2850 cm^{-1} are attributed to symmetric and asymmetric C–H stretching in PEI, respectively [131]. The bands at 1600 and 1450 cm^{-1} are assigned to NH bending [131, 167, 168]. The DETA-GO demonstrates new band at 1200 cm^{-1} which can be attributed to CN stretch.

(a)



(b)



(c)

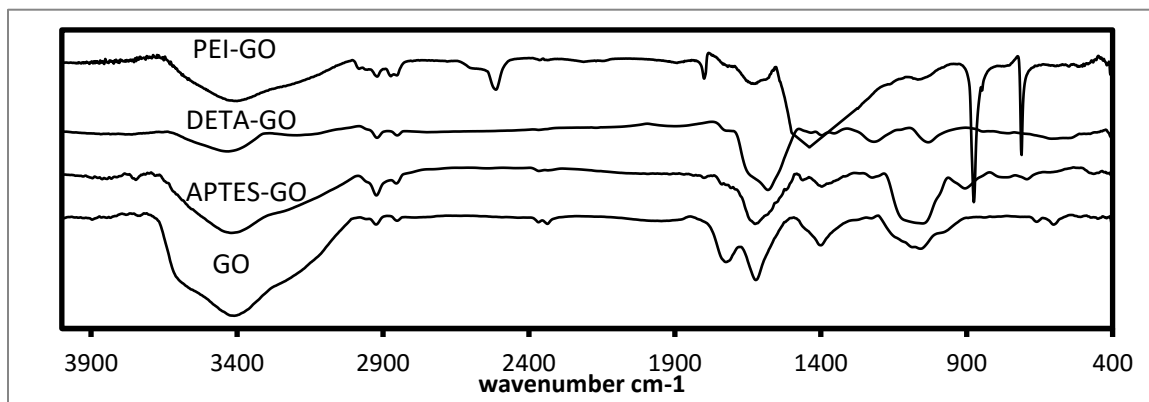


Figure 4-1 (a) FTIR patterns of GO, RGO-1, RGO-2 and RGO-3, (B) FTIR patterns of APTES-GO for variants ratio of APTES/GO, (C) FTIR patterns of GO and amine factionalized GO.

The XRD patterns of GO, RGO-1, APTES-GO, and APTES-RGO-1 are presented in Fig. 2. According to the reported result in the literature, The pristine graphite exhibits a very intense and narrow sharp peak around 26° , which corresponding to the standard graphite spacing about 0.34 nm [100, 169]. Concerning the obtained result of graphite oxide, a sharp diffraction peak appeared around 10° . This typical shifting of the sharp peak toward a lower peak angle is assigned to the attachment of a large amount of oxygen-containing groups to the carbon atoms such as hydroxyl, epoxy, and carboxyl groups that give rise to expand the interlayer distance between graphite layers [34, 127]. Moreover, a small diffraction peak of about 43° is attributed to a short-range order in stacked graphene layers [107]. In the case of reduced graphite oxide, a sharp peak around 10° has disappeared. As a result, the narrow graphite peak around 26° has been restored around 23.5° as a broad and less intense peak. This result indicates that the interlayer distance has decreased after GO reduction, and some of the oxygen functional group was removed [115, 127, 169, 170]. APTES-GO and APTES-RGO-1 obtained less intense diffraction peak and have been shifted toward a lower peak angle around 6.5° and 15.2° , respectively. These results indicate that after amine modification of GO, and RGO-1, they exhibited a further expanding in d-spacing, which can be regarded to the amine molecules intercalation among the layers [131, 171].

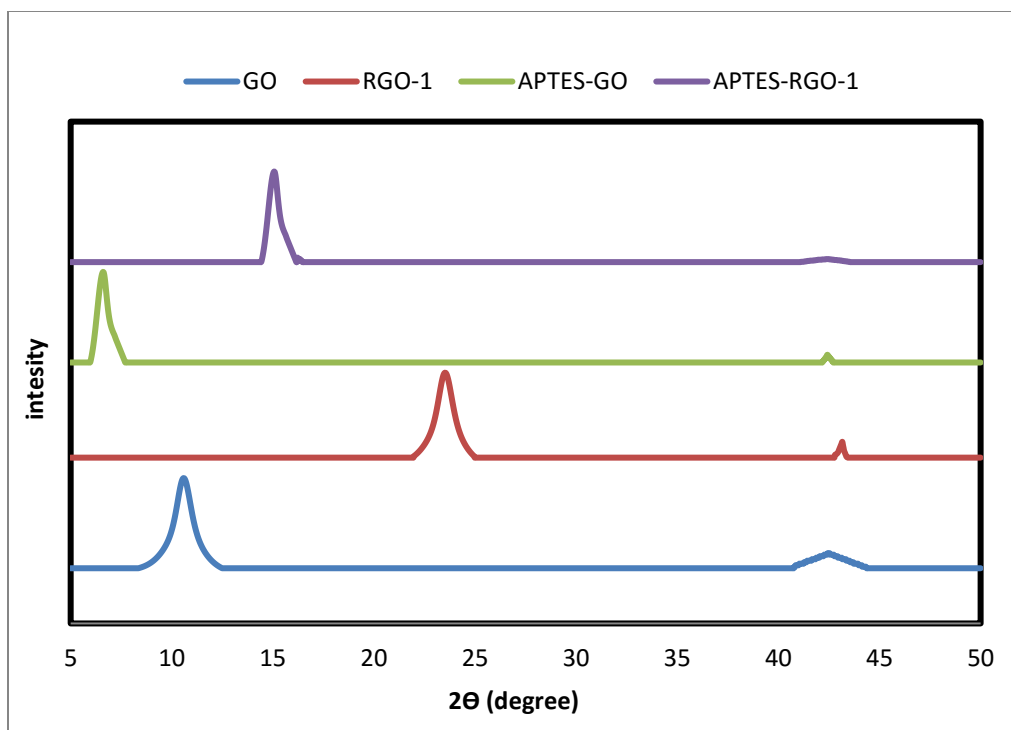


Figure 4-2 XRD pattern of GO, RGO, APTES-GO-1 and APTES-RGO-1

Table 1 presents the textural properties of the synthesized GO, RGO-1, APTES-GO, and APTES-RGO-1. The N₂-physisorption measurement at 77 K was applied to determine the surface textural properties of produced adsorbents, including surface area, pore size, and pore volume. According to the IUPAC standard, all of the samples fall in microporous order according to the measured pore size of prepared samples. Thus, microporous pores could have a positive impact of high selectivity towards CO₂ molecules of 0.33 nm of kinetic radius as previously reported [172, 173]. However, the synthesized GO using hummer modified method has obtained equivalence textural properties to the reported value in literature with 53.7 m²/g surface area, 0.023 cm³/g pore volume, and 1.74 nm pore size [132, 168]. On the other hand, the prepared RGO-1 has achieved a minimal surface area and pore volume which can be attributed to the influence of reducing agents and

experiments condition [174, 175]. After amine modification of GO and RGO-1 surface, the surface area, pore-volume, and pore size have further reduced as a result of amine attachment to the GO and RGO-1 structure.

Table 4-1 textural properties of GO, RGO-1, APTES-GO and APTES-RGO-1

Samples	Surface area	Pore volume	Pore size
	(BET) (m ² /g)	(cm ³ /g)	(nm)
GO	53.7	0.023	1.74
RGO-1	5.3	0.002	1.50
APTES-GO	29.1	0.012	1.61
APTES-RGO-1	8.6	0.003	1.43

The surface microscopic and morphology of the selected samples was investigated using the scanning electron microscopic. Fig. 3 displays the SEM image of GO, RGO-1, APTES-GO, and APTES-RGO-1. As shown in Fig. 3(a), GO shows lamellar morphology that composed of flakes and folded graphitic sheets due to oxidization with concentrated acid and dispersive forces of the formed surface groups [130, 131]. RGO-1 as well demonstrates the crumpled and wrinkled structure of randomly aggregated sheets. The wrinkled and folded sheet reflects the extent of reduction in which the more crumpled structure the highest achieved reduction degree [165]. After amine modification of GO and RGO-1, as shown in Fig. 3(c) and (d), the adsorbents still pertain the same morphology of crumpled and randomly aggregated sheets but with higher dense and less flexible solid structure due to amine grafting on the surface. Also, the surface area and pore volume have

further reduced as a result of chemical functionalization, which is in good agreement with BET surface area analysis.

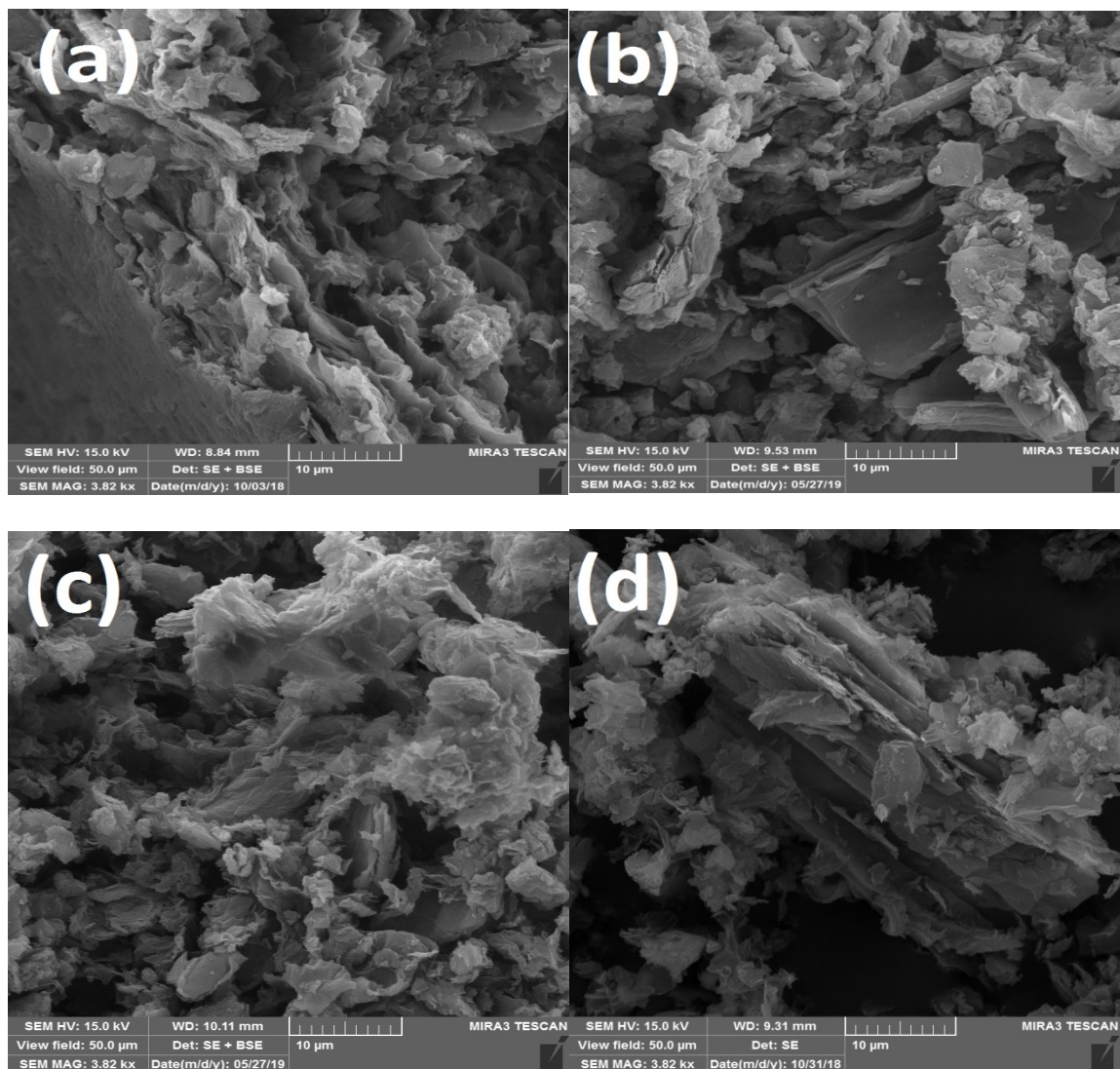


Figure 4-3 SEM of GO, RGO-1, APTES-GO and APTES-RGO-1 in (a), (b), (c) and (d) accordingly.

Table 2 summarizes the elemental composition (C, O, and N) of GO, RGO-1, RGO-2, RGO-3, APTES-GO, DETA-GO, and PEI- GO. As illustrated in Table 2, GO has the highest oxygen content as a result of containing a large number of oxygen functional groups on the surface. After the chemical reduction, carbon content has increased while oxygen has reduced due to the removal of some oxygen functional groups. Concerning the shown result in Table 2, RGO-1 which was prepared by Zn/HCl reduction of GO has reached a greater extent of reduction. Concerning the amine-modified GO, including APTES-GO, PEI-GO, and DETA-GO, the existing of nitrogen content has confirmed the successful functionalization of amine. It should be notified that PEI-GO contains higher nitrogen content comparing to DETA-GO and APTES-GO.

Table 4-2 Elemental compositions of the synthesized samples.

Samples	C % w/w	O % w/w	N % w/w
GO	57.87	42.13	—
RGO-1	89.4	10.6	—
RGO-2	88.2	11.8	—
RGO-3	85.4	14.6	—
APTES-GO	49.9	39.98	10.12
APTES-RGO-1	86.1	8.3	5.6
DETA-GO	51.51	35.99	12.5
PEI-GO	55.11	26.51	18.38

4.5.2 The CO₂ adsorption capacity of the synthesized samples

Studying of CO₂ adsorption capacity for the recently founded materials is one of the most reliable parameters to examine the material suitability for CO₂ removal. In the current study, TGA was used to evaluate the CO₂ adsorption extent of all the synthesized adsorbents under 100 ml/min flow of CO₂ for 90 minutes. The experiments conducted at the ambient condition of 30 °C and atmospheric pressure, as shown in Fig. (4-7). The abscissa axis indicates the interval time of CO₂ adsorption, and the ordinate presents the adsorption capacity. However, the evaluation of CO₂ uptake capacity of graphene derivatives based adsorbent has started by comparing the adsorption capacity of GO and RGO-1, as shown in Fig. 4. As a result, the GO has higher adsorption than RGO-1 did with a capacity of 45 mg/g. The considerable difference in adsorption capacity of GO and RGO-1 can be attributed to the existence of oxygen functional groups such as carboxyls and hydroxyls on GO surface that play essential role to increase CO₂ adsorption capacity [176, 177]. As well, the higher surface area of GO compared to RGO-1 has also significant influence toward CO₂ capture enhancement. To assess the impact of increasing the basicity of adsorbent surface on CO₂ adsorption, a mass ratio of 1:1 of APTES was grafting over the GO and RGO surfaces. Fig. 5 exhibited the uptake capacity of APTES-GO and APTES-RGO-1. As a result, APTES-GO and APTES-RGO-1 had a significant increase in CO₂ capture up to 63.29 mg/g and 20.62 mg/g, respectively. In this sense, the reason of higher CO₂ adsorption on APTES modified GO, and RGO-1 is not attributed to surface area while it is attributed to the higher affinity of CO₂ to react with amine groups (acid & base interaction) and yields carbamates than CO₂ quadrupole-dipole interaction with oxygen functional groups on GO and RGO-1 [178]. According to the obtained result, GO would

be more suitable based adsorbent for CO₂ capture. Thus, GO was further considered as a base adsorbent to investigate the influence of different kind of amines on enhancing CO₂ removal.

Fig. 6 compares the adsorption capacity of GO and variants type of amines modified GO, including APTES-GO, DETA-GO, PEI GO, and Hexamine-GO with a mass ratio of 1:1. As a result, both APTES-GO and DETA-GO had shown improvement in CO₂ capture comparing to GO with a capacity of 63.29 mg/g for APTES-GO which is in good agreement with the reported result in literature [130, 131] and DETA-GO has 56.64 mg/g which is higher than the earlier conducted work [179].

On the other hand, both PEI-GO and Hexamine-GO had less uptake capacity of CO₂ in contrast to unmodified GO with a capacity of 17.95 mg/g and 28.99 mg/g respectively. The positive impact of APTES and DETA grafting and the adverse effect of PEI and hexamine impregnation, it can be well explained to the less loss of oxygen functional groups after APTES and DETA modification for GO surface [131]. Thus, the addition of PEI and hexamine did not compensate for the vast lost in an oxygen functional group, which cause a higher reduction in GO surface that results in less adsorption as observed in APTES-RGO-1. Moreover, the long chain of PEI and high molecular weight of both PEI and Hexamine could restrict the pathway of CO₂ and reduce the adsorption capacity [180]. As APTES-GO was the highest adsorbent capacity among the synthesized amine-modified GO adsorbents, it was further examined to identify the optimum APTES/GO mass ratio of the produced APTES-GO which can have higher adsorption capacity of CO₂.

Fig. 7 shows the adsorption capacity of variants APTES-GO adsorbents prepared by different solution mass ratio including 0.5:1, 1:1, 5:1, 10:1 and 15:1 APTES/GO mass ratio. As a result, only APSET-GO with 1:1 and 5:1 mass ratio had better enhancement on CO₂ capture. Thus, the higher mass ratio can restrict the CO₂ pathway as well the GO would be much reduced. For the low mass ratio of APTES/GO, which is 0.5:1 in this study, it seems to be not adequate to compensate for the loss of oxygen functional groups on the GO surface. Therefore, the optimum mass ratio that compromises the loss of surface area and oxygen functional group and obtains the highest adsorption capacity has to be a value between 1 and 5.

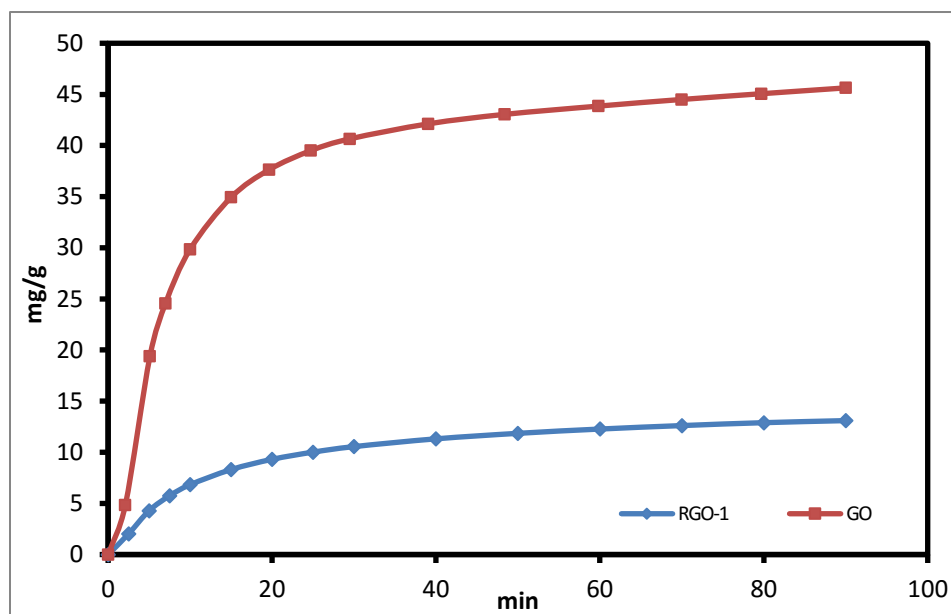


Figure 4-4 CO₂ adsorption capacity of GO and RGO-1 at 30 °C under atmospheric pressure.

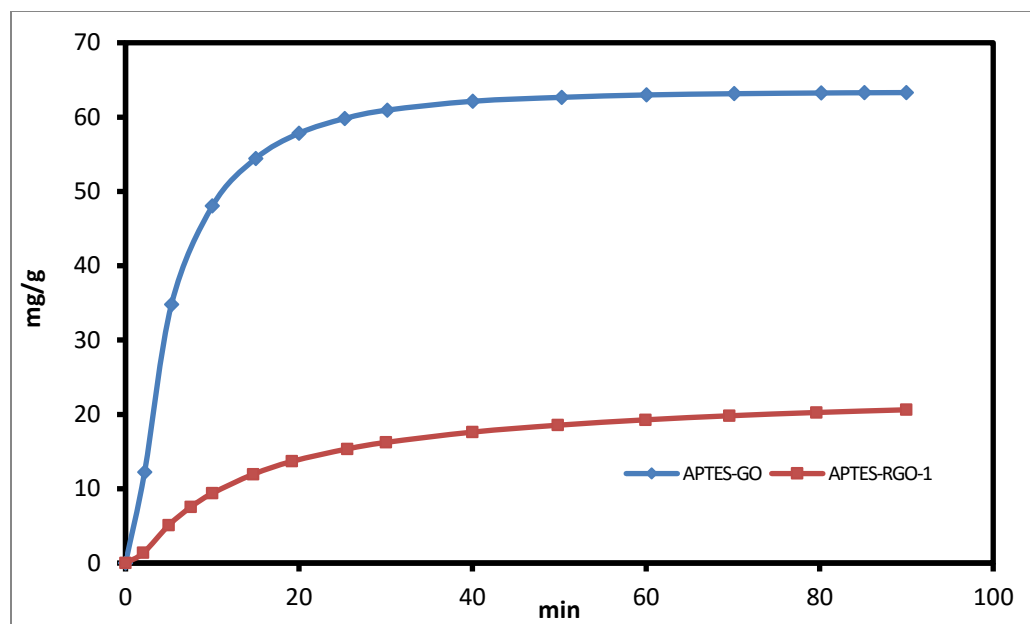


Figure 4-5 CO₂ adsorption capacity of APTES-GO and APTES-RGO-1 at 30 °C under atmospheric pressure.

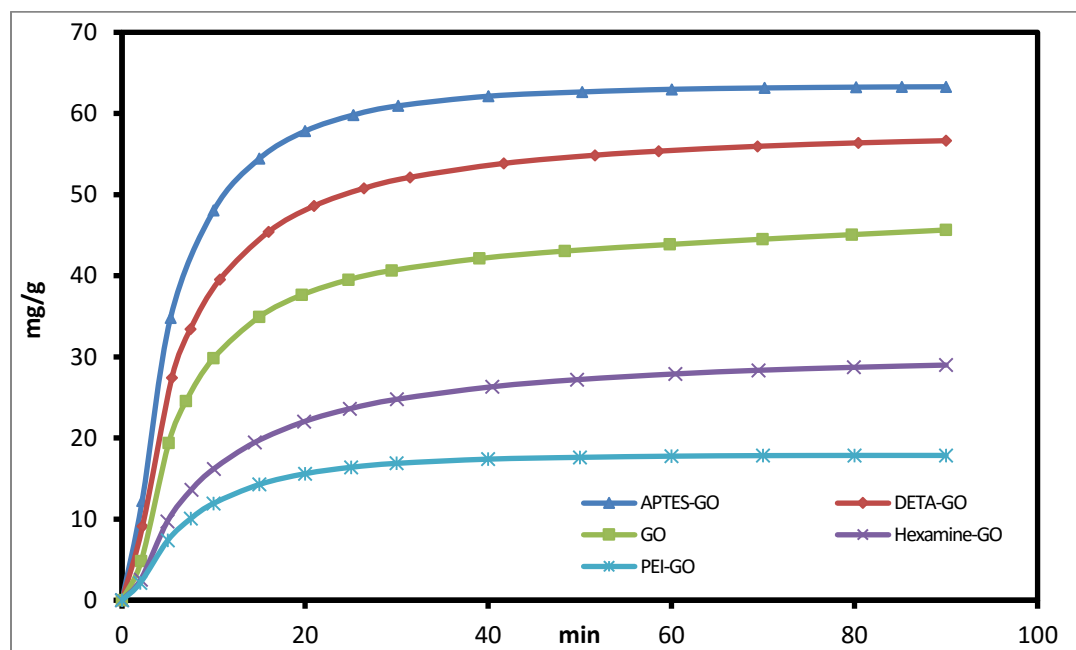


Figure 4-6 CO₂ adsorption capacity of GO, APTES-GO, DETA-GO, Hexamine-GO and PEI-GO at 30 °C under atmospheric pressure.

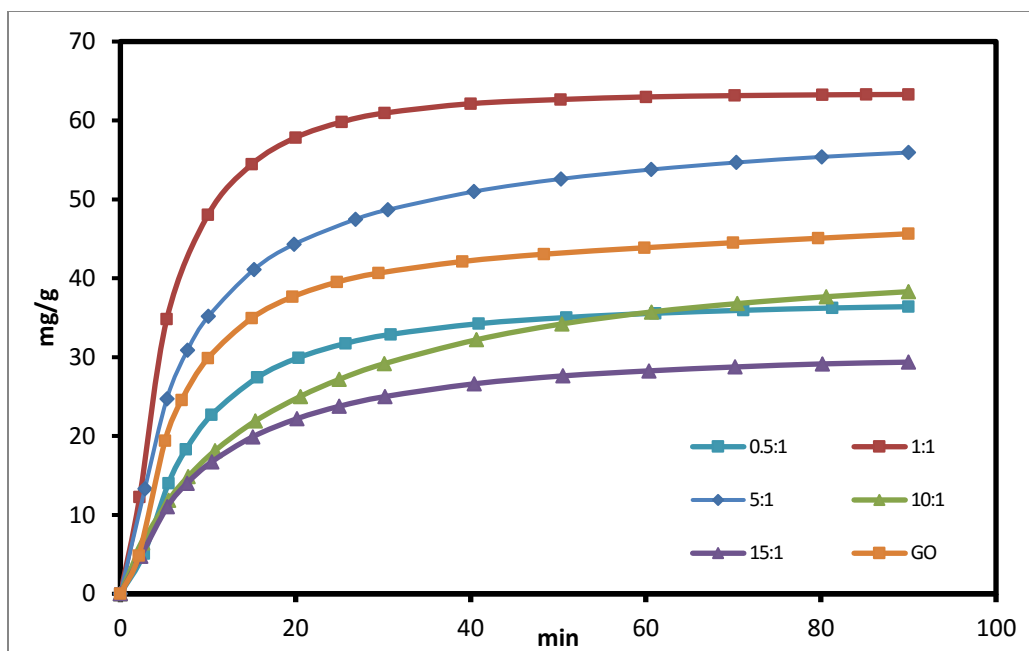


Figure 4-7 CO₂ adsorption capacity at 30 °C and 1 bar for GO and APTES-GO at variants APTES/GO ratio.

4.6 Conclusion

This work was aimed to highlight the efficient utilization of graphene derivatives Nano-composites as base adsorbent of CO₂ capture at ambient operating condition of 30°C and atmospheric pressure. First of all, Graphite oxide was typically produced using hummer modified method through the graphite oxidization by KMnO₄ in strong acid. Three reduced graphite oxides were consecutively produced by chemical reduction using Zn powder and Al foil as reducing agent, respectively. As a result, the Zn powder reducing agent shows the highest reduction degree for GO in acidic media. However, the comparison of GO and RGO-1 adsorption capacity for CO₂ capture has demonstrated the suitability of GO as based adsorbent than RGO due to the abundance of oxygen functional group on GO surface. The influence of the basicity and amine modification for the GO surface on the

CO₂ uptake capacity was investigated in detail. Four types of amine, including APTES, DETA, PEI, and hexamine with the same mass ratio of amine/GO, were employed separately to modified GO. Among these four synthesized adsorbents, only APTES-GO and DETA-GO have shown an excellent enhancement in the CO₂ uptake capacity comparing to the unmodified GO with a capacity of 63 mg/g and 56 mg/g respectively. Moreover, the effect of APTES dissolved quantities in the APTES/GO solution was studied in detail to identify the optimum APTES/GO mass ratio. Results indicate that the optimum ratio has to be in the range of 1 to 5.

CHAPTER 5

CONCLUSION & RECOMMENDATIONS

5.1 Conclusion

The following statements are the main conclusions of the experimental work.

- i. Three different forms of MgO micro porous were successfully synthesized by a facile sol-gel technique using magnesium nitrate as a manganese source.
- ii. Among these three based adsorbents, MgO-A, which was formed by the utilization of ammonia precipitate agent has exhibited the highest CO₂ uptake capacity of 30 mg/g along with the highest surface area of 246.4m²/g.
- iii. In addition to the synthesis route, the calcination temperature plays essential role in altering the textural properties which result in variants adsorption capacity. Accordingly, Calcination at 400 °C results in higher CO₂ adsorption compared to 500 °C and 300 °C due to a certain level of agglomeration at high calcination temperature and in incomplete oxidation of the as-prepared adsorbent at low calcination temperature.
- iv. The modification of MgO with APTES and DETA resulted in higher adsorption capacity for CO₂ up to 65 mg/g and 47.6 mg/g, respectively, while the functionalization with PEI caused a severe drop by 25% of the original capacity because the reduced surface area was severely not compromised by the impregnated PEI.

- v. The stability and complete regeneration of APTES-MgO-A at mild regeneration temperature suggested the practical application of APTES-MgO-A as CO₂ adsorbent with low-energy consumption.
- vi. The oxidized form of graphene derivatives (GO) showed higher adsorption capacity of 45 mg/g compared to the reduced form (RGO) due to the abundance of oxygen functional groups in GO which favor the reaction with CO₂.
- vii. The highest degree of reduction was achieved by the chemical reduction of GO using Zn powder in acidic media.
- viii. The functionalization of GO with APTES and DETA have compromised the removal of oxygen functional groups and resulted in higher adsorption.
- ix. The APTES/GO ratio 1:1 demonstrated the critical role of compromising between surface area, pore filling with amine, oxygen functional removal and CO₂ adsorption capacity.

5.2 Recommendation

The following points are the recommendations suggested to be addressed for the upcoming researches in this topic:

- i. Considering the enhancement of the MgO surface area and pore size distribution before the functionalization with amines.
- ii. Studying the simultaneous removal of CO₂ and H₂S from natural gas for both base adsorbent MgO and graphene derivatives.
- iii. Using different amines which can lead to obtain higher adsorption and study the adsorption performance at different temperature.

References

- [1] T.-L. Chew, A.L. Ahmad, S. Bhatia, Ordered mesoporous silica (OMS) as an adsorbent and membrane for separation of carbon dioxide (CO₂), *Advances in Colloid and Interface Science*, 153 (2010) 43-57.
- [2] C.H. Yu, C.H. Huang, C.S. Tan, A Review of CO₂ Capture by Absorption and Adsorption, *Aerosol and Air Quality Research*, 12 (2012) 745-769.
- [3] A.A. Olajire, CO₂ capture and separation technologies for end-of-pipe applications *energy* 35 (2010) 2610-2628.
- [4] R. Strube, G. Pellegrini, G. Manfredi, The environmental impact of post-combustion CO₂ capture with MEA, with aqueous ammonia, and with an aqueous ammonia-ethanol mixture for a coal-fired power plant, *Energy*, 36 (2011) 3763-3770.
- [5] P. Luis, Use of monoethanolamine (MEA) for CO₂ capture in a global scenario: Consequences and alternatives, *Desalination*, 380 (2016) 93-99.
- [6] G. Gómez-Pozuelo, E.S. Sanz-Pérez, A. Arencibia, P. Pizarro, R. Sanz, D.P. Serrano, CO₂ adsorption on amine-functionalized clays, *Microporous and Mesoporous Materials*, 282 (2019) 38-47.
- [7] U.S.E.P. Agency, inventory of U.S. Greenhouse Gas Emission and sinks, in, <https://www.epa.gov/ghgemissions>, 2018.
- [8] P.J.G. Huttenhuis, N.J. Agrawal, J.A. Hogendoorn, G.F. Versteeg, Gas solubility of H₂S and CO₂ in aqueous solutions of N-methyldiethanolamine, *Journal of Petroleum Science and Engineering*, 55 (2007) 122-134.
- [9] H. Zare Aliabad, S. Mirzaei, Removal of CO₂ and H₂S using Aqueous Alkanolamine Solutions, *World Academy of Science, Engineering and Technology*, 3 (2009) 50-59.
- [10] E.B. Rinker, S.S. Ashour, O.C. Sandall, Absorption of carbon dioxide into aqueous blends of diethanolamine and methyldiethanolamine, *Industrial & engineering chemistry research*, 39 (2000) 4346-4356.
- [11] K. Maqsood, A. Mullick, A. Ali, K. Kargupta, S. Ganguly, Cryogenic carbon dioxide separation from natural gas: A review based on conventional and novel emerging technologies, *Reviews in Chemical Engineering*, 30 (2014) 453-477
- [12] H. Bamdad, K. Hawboldt, S. MacQuarrie, A review on common adsorbents for acid gases removal: Focus on biochar, *Renewable and Sustainable Energy Reviews*, 81 (2018) 1705-1720.

- [13] F.D. Lamari, P. Langlois, M. Dicko, C. Chile, C. Chilev, I. Pentchev, CARBON DIOXIDE CAPTURE BY ADSORPTION, *Journal of Chemical Technology and Metallurgy*, 51 (2016) 609-626.
- [14] G. George, N. Bhorla, S. AlHallaq, A. Abdala, V. Mittal, Polymer membranes for acid gas removal from natural gas, *Separation and Purification Technology*, 158 (2016) 333-356.
- [15] B. Belaissaoui, E. Favre, Membrane Separation Processes for Post-Combustion Carbon Dioxide Capture: State of the Art and Critical Overview, *Oil Gas Sci. Technol. – Rev. IFP Energies nouvelles*, 69 (2014) 1005-1020.
- [16] J. Liu, S. Wang, B. Zhao, H. Tong, C. Chen, Absorption of carbon dioxide in aqueous ammonia, *Energy Procedia*, 1 (2009) 933-940.
- [17] D. Im, K. Roh, J. Kim, Y. Eom, J.H. Lee, Economic assessment and optimization of the Selexol process with novel additives, *International Journal of Greenhouse Gas Control*, 42 (2015) 109-116.
- [18] S. Faramawy, T. Zaki, A.A.E. Sakr, Natural gas origin, composition, and processing: A review, *Journal of Natural Gas Science and Engineering*, 34 (2016) 34-54.
- [19] Y. Alcheikhhamdon, M. Hoorfar, Natural gas quality enhancement: A review of the conventional treatment processes, and the industrial challenges facing emerging technologies, *Journal of Natural Gas Science and Engineering*, 34 (2016) 689-701.
- [20] Y. Alcheikhhamdon, M. Hoorfar, Natural gas purification from acid gases using membranes: A review of the history, features, techno-commercial challenges, and process intensification of commercial membranes, *Chemical Engineering and Processing: Process Intensification*, 120 (2017) 105-113.
- [21] M.S. Suleman, K.K. Lau, Y.F. Yeong, Plasticization and Swelling in Polymeric Membranes in CO₂ Removal from Natural Gas, *Chemical Engineering & Technology*, 39 (2016) 1604-1616.
- [22] S. Choi, J.H. Drese, C.W. Jones, Adsorbent Materials for Carbon Dioxide Capture from Large Anthropogenic Point Sources, *ChemSusChem*, 2 (2009) 796-854.
- [23] H. Pourzolfaghar, M.H.S. Ismail, S. Izhar, Z. MagharehEsfahan, Review of H₂S Sorbents at Low-Temperature Desulfurization of Biogas, *International Journal of Chemical and Environmental Engineering*, 5 (2014) 22-28.
- [24] X. Liu, J. Li, L. Zhou, D. Huang, Y. Zhou, Adsorption of CO₂, CH₄ and N₂ on ordered mesoporous silica molecular sieve, *Chemical Physics Letters*, 415 (2005) 198-201.

- [25] S.-H. Liu, Y.-C. Lin, Y.-C. Chien, H.-R. Hyu, Adsorption of CO₂ from Flue Gas Streams by a Highly Efficient and Stable Aminosilica Adsorbent, *Journal of the Air & Waste Management Association*, 61 (2011) 226-233.
- [26] M.M. Maroto-Valer, Z. Tang, Y. Zhang, CO₂ capture by activated and impregnated anthracites, *Fuel Processing Technology*, 86 (2005) 1487-1502.
- [27] M.C. Castrillon, K.O. Moura, C.A. Alves, M. Bastos-Neto, D.C.S. Azevedo, J. Hofmann, J. Möllmer, W.-D. Einicke, R. Gläser, CO₂ and H₂S Removal from CH₄-Rich Streams by Adsorption on Activated Carbons Modified with K₂CO₃, NaOH, or Fe₂O₃, *Energy & Fuels*, 30 (2016) 9596-9604.
- [28] L. Li, X. Wen, X. Fu, F. Wang, N. Zhao, F. Xiao, W. Wei, Y. Sun, MgO/Al₂O₃ Sorbent for CO₂ Capture, *Energy & Fuels*, 24 (2010) 5773-5780.
- [29] A. Hakim, T.S. Marliza, N.M. Abu Tahari, R.W.N. Wan Isahak, R.M. Yusop, W.M. Mohamed Hisham, A.M. Yarmo, Studies on CO₂ Adsorption and Desorption Properties from Various Types of Iron Oxides (FeO, Fe₂O₃, and Fe₃O₄), *Industrial & Engineering Chemistry Research*, 55 (2016) 7888-7897.
- [30] T. Remy, S.A. Peter, S. Van der Perre, P. Valvekens, D.E. De Vos, G.V. Baron, J.F.M. Denayer, Selective Dynamic CO₂ Separations on Mg-MOF-74 at Low Pressures: A Detailed Comparison with 13X, *The Journal of Physical Chemistry C*, 117 (2013) 9301-9310.
- [31] S. Couck, J.F.M. Denayer, G.V. Baron, T. Rémy, J. Gascon, F. Kapteijn, An Amine-Functionalized MIL-53 Metal–Organic Framework with Large Separation Power for CO₂ and CH₄, *Journal of the American Chemical Society*, 131 (2009) 6326-6327.
- [32] B. Wang, J. Park, C. Wang, H. Ahn, G. Wang, Mn₃O₄ nanoparticles embedded into graphene nanosheets: Preparation, characterization, and electrochemical properties for supercapacitors, *Electrochimica Acta*, 55 (2010) 6812-6817.
- [33] T.S. Sreeprasad, S.M. Maliyekkal, K.P. Lisha, T. Pradeep, Reduced graphene oxide–metal/metal oxide composites: Facile synthesis and application in water purification, *Journal of Hazardous Materials*, 186 (2011) 921-931.
- [34] C. Wang, J. Zhu, S. Liang, H. Bi, Q. Han, X. Liu, X. Wang, Reduced graphene oxide decorated with CuO–ZnO hetero-junctions: towards high selective gas-sensing property to acetone, *Journal of Materials Chemistry A*, 2 (2014) 18635-18643.
- [35] N. Li, M. Zheng, X. Chang, G. Ji, H. Lu, L. Xue, L. Pan, J. Cao, Preparation of magnetic CoFe₂O₄-functionalized graphene sheets via a facile hydrothermal method and their adsorption properties, *Journal of Solid State Chemistry*, 184 (2011) 953-958.

- [36] M.W. Ackley, S.U. Rege, H. Saxena, Application of natural zeolites in the purification and separation of gases, *Microporous and Mesoporous Materials*, 61 (2003) 25-42.
- [37] J. Zhang, R. Singh, P.A. Webley, Alkali and alkaline-earth cation exchanged chabazite zeolites for adsorption based CO₂ capture, *Microporous and Mesoporous Materials*, 111 (2008) 478-487.
- [38] N. Konduru, P. Lindner, N.M. Assaf-Anid, Curbing the greenhouse effect by carbon dioxide adsorption with Zeolite 13X, *AIChE Journal*, 53 (2007) 3137-3143.
- [39] A. Alonso-Vicario, J.R. Ochoa-Gómez, S. Gil-Río, O. Gómez-Jiménez-Aberasturi, C.A. Ramírez-López, J. Torrecilla-Soria, A. Domínguez, Purification and upgrading of biogas by pressure swing adsorption on synthetic and natural zeolites, *Microporous and Mesoporous Materials*, 134 (2010) 100-107.
- [40] M.R. Othman, N.M. Rasid, W.J.N. Fernando, Mg–Al hydrotalcite coating on zeolites for improved carbon dioxide adsorption, *Chemical Engineering Science*, 61 (2006) 1555-1560.
- [41] R.T. Yang, *ADSORBENTS: FUNDAMENTALS AND APPLICATIONS*, John Wiley & Sons, Inc., 2003.
- [42] Y. Sun, X.-W. Liu, W. Su, Y. Zhou, L. Zhou, Studies on ordered mesoporous materials for potential environmental and clean energy applications, *Applied Surface Science*, 253 (2007) 5650-5655.
- [43] X. Xu, C. Song, J.M. Andresen, B.G. Miller, A.W. Scaroni, Novel Polyethylenimine-Modified Mesoporous Molecular Sieve of MCM-41 Type as High-Capacity Adsorbent for CO₂ Capture, *Energy & Fuels*, 16 (2002) 1463-1469.
- [44] S. Kim, J. Ida, V.V. Guliants, Y.S. Lin, Tailoring Pore Properties of MCM-48 Silica for Selective Adsorption of CO₂, *The Journal of Physical Chemistry B*, 109 (2005) 6287-6293.
- [45] S.-H. Liu, W.-C. Hsiao, W.-H. Sie, Tetraethylenepentamine-modified mesoporous adsorbents for CO₂ capture: effects of preparation methods, *Adsorption*, 18 (2012) 431-437.
- [46] J. Wang, L. Wang, H. Fan, H. Wang, Y. Hu, Z. Wang, Highly porous copper oxide sorbent for H₂S capture at ambient temperature, *Fuel*, 209 (2017) 329-338.
- [47] J. Wang, L. Huang, R. Yang, Z. Zhang, J. Wu, Y. Gao, Q. Wang, D. O'Hare, Z. Zhong, Recent advances in solid sorbents for CO₂ capture and new development trends, *Energy & Environmental Science*, 7 (2014) 3478-3518.

- [48] S. Kumar, S.K. Saxena, A comparative study of CO₂ sorption properties for different oxides, *Materials for Renewable and Sustainable Energy*, 3 (2014) 30.
- [49] G.-B. Elvira, G.-C. Francisco, S.-M. Víctor, M.-L.R. Alberto, MgO-based adsorbents for CO₂ adsorption: Influence of structural and textural properties on the CO₂ adsorption performance, *Journal of Environmental Sciences*, 57 (2017) 418-428.
- [50] Z.-X. Tang, B.-F. Lv, MgO nanoparticles as antibacterial agent: preparation and activity, *Brazilian Journal of Chemical Engineering*, 31 (2014) 591-601.
- [51] P. Ouraipryvan, T. Sreethawong, S. Chavadej, Synthesis of crystalline MgO nanoparticle with mesoporous-assembled structure via a surfactant-modified sol-gel process, *Materials Letters*, 63 (2009) 1862-1865.
- [52] J. Hu, Z. Song, L. Chen, H. Yang, J. Li, R. Richards, Adsorption Properties of MgO(111) Nanoplates for the Dye Pollutants from Wastewater, *Journal of Chemical & Engineering Data*, 55 (2010) 3742-3748.
- [53] J.H. Lunsford, P. Qiu, M.P. Rosynek, Z. Yu, Catalytic Conversion of Methane and Ethylene to Propylene, *The Journal of Physical Chemistry B*, 102 (1998) 167-173.
- [54] D. Szmigiel, W. Raróg-Pilecka, E. Miśkiewicz, M. Gliński, M. Kielak, Z. Kaszkur, Z. Kowalczyk, Ammonia synthesis over ruthenium catalysts supported on high surface area MgO and MgO–Al₂O₃ systems, *Applied Catalysis A: General*, 273 (2004) 105-112.
- [55] B. Miller, 8 - Greenhouse gas – carbon dioxide emissions reduction technologies, in: B. Miller (Ed.) *Fossil Fuel Emissions Control Technologies*, Butterworth-Heinemann, 2015, pp. 367-438.
- [56] E. Alvarado, L.M. Torres-Martinez, A.F. Fuentes, P. Quintana, Preparation and characterization of MgO powders obtained from different magnesium salts and the mineral dolomite, *Polyhedron*, 19 (2000) 2345-2351.
- [57] T. Yoshida, T. Tanaka, H. Yoshida, T. Funabiki, S. Yoshida, T. Murata, Study of Dehydration of Magnesium Hydroxide, *The Journal of Physical Chemistry*, 99 (1995) 10890-10896.
- [58] M. Hartman, O. Trnka, V. Veselý, Thermal dehydration of magnesium hydroxide and sintering of nascent magnesium oxide, *AIChE Journal*, 40 (1994) 536-542.
- [59] Q. Huang, G. Lu, J. Wang, J. Yu, Thermal decomposition mechanisms of MgCl₂·6H₂O and MgCl₂·H₂O, *Journal of Analytical and Applied Pyrolysis*, 91 (2011) 159-164.
- [60] A.K. Galwey, G.M. Laverty, The thermal decomposition of magnesium chloride dihydrate, *Thermochimica Acta*, 138 (1989) 115-127.

- [61] J. Roggenbuck, M. Tiemann, Ordered Mesoporous Magnesium Oxide with High Thermal Stability Synthesized by Exotemplating Using CMK-3 Carbon, *Journal of the American Chemical Society*, 127 (2005) 1096-1097.
- [62] M. Bhagiyalakshmi, J.Y. Lee, H.T. Jang, Synthesis of mesoporous magnesium oxide: Its application to CO₂ chemisorption, *International Journal of Greenhouse Gas Control*, 4 (2010) 51-56.
- [63] T. Harada, F. Simeon, E.Z. Hamad, T.A. Hatton, Alkali Metal Nitrate-Promoted High-Capacity MgO Adsorbents for Regenerable CO₂ Capture at Moderate Temperatures, *Chemistry of Materials*, 27 (2015) 1943-1949.
- [64] A.-T. Vu, K. Ho, S. Jin, C.-H. Lee, Double sodium salt-promoted mesoporous MgO sorbent with high CO₂ sorption capacity at intermediate temperatures under dry and wet conditions, *Chemical Engineering Journal*, 291 (2016) 161-173.
- [65] Y.-D. Ding, G. Song, X. Zhu, R. Chen, Q. Liao, Synthesizing MgO with a high specific surface for carbon dioxide adsorption, *RSC Advances*, 5 (2015) 30929-30935.
- [66] G. Song, X. Zhu, R. Chen, Q. Liao, Y.-D. Ding, L. Chen, An investigation of CO₂ adsorption kinetics on porous magnesium oxide, *Chemical Engineering Journal*, 283 (2016) 175-183.
- [67] W. Dong, X. Chen, F. Yu, Y. Wu, Na₂CO₃/MgO/Al₂O₃ Solid Sorbents for Low-Temperature CO₂ Capture, *Energy & Fuels*, 29 (2015) 968-973.
- [68] S.C. Lee, H.J. Chae, S.J. Lee, B.Y. Choi, C.K. Yi, J.B. Lee, C.K. Ryu, J.C. Kim, Development of Regenerable MgO-Based Sorbent Promoted with K₂CO₃ for CO₂ Capture at Low Temperatures, *Environmental Science & Technology*, 42 (2008) 2736-2741.
- [69] X. Fu, N. Zhao, J. Li, F. Xiao, W. Wei, Y. Sun, Carbon Dioxide Capture by MgO-modified MCM-41 Materials, *Adsorption Science & Technology*, 27 (2009) 593-601.
- [70] M.S. Shafeeyan, W.M.A.W. Daud, A. Houshmand, A. Shamiri, A review on surface modification of activated carbon for carbon dioxide adsorption, *Journal of Analytical and Applied Pyrolysis*, 89 (2010) 143-151.
- [71] F. Adib, A. Bagreev, T.J. Bandosz, Effect of pH and Surface Chemistry on the Mechanism of H₂S Removal by Activated Carbons, *Journal of Colloid and Interface Science*, 216 (1999) 360-369.
- [72] J. Wang, H. Chen, H. Zhou, X. Liu, W. Qiao, D. Long, L. Ling, Carbon dioxide capture using polyethylenimine-loaded mesoporous carbons, *Journal of Environmental Sciences*, 25 (2013) 124-132.

- [73] Z. Zhang, B. Wang, Q. Sun, Fly Ash-derived Solid Amine Sorbents for CO₂ Capture from Flue Gas, *Energy Procedia*, 63 (2014) 2367-2373.
- [74] B. Shimekit, H. Mukhtar, Natural gas purification technologies-major advances for CO₂ separation and future directions, in: *Advances in natural gas technology*, InTech, 2012.
- [75] H. Furukawa, K.E. Cordova, M. O'Keeffe, O.M. Yaghi, The Chemistry and Applications of Metal-Organic Frameworks, *Science*, 341 (2013).
- [76] M. Alhamami, H. Doan, C.-H. Cheng, A Review on Breathing Behaviors of Metal-Organic-Frameworks (MOFs) for Gas Adsorption, *Materials*, 7 (2014) 3198-3248.
- [77] O.M. Yaghi, M. O'Keeffe, N.W. Ockwig, H.K. Chae, M. Eddaoudi, J. Kim, Reticular synthesis and the design of new materials, *Nature*, 423 (2003) 705-714.
- [78] H.-C. Zhou, J.R. Long, O.M. Yaghi, Introduction to Metal–Organic Frameworks, *Chemical Reviews*, 112 (2012) 673-674.
- [79] Z. Liang, M. Marshall, A.L. Chaffee, CO₂ Adsorption-Based Separation by Metal Organic Framework (Cu-BTC) versus Zeolite (13X), *Energy & Fuels*, 23 (2009) 2785-2789.
- [80] A.K. Geim, K.S. Novoselov, The rise of graphene, *Nature Materials*, 6 (2007) 183.
- [81] C.N.R. Rao, A.K. Sood, K.S. Subrahmanyam, A. Govindaraj, Graphene: The New Two-Dimensional Nanomaterial, *Angewandte Chemie International Edition*, 48 (2009) 7752-7777.
- [82] M. Khan, M.N. Tahir, S.F. Adil, H.U. Khan, M.R.H. Siddiqui, A.A. Al-warthan, W. Tremel, Graphene based metal and metal oxide nanocomposites: synthesis, properties and their applications, *Journal of Materials Chemistry A*, 3 (2015) 18753-18808.
- [83] Y. Zhu, S. Murali, W. Cai, X. Li, J.W. Suk, J.R. Potts, R.S. Ruoff, Graphene and Graphene Oxide: Synthesis, Properties, and Applications, *Advanced Material*, 22 (2010) 3906-3924.
- [84] X. Huang, Z. Yin, S. Wu, X. Qi, Q. He, Q. Zhang, Q. Yan, F. Boey, H. Zhang, Graphene-Based Materials: Synthesis, Characterization, Properties, and Applications, *Small*, 7 (2011) 1876-1902.
- [85] H. Kim, A.A. Abdala, C.W. Macosko, Graphene/Polymer Nanocomposites, *Macromolecules*, 43 (2010) 6515-6530.
- [86] G. Yazdi, T. Iakimov, R. Yakimova, Epitaxial Graphene on SiC: A Review of Growth and Characterization, *Crystals*, 6 (2016) 1-45.

- [87] Z. Yan, Z. Peng, J.M. Tour, Chemical Vapor Deposition of Graphene Single Crystals, *Accounts of Chemical Research*, 47 (2014) 1327-1337.
- [88] X. Li, W. Cai, L. Colombo, R.S. Ruoff, Evolution of Graphene Growth on Ni and Cu by Carbon Isotope Labeling, *Nano Letters*, 9 (2009) 4268-4272.
- [89] I. Salzmann, A. Moser, M. Oehzelt, T. Breuer, X. Feng, Z.-Y. Juang, D. Nabok, R.G. Della Valle, S. Duhm, G. Heimel, A. Brillante, E. Venuti, I. Bilotti, C. Christodoulou, J. Frisch, P. Puschnig, C. Draxl, G. Witte, K. Müllen, N. Koch, Epitaxial Growth of π -Stacked Perfluoropentacene on Graphene-Coated Quartz, *ACS Nano*, 6 (2012) 10874-10883.
- [90] K.S. Novoselov, D. Jiang, F. Schedin, T.J. Booth, V.V. Khotkevich, S.V. Morozov, A.K. Geim, Two-dimensional atomic crystals, *Proceedings of the National Academy of Sciences of the United States of America*, 102 (2005) 10451-10453.
- [91] S. Park, R.S. Ruoff, Chemical methods for the production of graphenes, *Nature Nanotechnology*, 4 (2009) 217-225.
- [92] A.B. Bourlinos, V. Georgakilas, R. Zboril, T.A. Steriotis, A.K. Stubos, Liquid-Phase Exfoliation of Graphite Towards Solubilized Graphenes, *Small*, 5 (2009) 1841-1845.
- [93] N. Liu, F. Luo, H. Wu, Y. Liu, C. Zhang, J. Chen, One-Step Ionic-Liquid-Assisted Electrochemical Synthesis of Ionic-Liquid-Functionalized Graphene Sheets Directly from Graphite, *Advanced Functional Materials*, 18 (2008) 1518-1525.
- [94] S. Pei, H.-M. Cheng, The reduction of graphene oxide, *Carbon*, 50 (2012) 3210-3228.
- [95] J.G.S. Moo, B. Khezri, R.D. Webster, M. Pumera, Graphene Oxides Prepared by Hummers', Hofmann's, and Staudenmaier's Methods: Dramatic Influences on Heavy-Metal-Ion Adsorption, *ChemPhysChem*, 15 (2014) 2922-2929.
- [96] F. Pendolino, N. Armata, Synthesis, Characterization and Models of Graphene Oxide, in: F. Pendolino, N. Armata (Eds.) *Graphene Oxide in Environmental Remediation Process*, Springer International Publishing, Cham, 2017, pp. 5-21.
- [97] B.C. Brodie, F.R. S., XIII. On the atomic weight of graphite, *Phil. Trans. R. Soc. Lond.*, 19 (1859) 249-259.
- [98] W.S. Hummers, R.E. Offeman, Preparation of Graphitic Oxide, *Journal of the American Chemical Society*, 80 (1958) 1339-1339.
- [99] A.M. Dimiev, J.M. Tour, Mechanism of Graphene Oxide Formation, *ACS Nano*, 8 (2014) 3060-3068.

- [100] Q. Huang, H.J. Sun, T.J. Peng, The Influence of Temperature and Oxidation Time on the Preparation of Graphite Oxide, *Advanced Materials Research*, 366 (2012) 291-295.
- [101] A.C. Ferrari, Raman spectroscopy of graphene and graphite: Disorder, electron–phonon coupling, doping and nonadiabatic effects, *Solid State Communications*, 143 (2007) 47-57.
- [102] L.M. Malard, M.A. Pimenta, G. Dresselhaus, M.S. Dresselhaus, Raman spectroscopy in graphene, *Physics Reports*, 473 (2009) 51-87.
- [103] A.A. Dubale, W.-N. Su, A.G. Tamirat, C.-J. Pan, B.A. Aragaw, H.-M. Chen, C.-H. Chen, B.-J. Hwang, The synergetic effect of graphene on Cu₂O nanowire arrays as a highly efficient hydrogen evolution photocathode in water splitting, *Journal of Materials Chemistry A*, 2 (2014) 18383-18397.
- [104] G. Binnig, G. Ch, E. Stoll, T.R. Albrecht, C.F. Quate, Atomic Resolution with Atomic Force Microscope, *EPL (Europhysics Letters)*, 3 (1987) 1-6.
- [105] J.C. Meyer, 5 - Transmission electron microscopy (TEM) of graphene, in: V. Skákalová, A.B. Kaiser (Eds.) *Graphene*, Woodhead Publishing, 2014, pp. 101-123.
- [106] K. Grodecki, I. Jozwik, J.M. Baranowski, D. Teklinska, W. Strupinski, SEM and Raman analysis of graphene on SiC(0001), *Micron*, 80 (2016) 20-23.
- [107] L. Stobinski, B. Lesiak, A. Malolepszy, M. Mazurkiewicz, B. Mierzwa, J. Zemek, P. Jiricek, I. Bieloshapka, Graphene oxide and reduced graphene oxide studied by the XRD, TEM and electron spectroscopy methods, *Journal of Electron Spectroscopy and Related Phenomena*, 195 (2014) 145-154.
- [108] F. Najafi, M. Rajabi, Thermal gravity analysis for the study of stability of graphene oxide–glycine nanocomposites, *International Nano Letters*, 5 (2015) 187-190.
- [109] S. Stankovich, R.D. Piner, X. Chen, N. Wu, S.T. Nguyen, R.S. Ruoff, Stable aqueous dispersions of graphitic nanoplatelets via the reduction of exfoliated graphite oxide in the presence of poly(sodium 4-styrenesulfonate), *Journal of Materials Chemistry*, 16 (2006) 155-158.
- [110] Rattana, S. Chaiyakun, N. Witit-anun, N. Nuntawong, P. Chindaudom, S. Oaew, C. Kedkeaw, P. Limsuwan, Preparation and characterization of graphene oxide nanosheets, *Procedia Engineering*, 32 (2012) 759-764.
- [111] S. Stankovich, D.A. Dikin, R.D. Piner, K.A. Kohlhaas, A. Kleinhammes, Y. Jia, Y. Wu, S.T. Nguyen, R.S. Ruoff, Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide, *Carbon*, 45 (2007) 1558-1565.

- [112] H.-J. Shin, K.K. Kim, A. Benayad, S.-M. Yoon, H.K. Park, I.-S. Jung, M.H. Jin, H.-K. Jeong, J.M. Kim, J.-Y. Choi, Y.H. Lee, Efficient Reduction of Graphite Oxide by Sodium Borohydride and Its Effect on Electrical Conductance, *Advanced Functional Materials*, 19 (2009) 1987-1992.
- [113] J.-L. Shi, W.-C. Du, Y.-X. Yin, Y.-G. Guo, L.-J. Wan, Hydrothermal reduction of three-dimensional graphene oxide for binder-free flexible supercapacitors, *Journal of Materials Chemistry A*, 2 (2014) 10830-10834.
- [114] X. Zhang, X. Sun, Y. Chen, D. Zhang, Y. Ma, One-step solvothermal synthesis of graphene/Mn₃O₄ nanocomposites and their electrochemical properties for supercapacitors, *Materials Letters*, 68 (2012) 336-339.
- [115] S. Dubin, S. Gilje, K. Wang, V.C. Tung, K. Cha, A.S. Hall, J. Farrar, R. Varshneya, Y. Yang, R.B. Kaner, A One-Step, Solvothermal Reduction Method for Producing Reduced Graphene Oxide Dispersions in Organic Solvents, *ACS Nano*, 4 (2010) 3845-3852.
- [116] S.J. An, Y. Zhu, S.H. Lee, M.D. Stoller, T. Emilsson, S. Park, A. Velamakanni, J. An, R.S. Ruoff, Thin Film Fabrication and Simultaneous Anodic Reduction of Deposited Graphene Oxide Platelets by Electrophoretic Deposition, *The Journal of Physical Chemistry Letters*, 1 (2010) 1259-1263.
- [117] Z. Wang, X. Zhou, J. Zhang, F. Boey, H. Zhang, Direct Electrochemical Reduction of Single-Layer Graphene Oxide and Subsequent Functionalization with Glucose Oxidase, *The Journal of Physical Chemistry C*, 113 (2009) 14071-14075.
- [118] H.C. Schniepp, J.-L. Li, M.J. McAllister, H. Sai, M. Herrera-Alonso, D.H. Adamson, R.K. Prud'homme, R. Car, D.A. Saville, I.A. Aksay, Functionalized Single Graphene Sheets Derived from Splitting Graphite Oxide, *The Journal of Physical Chemistry B*, 110 (2006) 8535-8539.
- [119] Z.-S. Wu, W. Ren, L. Gao, J. Zhao, Z. Chen, B. Liu, D. Tang, B. Yu, C. Jiang, H.-M. Cheng, Synthesis of Graphene Sheets with High Electrical Conductivity and Good Thermal Stability by Hydrogen Arc Discharge Exfoliation, *ACS Nano*, 3 (2009) 411-417.
- [120] X. Wang, L. Zhi, K. Müllen, Transparent, Conductive Graphene Electrodes for Dye-Sensitized Solar Cells, *Nano Letters*, 8 (2008) 323-327.
- [121] Y. Zhu, S. Murali, M.D. Stoller, A. Velamakanni, R.D. Piner, R.S. Ruoff, Microwave assisted exfoliation and reduction of graphite oxide for ultracapacitors, *Carbon*, 48 (2010) 2118-2122.
- [122] C.K. Chua, M. Pumera, Chemical reduction of graphene oxide: a synthetic chemistry viewpoint, *Chemical Society Reviews*, 43 (2014) 291-312.

- [123] X. Zhou, J. Zhang, H. Wu, H. Yang, J. Zhang, S. Guo, Reducing Graphene Oxide via Hydroxylamine: A Simple and Efficient Route to Graphene, *The Journal of Physical Chemistry C*, 115 (2011) 11957-11961.
- [124] M.J. Fernández-Merino, L. Guardia, J.I. Paredes, S. Villar-Rodil, P. Solís-Fernández, A. Martínez-Alonso, J.M.D. Tascón, Vitamin C Is an Ideal Substitute for Hydrazine in the Reduction of Graphene Oxide Suspensions, *The Journal of Physical Chemistry C*, 114 (2010) 6426-6432.
- [125] X. Mei, J. Ouyang, Ultrasonication-assisted ultrafast reduction of graphene oxide by zinc powder at room temperature, *Carbon*, 49 (2011) 5389-5397.
- [126] Y. Liu, Y. Li, M. Zhong, Y. Yang, W. Yuefang, M. Wang, A green and ultrafast approach to the synthesis of scalable graphene nanosheets with Zn powder for electrochemical energy storage, *Journal of Materials Chemistry*, 21 (2011) 15449-15455.
- [127] Z. Fan, K. Wang, T. Wei, J. Yan, L. Song, B. Shao, An environmentally friendly and efficient route for the reduction of graphene oxide by aluminum powder, *Carbon*, 48 (2010) 1686-1689.
- [128] N.H. Kim, T. Kuila, C.F. Zhang, J.H. Lee, Tin-Powder Mediated Facile Route for the Reduction of Graphene Oxide, *Advanced Materials Research*, 747 (2013) 238-241.
- [129] S. Yang, L. Zhan, X. Xu, Y. Wang, L. Ling, X. Feng, Graphene-Based Porous Silica Sheets Impregnated with Polyethyleneimine for Superior CO₂ Capture, *Advanced Materials*, 25 (2013) 2130-2134.
- [130] S.-M. Hong, S.H. Kim, a.K.B. Lee, Adsorption of Carbon Dioxide on 3-Aminopropyl-Triethoxysilane Modified Graphite Oxide, *energy & fuels*, 27 (2013) 3358-3363.
- [131] J. Pokhrel, N. Bhorla, S. Anastasiou, T. Tsoufis, D. Gournis, G. Romanos, G.N. Karanikolos, CO₂ adsorption behavior of amine-functionalized ZIF-8, graphene oxide, and ZIF-8/graphene oxide composites under dry and wet conditions, *Microporous and Mesoporous Materials*, 267 (2018) 53-67.
- [132] Y. Zhang, Y. Chi, C. Zhao, Y. Liu, Y. Zhao, L. Jiang, Y. Song, CO₂ Adsorption Behavior of Graphite Oxide Modified with Tetraethylenepentamine, *Journal of Chemical & Engineering Data*, 63 (2018) 202-207.
- [133] D. Zhou, Q. Liu, Q. Cheng, Y. Zhao, Y. Cui, T. Wang, B. Han, Graphene-manganese oxide hybrid porous material and its application in carbon dioxide adsorption, *Chinese Science Bulletin*, 57 (2012) 3059-3064.
- [134] M. Fasihi, O. Efimova, C. Breyer, Techno-economic assessment of CO₂ direct air capture plants, *Journal of Cleaner Production*, 224 (2019) 957-980.

- [135] CO₂ EMISSIONS FROM FUEL COMBUSTION Highlights, in, INTERNATIONAL ENERGY AGENCY, <http://www.iea.org/publications/>, 2017.
- [136] S. Kumar, S.K. Saxena, A comparative study of CO₂ sorption properties for different oxides, *Materials for Renewable and Sustainable Energy*, 3 (2014) 1-30.
- [137] A.M. Kierzkowska, R. Pacciani, C.R. Müller, CaO-Based CO₂ Sorbents: From Fundamentals to the Development of New, Highly Effective Materials, *ChemSusChem*, 6 (2013) 1130-1148.
- [138] H. Lu, E.P. Reddy, P.G. Smirniotis, Calcium Oxide Based Sorbents for Capture of Carbon Dioxide at High Temperatures, *Industrial & Engineering Chemistry Research*, 45 (2006) 3944-3949.
- [139] R. Quinn, R.J. Kitzhoffer, J.R. Hufton, T.C. Golden, A High Temperature Lithium Orthosilicate-Based Solid Absorbent for Post Combustion CO₂ Capture, *Industrial & Engineering Chemistry Research*, 51 (2012) 9320-9327.
- [140] A. Hanif, S. Dasgupta, A. Nanoti, Facile Synthesis of High-Surface-Area Mesoporous MgO with Excellent High-Temperature CO₂ Adsorption Potential, *Industrial & Engineering Chemistry Research*, 55 (2016) 8070-8078.
- [141] G.S. Grasa, J.C. Abanades, CO₂ Capture Capacity of CaO in Long Series of Carbonation/Calcination Cycles, *Industrial & Engineering Chemistry Research*, 45 (2006) 8846-8851.
- [142] G. Xiao, R. Singh, A. Chaffee, P. Webley, Advanced adsorbents based on MgO and K₂CO₃ for capture of CO₂ at elevated temperatures, *International Journal of Greenhouse Gas Control*, 5 (2011) 634-639.
- [143] X. Zhao, G. Ji, W. Liu, X. He, E.J. Anthony, M. Zhao, Mesoporous MgO promoted with NaNO₃/NaNO₂ for rapid and high-capacity CO₂ capture at moderate temperatures, *Chemical Engineering Journal*, 332 (2018) 216-226.
- [144] E.M. van der Merwe, C.A. Strydom, Hydration of medium reactive magnesium oxide using hydration agents, *Journal of Thermal Analysis and Calorimetry*, 84 (2006) 467-471.
- [145] H. Kurama, L. Hoşgün, Magnesium Hydroxide Recovery from Magnesia Waste by Calcinations and Hydration Processes, *Physicochemical Problems of Mineral Processing*, 51 (2015) 233-245.
- [146] A. Kumar, J. Kumar, On the synthesis and optical absorption studies of nano-size magnesium oxide powder, *Journal of Physics and Chemistry of Solids*, 69 (2008) 2764-2772.

- [147] R. Wahab, S.G. Ansari, M.A. Dar, Y.S. Kim, H.S. Shin, Synthesis of Magnesium Oxide Nanoparticles by Sol-Gel Process, *Materials Science Forum*, 558-559 (2007) 983-986.
- [148] X. Xu, C. Song, J.M. Andrésen, B.G. Miller, A.W. Scaroni, Preparation and characterization of novel CO₂ “molecular basket” adsorbents based on polymer-modified mesoporous molecular sieve MCM-41, *Microporous and Mesoporous Materials*, 62 (2003) 29-45.
- [149] I.F. Mironyuk, V.M. Gun’ko, M.O. Povazhnyak, V.I. Zarko, V.M. Chelyadin, R. Leboda, J. Skubiszewska-Zięba, W. Janusz, Magnesia formed on calcination of Mg(OH)₂ prepared from natural bischofite, *Applied Surface Science*, 252 (2006) 4071-4082.
- [150] G. Song, S. Ma, G. Tang, X. Wang, Ultrasonic-assisted synthesis of hydrophobic magnesium hydroxide nanoparticles, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 364 (2010) 99-104.
- [151] M. Rezaei, M. Khajenoori, B. Nematollahi, Synthesis of high surface area nanocrystalline MgO by pluronic P123 triblock copolymer surfactant, *Powder Technology*, 205 (2011) 112-116.
- [152] F. Meshkani, M. Rezaei, Facile synthesis of nanocrystalline magnesium oxide with high surface area, *Powder Technology*, 196 (2009) 85-88.
- [153] H.Y. Huang, R.T. Yang, D. Chinn, C.L. Munson, Amine-Grafted MCM-48 and Silica Xerogel as Superior Sorbents for Acidic Gas Removal from Natural Gas, *Industrial & Engineering Chemistry Research*, 42 (2003) 2427-2433.
- [154] S. Yan, Y. Yang, L. Song, X. Qi, Y. Xue, B. Fan, Influence of 3-aminopropyltriethoxysilane- graphite oxide composite on thermal stability and mechanical property of polyethersulfone, *High Performance Polymers*, 29 (2016) 960-975.
- [155] N. Rani, S. Chahal, A.S. Chauhan, P. Kumar, R. Shukla, S.K. Singh, X-ray Analysis of MgO Nanoparticles by Modified Scherer’s Williamson-Hall and Size-Strain Method, *Materials Today: Proceedings*, 12 (2019) 543-548.
- [156] N. Yang, P. Ning, K. Li, J. Wang, MgO-based adsorbent achieved from magnesite for CO₂ capture in simulate wet flue gas, *Journal of the Taiwan Institute of Chemical Engineers*, 86 (2018) 73-80.
- [157] Y. Liu, B. Sajjadi, W.-Y. Chen, R. Chatterjee, Ultrasound-assisted amine functionalized graphene oxide for enhanced CO₂ adsorption, *Fuel*, 247 (2019) 10-18.
- [158] W. Gao, T. Zhou, B. Louis, Q. Wang, Hydrothermal Fabrication of High Specific Surface Area Mesoporous MgO with Excellent CO₂ Adsorption Potential at Intermediate Temperatures, *Catalysts*, 7 (2017) 116.

- [159] K.K. Han, Y. Zhou, W.G. Lin, J.H. Zhu, One-pot synthesis of foam-like magnesia and its performance in CO₂ adsorption, *Microporous and Mesoporous Materials*, 169 (2013) 112-119.
- [160] R. Rajiv gandhi, J. Suresh, S. Gowri, D.S. Selvam, M. Sundrarajan, Effect of Calcination Temperature on Surface Morphology of Ionic Liquid Assisted MgO Nanoparticles by Sol–Gel Method, *Advanced Science Letters*, 16 (2012) 244-248.
- [161] G. Song, Y.-D. Ding, X. Zhu, Q. Liao, Carbon dioxide adsorption characteristics of synthesized MgO with various porous structures achieved by varying calcination temperature, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 470 (2015) 39-45.
- [162] F. Karadas, M. Atilhan, S. Aparicio, Review on the use of ionic liquids (ILs) as alternative fluids for CO₂ capture and natural gas sweetening, *Energy & Fuels*, 24 (2010) 5817-5828.
- [163] L. Shahriary, A. Athawale, Graphene oxide synthesized by using modified Hummers approach, *Renew. Energy Environ. Eng.*, 2 (2014) 58-63.
- [164] S.M. Hong, K.B. Lee, Solvent-assisted amine modification of graphite oxide for CO₂ adsorption, *RSC Advances*, 4 (2014) 56707-56712.
- [165] V.H. Pham, H.D. Pham, T.T. Dang, S.H. Hur, E.J. Kim, B.S. Kong, S. Kim, J.S. Chung, Chemical reduction of an aqueous suspension of graphene oxide by nascent hydrogen, *Journal of Materials Chemistry*, 22 (2012) 10530-10536.
- [166] Y. Matsuo, Y. Nishino, T. Fukutsuka, Y. Sugie, Introduction of amino groups into the interlayer space of graphite oxide using 3-aminopropylethoxysilanes, *Carbon*, 45 (2007) 1384-1390.
- [167] A. Huang, B. Feng, Facile synthesis of PEI-GO@ZIF-8 hybrid material for CO₂ capture, *International Journal of Hydrogen Energy*, 43 (2018) 2224-2231.
- [168] G.-J. Shin, K. Rhee, S.-J. Park, Improvement of CO₂ capture by graphite oxide in presence of polyethylenimine, *International Journal of Hydrogen Energy*, 41 (2016) 14351-14359.
- [169] P. Liu, Y. Huang, L. Wang, A facile synthesis of reduced graphene oxide with Zn powder under acidic condition, *Materials Letters*, 91 (2013) 125-128.
- [170] M. Khan, A.H. Al-Marri, M. Khan, M.R. Shaik, N. Mohri, S.F. Adil, M. Kuniyil, H.Z. Alkhathlan, A. Al-Warthan, W. Tremel, M.N. Tahir, M.R.H. Siddiqui, Green Approach for the Effective Reduction of Graphene Oxide Using *Salvadora persica* L. Root (Miswak) Extract, *Nanoscale Research Letters*, 10 (2015) 281-290.

- [171] S.-M. Hong, S.H. Kim, K.B. Lee, Adsorption of Carbon Dioxide on 3-Aminopropyl-Triethoxysilane Modified Graphite Oxide, *Energy & Fuels*, 27 (2013) 3358-3363.
- [172] J. Li, B. Michalkiewicz, J. Min, C. Ma, X. Chen, J. Gong, E. Mijowska, T. Tang, Selective preparation of biomass-derived porous carbon with controllable pore sizes toward highly efficient CO₂ capture, *Chemical Engineering Journal*, 360 (2019) 250-259.
- [173] J. Serafin, U. Narkiewicz, A.W. Morawski, R.J. Wróbel, B. Michalkiewicz, Highly microporous activated carbons from biomass for CO₂ capture and effective micropores at different conditions, *Journal of CO₂ Utilization*, 18 (2017) 73-79.
- [174] T. Strachowski, M. Woluntarski, M. Djas, K. Kowiorski, Z. Wiliński, M. Baran, J. Jagiełło, M. Winkowska, L. Lipińska, the influence of reducing agents on the reduced graphene oxide specific surface area determined on the basis of nitrogen adsorption isotherm, *Electronic Materials*, 45 (2017) 2-4.
- [175] W. Hooch Antink, Y. Choi, K.-d. Seong, J.M. Kim, Y. Piao, Recent Progress in Porous Graphene and Reduced Graphene Oxide-Based Nanomaterials for Electrochemical Energy Storage Devices, *Advanced Materials Interfaces*, 5 (2018) 1-19.
- [176] S. Furmaniak, P. Kowalczyk, A.P. Terzyk, P.A. Gauden, P.J.F. Harris, Synergetic effect of carbon nanopore size and surface oxidation on CO₂ capture from CO₂/CH₄ mixtures, *Journal of Colloid and Interface Science*, 397 (2013) 144-153.
- [177] Y. Liu, J. Wilcox, Effects of Surface Heterogeneity on the Adsorption of CO₂ in Microporous Carbons, *Environmental Science & Technology*, 46 (2012) 1940-1947.
- [178] J.H. Lee, H.J. Lee, J.W. Choi, Unveiling anomalous CO₂-to-N₂ selectivity of graphene oxide, *Physical Chemistry Chemical Physics*, 19 (2017) 22743-22748.
- [179] Y. Zhao, H. Ding, Q. Zhong, Preparation and characterization of aminated graphite oxide for CO₂ capture, *Applied Surface Science*, 258 (2012) 4301-4307.
- [180] Z. Liu, D. Pudasainee, Q. Liu, R. Gupta, Post-combustion CO₂ capture using polyethyleneimine impregnated mesoporous cellular foams, *Separation and Purification Technology*, 156 (2015) 259-268.

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Patents

Sagheer A. Onaizi, Ali A. Alkadhem, an Amine-Functionalized Magnesium Oxide Adsorbent for CO₂ Capture. Submitted in Nov 2019. In progress.

Sagheer A. Onaizi, Ali A. Alkadhem Modification of Magnesium Oxide using Diethylenetriamine for Effective CO₂ Capture. Submitted in Nov 2019. In progress.