GRAPHENE COMPOSITED ACTIVATED CARBON NANOFIBERS FOR CARBON DIOXIDE ADSORPTION

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A thesis submitted in fulfilment of the
requirements for the award of the degree of
Doctor of Philosophy

School of Chemical and Energy Engineering
Faculty of Engineering
Universiti Teknologi Malaysia

FEBRUARY 2021

ACKNOWLEDGEMENT

In preparing this thesis, I was in contact with many people, researchers, academicians, and practitioners. They have contributed towards my understanding and thoughts. In particular, I wish to express my sincere appreciation to my mainsupervisor, Dr. Norhaniza Yusof, for encouragement, guidance, critics and friendship. I am also very thankful to my co-supervisor Professor Datuk Dr. Ahmad Fauzi Ismail for his guidance, advices, and motivation. Without their continued support and interest, this thesis would not have been the same as presented here.

I am also indebted to Universiti Teknologi Malaysia (UTM) for funding my Ph.D study. My internship supervisors, Dr. Sadaki Samitsu in National Institute for Materials Science, Japan and Professor Gregory Patience in Polytechnique Montreal, Canada also deserve special thanks for their assistance in supplying the relevant advices, helps, and supports during my internships.

My fellow postgraduate student should also be recognised for their support. My sincere appreciation also extends to all my colleagues and others who have provided assistance at various occasions. Their views and tips are useful indeed. Unfortunately, it is not possible to list all of them in this limited space. I am grateful to all my family member.

ABSTRACT

Activated carbon nanofibers (ACNFs) is a newly modified structure of carbon-based adsorbent that could adsorb carbon dioxide (CO_2) due to its high specific surface area (SSA), wide distribution of pores as well as high volume of active sites on its fibrous structure. Meanwhile, graphene is a single layer of pure carbon atoms known for its great properties such as high SSA, high thermal and chemical stability, and high electrical and thermal conductivities. It is hypothesized that the incorporation of graphene as nanofiller in the polyacrylonitrile (PAN)-based ACNFs may improve the overall properties of the ACNFs. Nevertheless, pure graphene has been found to be very expensive and this factor hindered its utilization in wide range of applications. Due to that, rice husk which is known as abundantly available agricultural waste was introduced in this study to obtain cost-effective graphene-based materials. Herein, the main highlight of this current study is to fabricate PAN-based graphene composited activated carbon nanofibers (gACNFs) with enhanced physicochemical properties and to evaluate its adsorption performance behaviours towards CO_2, especially in flue gas. The study was performed by varying several experimental and adsorption parameters including the PAN to graphene ratio (0, 1, 5, 10% of graphene-derived rice husk char (GRHC) relative to PAN weight), types of graphene-based materials (GRHC and reduced graphene oxide (rGO)), polyethyleneimine (PEI)-impregnated and non-impregnated gACNFs, as well as variation of pressure (5, 10, and 15 bar) and temperature of adsorption (0, 25, 50 °C). The resultant gACNFs with 1 wt.% of GRHC displayed the greatest improvement in their porous structure including largest SSA up to 597 m^2/g and highest micropore volume (0.2606 cm^3/g) which was twice the values of pristine ACNFs (202 m^2/g and 0.0976 cm^3/g). These tailorable surface properties are superior factors for effective CO_2 adsorption. Additionally, gACNFs with diameter ranging between 250-350 nm was obtained, which was smaller than the pristine ACNFs. This was due to electrical conductivity contributed by the GRHC that enhanced the solution conductivity during electrospinning, resulting in fibers with smaller diameter. Moreover, under the activation temperature of 700 °C, the yield of gACNFs obtained (44.5%), was almost double the value of pristine ACNFs (25.1%) due to the thermal stability properties of GRHC. The resultant GRHC/ACNF0.01 with the best porous structures and physicochemical properties exhibited the highest volume of CO_2 uptakes among other samples up to 3.1 mmol/g at atmospheric pressure and 25 °C. Meanwhile, the PEI-gACNFs have shown increment in CO_2 uptake from 3.1 to 4.8 mmol/g under the same conditions. Notably, the adsorption performance of CO_2 was directly proportional with the pressure increment, however it was inversely proportional with the increased temperature. Interestingly, both gACNFs and PEI-gACNFs fitted the pseudo-first order kinetic model (physisorption) at 1 bar, however, best fitted the pseudo-second order kinetic model (chemisorption) at 15 bar. Both gACNFs samples obeyed the Langmuir adsorption isotherm model. The stability performance of both gACNFs was reduced up to 23% after 5 complete cycles at 50 °C and atmospheric pressure.

ABSTRAK

Gentian nano karbon teraktif (ACNFs) adalah struktur penjerap berasaskan karbon yang baharu diubahsuai yang boleh menjerap karbon dioksida (CO_2) kerana luas permukaan tentunya (SSA) yang tinggi, serakan struktur pori yang luas, serta jumlah bahagian aktif yang tinggi pada struktur gentiannya. Sementara itu, grafin adalah satu lapisan atom karbon tulen yang terkenal dengan sifatnya yang bagus seperti SSA yang tinggi, kestabilan yang tinggi terhadap haba dan bahan kimia, dan konduktiviti elektrik dan haba yang tinggi. Berdasarkan hipotesis, penggabungan grafin sebagai pengisi-nano dalam ACNFs yang berasaskan poliakrilonitril (PAN) dapat meningkatkan sifat keseluruhan ACNFs. Walaupun begitu, grafin tulen adalah sangat mahal dan ini merupakan faktor yang menghalang penggunaannya di dalam pelbagai aplikasi. Kajian ini telah memperkenalkan bahan berasaskan grafin daripada sisa-sisa pertanian yang mudah diperoleh dan murah seperti sekam padi. Perkara utama yang ditekankan di dalam kajian ini adalah untuk membuat komposit grafin dan gentian nano karbon teraktif (gACNFs) berasaskan PAN dengan peningkatan sifat fizikokimia dan menilai kebolehan penjerapannya terhadap CO_2, terutamanya gas serombong. Kajian ini dilakukan dengan mempelbagaikan beberapa parameter ujikaji dan penjerapan termasuklah nisbah PAN kepada grafin (0, 1, 5, 10% grafin berasaskan arang sekam padi (GRHC) berbanding dengan berat PAN), jenis-jenis bahan yang berasaskan grafin (GRHC dan grafin kurang oksida (rGO)), gACNFs yang diresapi dan tidak diresapi dengan polietilenaimina (PEI), serta pelbagai tekanan (5, 10, 15 bar) dan suhu penjerapan (0, 25, 50 °C). gACNFs yang dihasilkan dengan berat GRHC 1% menunjukkan peningkatan terbesar dalam struktur berliang termasuklah SSA yang terbesar sehingga 597 m^2/g dan isipadu liang mikro yang tertinggi (0.2606 cm^3/g) yang menunjukkan peningkatan dua kali ganda berbanding nilai ACNFs asli (202 m^2/g dan 0.0976 cm^3/g). Sifat permukaan yang diubahsuai ini merupakan penyumbang utama untuk penjerapan CO_2 yang lebih berkesan. Selain itu, diameter gACNFs yang diperoleh di antara 250-350 nm adalah lebih kecil berbanding diameter ACNFs asli. Ini disebabkan oleh kekonduksian elektrik yang disumbangkan oleh GRHC telah meningkatkan kekonduksian larutan semasa proses putaran elektro yang dapat menghasilkan gentian dengan diameter yang lebih kecil. Tambahan pula, pada suhu pengaktifan 700 °C, hasil gACNFs yang diperoleh (44.5%) hampir dua kali ganda nilai ACNFs asli (25.1%) yang disebabkan oleh sifat kestabilan haba GRHC. GRHC/ACNF0.01 yang dihasilkan dengan struktur berliang dan sifat fizikokimia yang terbaik menunjukkan jumlah penjerapan CO_2 tertinggi iaitu 3.1 mmol/g berbanding sampel lain pada tekanan atmosfera dan 25 °C. Sementara itu, PEI-gACNFs menunjukkan peningkatan penjerapan CO_2 daripada 3.1 kepada 4.8 mmol/g dalam keadaan yang sama. Prestasi penjerapan CO_2 berkadar terus dengan kenaikan tekanan, namun berkadar songsang dengan kenaikan suhu. Menariknya, kedua-dua gACNFs dan PEI-gACNFs sesuai dengan model kinetik pseudo tertib pertama (penjerapan fizikal) pada 1 bar, namun menunjukkan kesesuaian dengan model kinetik pseudo tertib kedua (penjerapan kimia) pada 15 bar. Kedua-dua sampel gACNFs ini mematuhi model isoterma penjerapan Langmuir. Prestasi kestabilan kedua-dua gACNFs berkurang sehingga 23% selepas 5 kali kitaran lengkap pada suhu 50 °C dan tekanan atmosfera.

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LIST OF ABBREVIATIONS

AC	-	Activated carbon
ACNFs	-	Activated carbon nanofibers
AlO_4	-	Aluminium oxide
BET	-	Brunauer, Emmett and Teller
BJH	-	Barrett-Joyner-Halenda
CCSU	-	Carbon capture, storage, and utilization
CF	-	Carbon fibers
CH_4	-	Methane
CNF	-	Carbon nanofibers
CNTs	-	Carbon nanotubes
CO_2		Carbon dioxide
Co_3O_4	-	Cobalt spinel oxide
CuO	-	Copper oxide
CVD	-	Chemical vapor deposition
DEA	-	Diethylamine
DETA	-	Diethylenetriamine
DI	-	Deionised water
DMF	-	Dimethylformamide
DP_{ave}	-	Average pore diameter
EDX	-	Elemental dispersive X-ray
FTIR	-	Fourier transform infrared
GAC	-	Granular activated carbon
gACNFs	-	Activated carbon nanofibers/graphene composites
GHGs	-	Greenhouse gases
gNFs	-	Nanofibers/graphene composites
GO	-	Graphene oxide
GRHC	-	Graphene-derived rice husk char
H_3PO_4	-	Phosphoric acid
HiPCO	-	Carbon monoxide disproportionation
IUPAC	-	International Union of Pure and Applied Chemistry

K_2CO_3	-	Potassium carbonate
KOH	-	Potassium hydroxide
MEA	-	Monoethanolamine
MEGO	-	Microwave-exfoliated graphite oxide
MgO	-	Magnesium oxide
MnO_2	-	Manganese dioxide
MOFs	-	Metal organic frameworks
MWCNT	-	Multi-walled carbon nanotubes
N_2	-	Nitrogen
N_2O	-	Nitrous oxide
NaOH	-	Sodium hydroxide
NFs	-	Nanofibers
NLDFT	-	Non-local density functional theory
PAC	-	Powdered activated carbon
PAN	-	Polyacrylonitrile
PCP	-	Porous carbon polyhedral
PEHA	-	Pentaethylenehexamine
PEI	-	Polyethyleneimine
PMMA	-	Poly(methyl methacrylate)
ppm	-	Parts per million
PSD	-	Pore size distribution
Pt	-	Platinum
PVP	-	Polyvinylpyrrolidone
rGO	-	Reduced graphene oxide
SEM	-	Scanning electron microscopy
SiC	-	Silicon carbide
SiO_4	-	Silicon oxide
SnO_2	-	Tin oxide
SSA	-	Specific surface area
SWCNT	-	Single-walled carbon nanotubes
TEM	-	Transmission electron microscopy
TEPA	-	Tetraethylenepentamine
TGA	-	Thermogravimetric analysis

TPV	-	Total pore volume
V_{meso}	-	Mesopore volume
V_{micro}	-	Micropore volume
XRD	-	X-ray diffraction
$ZnCl_2$	-	Zinc cholride
$ZrCO_2$	-	Zirconium oxide

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LIST OF SYMBOLS

°C	-	Degree celsius
ΔH_{st}	-	Isosteric heat of adsorption
R^2	-	Linear regression
ρ	-	Resistivity
σ	-	Electrical conductivity
m	-	Mass of the adsorbent
q	-	Amount of gas adsorbed on the adsorbent at equilibrium
P	-	Pressure
T	-	Temperature
v	-	Volume
Z	-	Compressibility factor
sp^2	-	Two carbon atoms form a sigma bond in the molecule

CHAPTER 1

INTRODUCTION

1.1 Research Background

The massive emissions of anthropogenic carbon dioxide (CO_2) gas into the atmosphere are considered as the main reason for the occurrence of global warming and climate change (Acevedo et al., 2019; Huang et al., 2019). Human activities such as combustion of fossil fuels in industry, especially power generation sector, is one of the major emission sources of CO_2 to the atmosphere (Bains et al., 2019; Acevedo et al., 2020). In mid-August 2020, according to the latest update from Mouna Loa Observatory (2020), the increment of CO_2 concentration was recorded as 3.02 ppm from August 2019 to August 2020 and reached up to 412.97 ppm as compared to the previous year concentration, i.e., 409.95 ppm, which is an alarming rate since CO_2 concentration in the atmosphere at <350 ppm is considering safe (Willard, 2014). Even though, there was a temporary reduction in daily global CO_2 emissions during the COVID-19 forced confinement in April 2020 reported by Le Quéré et al. (2020), it does not really reflect the structural changes in the economic, transport or energy systems. Up to now, various agreements are developed among nations worldwide including Kyoto Protocol and Paris Agreement to face the challenges caused by carbon emissions, especially CO_2 emission. Accordingly, it has encouraged many research efforts around the globe to develop advanced materials, techniques and strategies to address the problems associated with CO_2 emission including the health problems. Popular strategies have been explored and adopted including the utilization of low carbon fuels and renewable energy sources, and CO_2 capture, storage and utilization (CCSU) from their source points (Chen et al., 2015).

CCSU is a promising approach to mitigate the anthropogenic CO_2 with the capacity to reduce up to 22% of CO_2 emissions in 2035 (Bains et al., 2017). In this technology, there are three basic CO_2 capture scenarios can be adopted which are post-combustion capture, pre-combustion capture, and oxy-fuel combustion. The main focus of this study is to capture the CO_2 from the flue gases after the burning of fossil fuels in power plants, post-combustion capture. These past few decades, absorption is the common method in post-combustion CO_2 capture and separation. However, CO_2 absorption via amine scrubbing possesses apparent disadvantages, such as release of toxic gases and chemicals, high energy requirement for regeneration, and extensive corrosion of the equipment, which limit the practical application of this technology. Due to its disadvantages, this method become less preferable and alternative technology processes were developed to overcome the drawbacks of this method. The development of practical yet sustainable alternatives are still highly desired (Abbasi et al., 2019; Romano et al., 2013). Consequently, other alternative and effective method such as adsorption have been suggested due to its simplicity in operation (Huang et al., 2019), low energy requirement, ease of regeneration, environmental-friendly, and cost-effective (Singh and Kumar, 2016). Moreover, adsorption can be done under ambient pressure at elevated temperatures which makes it suitable adsorbent for post-combustion CO_2 capture.

In CO_2 adsorption, there are various types of commonly employed adsorbents such as zeolites and clays-based adsorbents, carbon-based adsorbents, and metal organic frameworks (MOF)-based adsorbents (Gibson et al., 2016). Out of these mentioned adsorbents, carbon-based adsorbent is the most abundant and can be attained from inexpensive carbon precursors. Activated carbon (AC) (Guo et al., 2006), carbon fibers (CFs), carbon nanotubes (CNTs), graphene (Chowdhury and Balasubramaniam, 2016), activated carbon nanofibers (ACNFs) (Othman et al., 2016) are examples of carbon-based adsorbents that have been currently used in CO_2 adsorption. Amongst the available carbon-based adsorbents being investigated, porous ones such as activated carbons (ACs) were preferred due to its low cost, high surface area and porosity, high adsorption capability, high amenability to modify the pore structure and functionalize the surface, low energy requirements for regeneration as well as hydrophobicity (Pellerano et al., 2009; El-Sharkawy et al., 2015). ACs in granular and powdered form are the commonly used adsorbent (El-Sharkawy et al., 2015). Generally, ACs have relatively low micropore volume and multimodal pore size distribution which are the main factors to limit their adsorption capabilities. Conversely, in comparison with the conventional ACs, newly developed fibrous ACs, also known activated carbon nanofibers (ACNFs) have shown the improved adsorption capacity due to the fibrous structure and presence of accessible micropores from their external surface (Lee et al., 2014), which reduce the mass transfer resistance for adsorbate diffusion to reach the adsorption sites. Although the developed pristine ACNFs has shown the improved adsorption performance as compared with the commercial ACs, recent study disclosed that the inclusion of nanofillers/additives could further improve the surface area and micropore volume of the modified ACNFs (Tavanai et al., 2009).

In comparison with other additives, graphene and graphene oxide with novel properties and economical carbon-based materials have been the potential candidates for adsorbent materials due to their large theoretical specific surface area (SSA) and high porosity (Mishra and Ramaprabhu, 2011; Takeuchi et al., 2017). These excellent properties have opened up the utilisation of graphene in wide range of applications including supercapacitors, biomedicals, fuel cells, energy storage etc. (Wang et al., 2017). For instance, the addition of graphene-based materials from agricultural wastes such as rice husks as nanofiller have received major attention due to its abundant availability, cost-effective, and easy preparation as compared to other precursors. Besides that, determination of suitable experimental and fabrication parameters of ACNFs such as electrospinning and activation are also very crucial. Electrospinning process resulting to the formation of fine, homogenous, smooth, and aligned fibers structure under controllable electrospinning parameters with diameter ranging from 100-300 nm as compared to other NFs fabrication methods (Nayak et al., 2011).

Besides the fabrication method, the selection of carbon precursor should be deeply considered in order to produce ACNFs with excellent properties for CO_2 adsorption (Park and Heo, 2015). Polyacrylonitrile (PAN) has been reported to produce yield of high carbon percentage during carbonization process due to its high melting point to retain its structure (Yusof and Ismail, 2012; Huang, 2009). Furthermore, the physical or chemical activation is another factor that can also increase the porosity and surface area of the resultant ACNFs. In conclusion, it can be said that the main point that should be taken into consideration for maximum CO_2 adsorption performance is depending on the properties of the adsorbent used including the SSA and porosity, susceptibility to surface chemistry and structural modifications, selectivity towards adsorbates and many more (Osmond, 2000).

1.2 Problem Statements

The commercial graphene synthesized by Hummer's method produced single-layered pure graphene with high specific surface area (SSA), which makes them suitable to be utilized in wide range of applications (Gadipelli and Guo, 2015). However, this expensive and complex synthesis method have been the major concerns faced by the researchers nowadays. The alternative for abundant and cheap agricultural wastes with simple chemical activation method to produce graphene materials has been considered. However, another challenge of the synthesized agricultural-based graphene such as rice husk char (GRHC), is it's often suffered from the restacking between neighboring layers, due to the van der Waals force of attraction as reported by Cui et al. (2014). This led to a serious reduction of the accessible surface area and adsorption active sites. In order to prevent restacking in graphene-based materials, this GRHC can be used as nanofillers, and were incorporated into polymer activated carbon nanofibers (ACNFs). Moreover, the other problems in local agriculture industries related to the rice husks is its unmanageable disposal by land filling or open burning, which can lead to occupancy of landfill space as well as air pollution.

Electrospun pristine activated carbon nanofibers (ACNFs) fabricated via a simple electrospinning process demonstrated low to moderate CO_2 uptake, necessary to compete with commercial activated carbon (AC). This is because the pristine ACNFs possessed moderate SSA value as compared to AC or modified ACNFs resulting from its large fiber diameter. It is believed that fiber with smaller diameter can contribute to ACNFs with higher SSA (Wang, 2008). Apparently, these polymeric-based ACNFs suffered from very low carbon yield. Due to that, incorporation of thermally stable graphene is expected to improve the thermal stability of the ACNFs nanocomposites, especially during high activation temperature, thus producing graphene incorporated ACNFs (gACNFs) with higher carbon yield. Moreover, the resultant gACNFs with highly thermal-stable properties is more preferable in the elevated temperature (40-80°C) during post-combustion CO_2 capture in power plants. It is believed that graphene-based materials with large SSA values, high electrical and thermal conductivities, excellent thermal and chemical stabilities can potentially act as additive/nanofiller to produce composite ACNFs. The resultant composite ACNFs are believed to display smaller fiber diameter, larger SSA, and thermal-stable properties as well as enhanced adsorption performances (Gadipelli and Guo, 2015; Papageorgiou et al., 2017).

However, from previous study conducted by Zhang et al. (2015), they have found that carbon-based adsorbents such as activated carbon suffered from low CO_2 adsorption capacity. This could possibly be due to the uncontrollable pore size caused by the uncertain structures of various carbon-based precursors. Even though, the SSA, V_{micro}, and pore size appeared to be the key parameters in the design of porous adsorbents for CO_2. The surface chemistry also plays vital role that needs to be considered. For this issue, the surface properties can be tuned not only by the pre-design of precursors, but also by the post-modification of existing carbon materials. This is because the carbon-based adsorbents possess fewer basic functionalities which make the adsorbents do not significantly interact with acidic CO_2 molecules. Due to that, it is believed by adding the basicity of the adsorbent with amine-based chemicals will improve the adsorption capacity of the adsorbents due to high affinity of this functional groups towards CO_2.

1.3 Hypotheses

(a) Incorporation of GRHC with good conductivity and thermal stability properties would reduce the fiber diameter during electrospinning and producing ACNFs with higher yield after activation at high temperature.

(b) By varying the types of graphene-based materials and their loadings during synthesis, the gACNFs would possess differences in their physicochemical properties.

(c) CO_2 adsorption capacity of gACNFs composites will be enhanced by impregnating polyethyleneimine (PEI) due to introduction of basic N-functionalities that have stronger interaction with CO_2 molecules.

(d) The resultant PEI-gACNFs composites with specific and desirable physicochemical properties would give superior adsorption capacity toward CO_2 via physisorption and chemisorption, simultaneously.

1.4 Research Objectives

The aim of this study is to produce low-cost and simple synthesis method of graphene-derived rice husk char (GRHC) and its effects on the prepared activated carbon nanofibers nanocomposites (ACNFs) for carbon dioxide adsorption. In order to accomplish the aim of this study, the completion of each objective mentioned as follow need to be done:

(a) To optimize the synthesis conditions and method of graphene-derived rice husk char (GRHC) as nanofillers in activated carbon nanofibers (ACNFs).

(b) To evaluate the effects of GRHC on the physicochemical properties of the resultant graphene/activated carbon nanofibers nanocomposites (gACNFs).

(c) To improve the gACNFs surface chemistry properties for CO_2 adsorption by impregnating polyethyleneimine (PEI) on the prepared gACNFs.

(d) To examine the CO_2 adsorption characteristics of pristine ACNFs and gACNFs nanocomposites, as well as PEI-gACNFs via volumetric adsorption method.

1.5 Scopes of the Study

In order to accomplish the aforementioned aim and objectives, the scopes of this study were divided accordingly to the aforementioned objectives as enlisted below:

(a) To optimize the synthesis conditions and method of graphene-derived rice husk char (GRHC) as nanofillers in activated carbon nanofibers (ACNFs) by considering the following scopes:

i. Synthesis of graphene derived-rice husk char (GRHC) at different stabilization temperatures (100, 200, 300, 400°C) by using different RHC:KOH ratio (1:1, 1:2, 1:3,1:4, 1:5).

ii. Thermal reduction of reduced graphene oxide (rGO) from commercial graphene oxide (GO).

(b) To evaluate the effects of GRHC on the physicochemical properties of the resultant graphene/activated carbon nanofibers nanocomposites (gACNFs), the following scopes are conducted:

i. Preparation of dope solution with different concentration of polyacrylonitrile (8, 9, 10% relative to total solution weight) and graphene loadings (1, 2.5, 5, 10%).

ii. Effects of different types of graphene-like materials such as GRHC and rGO and their loadings on the properties of nanofibers/graphene composites (gNFs).

iii. Effects of physical activation on the resultant NFs by using carbon dioxide (CO_2) as activating agents under optimum activation parameters.

iv. Characterization of elemental, microstructural, and textural properties of the graphene-based materials (GRHC and rGO), pristine ACNFs and gACNFs composites by using thermogravimetric analysis (TGA), Fourier transform infrared (FTIR), Raman spectra, X-ray diffraction (XRD), Brunauer, Emmett and Teller (BET), N_2 adsorption/desorption isotherm by using BET method, and scanning electron microscopy (SEM), transmission electron microscopy (TEM), and elemental dispersive X-ray (EDX) analyses.

(c) To improve the gACNFs surface chemistry properties for CO_2 adsorption by impregnating polyethyleneimine (PEI) on the prepared gACNFs and the following scopes are considered:

i. Preparation of impregnated gACNFs nanocomposites with PEI containing N-functionalities by using impregnation method.

ii. Characterization of chemical, microstructural, and textural properties of the PEI-impregnated and non-impregnated gACNFs.

(d) To examine the CO_2 adsorption characteristics of pristine ACNFs and gACNFs nanocomposites, as well as PEI-gACNFs via volumetric adsorption method, the following scopes have been conducted:

i. Evaluation of CO_2 adsorption capacity of pristine ACNFs and gACNFs from low to moderate pressure conditions (5, 10, 15 bars) at 25°C.

ii. Evaluation of CO_2 adsorption capacity of the impregnated and non-impregnated ACNFs and gACNFs at atmospheric pressures (1 bar) and 25°C.

iii. Evaluation of CO_2 adsorption/desorption of the impregnated and non-impregnated gACNFs at different adsorption temperatures (0, 25, 50°C) at atmospheric pressure to mimic the real-life post-combustion conditions (> 40 - 80°C, 1 bar).

iv. Assessment of CO_2 adsorption characteristics; kinetics of the adsorption was described using pseudo-first order and pseudo-second order model. The adsorption equilibrium data were correlated with Langmuir and Freundlich isotherm models. Regeneration of the gACNFs was determined after several successive adsorption/desorption cycles at atmospheric pressure and 25°C.

1.6 Significance of the Study

This newly modified ACNFs with the incorporation of graphene are believed to be a potential candidate that will serve as an alternative CO_2 storage apart of current adsorbents that are available nowadays. This is probably due to its feasibility and high gas adsorption capacity. Recently, graphene derived from the agricultural wastes such as rice husk char have been found to be good additives in various research applications due to its abundant availability, low cost, large specific surface area, and thermally stable. Up to now, there is no previous research that have been extensively studied and discussed on the effects of incorporation of graphene derived rice husk charchar (GRHC) in ACNFs properties and their gas adsorption capacity. There are also only limited studies that have been discussed on the effects of incorporation of GRHC in the NFs and most of it, are focusing of the preparation of composite NFs and their advantages in other applications such as supercapacitor electrodes. Wherefore, this proposed study may provide better understanding in the fabrication of gACNFs nanocomposites with enhanced properties by selecting suitable graphene precursors and loadings by considering the optimum electrospinning and pyrolysis conditions from previously reported studies. Moreover, the CO_2 adsorption performance was improved by impregnating the resultant ACNFs with amine-based chemicals that rich in N-functional groups such as polyethyleneimine (PEI). In the end of this study, both resultant gACNFs nanocomposites either PEI-impregnated or non-impregnated have become potentially excellent adsorbents for CO_2 adsorption in post-combustion CO_2 capture step in CCS method. Consequently, mitigate the anthropogenic CO_2 emission to the atmosphere and reduced the greenhouse effects.

1.7 Limitation of the Study

(a) The temperature-dependent adsorption/desorption test of the gACNFs and PEI-gACNFs were conducted under atmospheric pressure due to the limitation of the equipment.

(b) The improvement of the surface chemistry of the gACNFs by surface functionalization only limited to one type of amine-based chemicals which is polyethyleneimine (PEI).

(c) The mechanical strength of the resultant GRHC and gACNFs were not studied in this current work.

(d) Due to time limitation, the stability study of the gACNFs and PEI-gACNFs were performed for only five cycles.

(e) Studies on kinetic modelling and equilibrium isotherms for adsorption studies only limited to two different models, which is pseudo-first order and pseudo-second order kinetic models, and Langmuir and Freundlich models.

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LIST OF PUBLICATIONS

Journal with Impact Factor

1. **Othman, F.E.-C.**, Yusof, N., Samitsu, S., Abdullah, N., Hamid, M.-F., Nagai, K., Abidin, M.N.-Z., Azali, A.A., Ismail, A.F., Jaafar, J., Aziz, F., Salleh, W.N.W. (2021). Activated carbon nanofibers incorporated metal oxides for CO_2 adsorption: Effects of different type of metal oxides, *Journal of CO_2 Utilization*, 45, 1-10 (**Q1, IF: 5.993**).
2. **Othman, F.E.-C.**, Yusof, N. González-Benito, J., Fan, X., Ismail and A.-F. (2020) 'Electrospun composites made of reduced graphene oxide and polyacrylonitrile-based activated carbon nanofibers (rGO/ACNF) for enhanced CO_2 adsorption', *Polymers*, 12, 2117, pp. 1-19 (**Q1, IF: 3.426**).
3. **Othman, F.E.-C.**, Yusof, N., Harun, N.-Y., Bilad, M.-R., Jaafar, J., Aziz, F., Salleh, W.N.-W. and Ismail, A.-F. (2020) 'Novel activated carbon nanofibers composited with cost-effective graphene-based materials for enhanced adsorption performance toward methane', *Polymers*, 12, 2064 (**Q1, IF: 3.426**).
4. **Othman, F.E.-C.**, Yusof, N. and Ismail, A.-F. (2020) 'Activated carbon nanofibers/graphene nanocomposites and its adsorption performance towards carbon dioxide', *Chemical Engineering and Technology*, 43, pp. 1-9 (**Q2, IF: 3.742**).
5. **Othman, F.E.-C.**, Sadaki, S., Yusof, N. and Ismail., A.-F. (2020) 'Effects of carbonization conditions on microporous structure and high-pressure methane adsorption behavior of glucose-derived graphene', *Korean Journal of Chemical Engineering*, 37(11), pp. 2068-2074 (**Q2, IF: 2.690**).

6. **Othman, F.E.-C.**, Yusof, N., Ismail, A.-F., Jaafar, J., Salleh, W.N.-W. and Aziz, F. (2020) 'Preparation and characterization of polyacrylonitrile-based activated carbon nanofibers/graphene (gACNFs) composite synthesized by electrospinning', *AIP Advances*, 10(5), 055117 (**Q4, IF: 1.337**).
7. **Othman, F.E.-C.**, Ismail, M.-S., Yusof, N., Samitsu, S., Yusop, M.Z.-M., Ariffin, N.F.-T., Alias, N.-H., Jaafar, J., Aziz, F., Salleh, W.H.-W. and Ismail, A.-F. (2020) 'Methane adsorption by porous graphene-derived from rice husks char under various stabilization temperatures', *Carbon Letters* (**Q3, IF: 1.992**).