# AMINE-BEARING ELECTROSPUN NANOFIBROUS ADSORBENT USING RADIATION INDUCED GRAFTING FOR CARBON DIOXIDE CAPTURING

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To my wife for her fabulous support and understanding

And

To my parents for their prayers for me

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#### ABSTRACT

Carbon dioxide (CO<sub>2</sub>) is the most polluting greenhouse gas released into the atmosphere in large quantities causing global warming. Immobilization of amine groups containing compounds on a solid substrate is a straightforward approach for CO<sub>2</sub> adsorption. The main aim of this study is to prepare new amine-containing adsorbents having nanofibrous structures for efficient capturing of CO<sub>2</sub> from different environments. The adsorbent preparation involved i) electrospinning of polypropylene (s-PP) solution, ii) radiation induced syndiotactic graft copolymerization of glycidyl methacrylate (GMA) onto the electrospun nanofibers, and iii) functionalization of poly-GMA grafted s-PP nanofibrous mats with different amines (ethanolamine, diethylamine and triethylamine). The effect of various electrospinning parameters such as voltage, needle tip to collector distance and flow rate on the morphological properties of the produced nanofibers was studied using the response surface method (RSM). The effects of grafting parameters such as absorbed dose, monomer concentration, time and temperature on the degree of grafting (DG) were also investigated. The Scanning electron microscopy (SEM), Fourier transform infra-red (FTIR), Differential scanning calorimetry (DSC), Thermogravimetric analysis (TGA) and Brunauer-Emmet-Teller (BET) techniques were used to determine morphological, chemical, thermal properties and stability, changes in the structure of the nanofibers after each modification step. Finally, the amine-bearing nanofibers were tested for CO<sub>2</sub> adsorption in a fixed bed column under different operating parameters such as DG in adsorbent, amine type, initial CO<sub>2</sub> concentration and temperature. The highest CO<sub>2</sub> adsorption capacity of 2.87 mmol CO<sub>2</sub>/g was achieved in an adsorbent having 300 % DG and functionalized with ethanolamine at 15 % initial CO<sub>2</sub> concentration, atmospheric pressure and 30 °C. This study showed that new class of CO<sub>2</sub> adsorbents can be successfully prepared by combining electrospinning with radiation induced grafting techniques followed by amine loading.

#### ABSTRAK

Karbon dioksida (CO<sub>2</sub>) merupakan gas rumah hijau paling mencemar yang dilepaskan dalam kuantiti yang tinggi ke dalam atmosfera dan menyebabkan pemanasan global. Immobilisasi kumpulan amina pada substrat pepejal merupakan pendekatan mudah untuk menjerap CO<sub>2</sub>. Matlamat utama kajian ini ialah menyediakan penjerap amina baru yang mempunyai struktur gentian nano untuk menjerap CO<sub>2</sub> dengan efisien dari pelbagai persekitaran. Penyediaan bahan penjerap elektroputar larutan polipropilena sindiotaktik melibatkan i) (s-PP), ii) pengkopolimeran cangkuk aruhan sinaran glisidil metakrilat (GMA) pada gentian nano elektroputar dan iii) pengfungsian poli-GMA cangkukan PP gentian nano dengan pelbagai amina (etanolamina, dietilamina dan trietilamina). Kesan daripada pelbagai parameter elektroputar seperti voltan, jarak antara hujung jarum dan drum pengumpulan dan kadar aliran ke atas sifat-sifat morfologi gentian nano yang dihasilkan dikaji menggunakan kaedah gerak balas permukaan (RSM). Kesan parameter cangkukan seperti dos terserap, kepekatan monomer, masa dan suhu ke atas kadar cangkukan (DG) juga disiasat. Teknik mikroskop pengimbasan electron (SEM), inframerah spektrometer transformasi Fourier (FT-IR), kalorimetri pengimbasan pembezaan (DSC), analisis termogravimetri (TGA) dan Brunauer-Emmett-Teller (BET) telah digunakan untuk menentukan sifat morfologi, sifat kimia, sifat haba dan kestabilan, perubahan dalam struktur gentian nano selepas setiap langkah pengubahsuaian. Akhirnya, gentian nano mengandungi amina telah diuji untuk penjerapan CO<sub>2</sub> menggunakan turus lapisan tetap di bawah parameter operasi yang berbeza seperti DG dalam penjerap, jenis amina, kepekatan asal CO<sub>2</sub> dan suhu. Kapasiti jerapan tertinggi iaitu 2.87 mmol CO<sub>2</sub>/g dicapai pada penjerap yang mempunyai 300 % DG dan difungsikan dengan etanolamina pada 15 % kepekatan asal CO<sub>2</sub>, tekanan atmosfera dan 30 °C. Kajian ini menunjukkan bahawa penjerap CO<sub>2</sub> yang baru berjaya disediakan dengan menggabungkan elektroputar dan teknik cangkukan aruhan sinaran diikuti dengan pemuatan amina.

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### LIST OF ABBREVIATIONS

AAc	-	Acrylic acid
AEAPDMS	-	N-(2-aminoethyl)-3-
		aminopropylmethyldimethoxysilane
AEM	-	Anion exchange membrane
APGDP	-	Atmospheric pressure glow discharge plasma
BET	-	Brauner Emmett Teller
BPO	-	Benzoyl peroxide
CEF	-	Cation exchange fiber
CEM	-	Cation exchange membrane
DBU	-	1,8-Diazabicyclo-[5.4.0]-undec-7-ene
DES	-	Diethylstilbestrol
DMAc	-	Dimethylacetamide
DS	-	Dienestrol
DSC	-	Differential scanning calorimetry
DVB	-	Divinylbenzene
EB	-	Electron beam
ECH	-	Epichlorohydrin
EPS	-	Expanded polystyrene
FTIR	-	Fourier transform infrared
GA	-	Glutaraldehyde
НА	-	Hydroxylamine
HEPA	-	High Efficiency Particulate Air filter
HEX	-	Hexestrol
HFP	-	Hexafluoropropylene
IEC	-	Ion exchange capacity
MAA	-	Methacrylic acid

MWNTs	- Multiwalled carbon nanotubes
NaSS	- Sodium styrene sulfonate
NFC	- Nanofibrillated cellulose
NFs	- Nanofibers
OMS	- Octahedral molecular sieve
PAN	- Polyacrylonitrile
PCLEEP	- Poly(ε-caprolactone-co-ethyl ethylene phosphate)
PE	- Polyethylene
PEGMA	- Poly(ethylene glycol) methyl ether methacrylate
PEI	- Polyethyleneimine
PEO	- Poly (ethylene oxide)
PES	- Poly ether sulfone
PET	- Polyethylene terephthalate
PGA	- Polyglycolic acid
PLLA	- Poly-L-lactide
РО	- Polyolefin
РР	- Polypropylene
PP150-g-Poly-GMA	- Polypropylene nanofibers grafted with 150%
	poly(GMA)
PP150-g-Poly-GMA-	- Polypropylene nanofibers grafted with 150%
EA30	poly(GMA) and 30% aminated by EA
PP150-g-Poly-GMA-	- Polypropylene nanofibers grafted with 150%
EA60	poly(GMA) and 60% aminated by EA
PP150-g-Poly-GMA-	- Polypropylene nanofibers grafted with 150%
EA94	poly(GMA) and 94% aminated by EA
PP300-g-Poly-GMA	- Polypropylene nanofibers grafted with 300%
	poly(GMA)
PP300-g-Poly-GMA-	- Polypropylene nanofibers grafted with 300%
DEA30	poly(GMA) and 30% aminated by DEA
PP300-g-Poly-GMA-	- Polypropylene nanofibers grafted with 300%
DEA85	poly(GMA) and 85% aminated by DEA
PP300-g-Poly-GMA-	- Polypropylene nanofibers grafted with 300%

DEA93		poly(GMA) and 93% aminated by DEA
PP300-g-Poly-GMA-	-	Polypropylene nanofibers grafted with 300%
EA30		poly(GMA) and 30% aminated by EA
PP300-g-Poly-GMA-	-	Polypropylene nanofibers grafted with 300%
EA60		poly(GMA) and 60% aminated by EA
PP300-g-Poly-GMA-	-	Polypropylene nanofibers grafted with 300%
EA94		poly(GMA) and 94% aminated by EA
PP300-g-Poly-GMA-	-	Polypropylene nanofibers grafted with 300%
TEA22		poly(GMA) and 22% aminated by TEA
PP300-g-Poly-GMA-	-	Polypropylene nanofibers grafted with 300%
TEA50		poly(GMA) and 50% aminated by TEA
PP300-g-Poly-GMA-	-	Polypropylene nanofibers grafted with 300%
TEA82		poly(GMA) and 82% aminated by TEA
PP400-g-Poly-GMA	-	Polypropylene nanofibers grafted with 400%
		poly(GMA)
PPNF	-	Polypropylene Nanofibers
PS	-	Polystyrene
PSU	-	Polysulfone
PTFE	-	Polytetrafluoroethylene
PVA	-	Polyvinyl alcohol
PVDF	-	Polyvinylidene fluoride
PVP	-	Polyvinylpyrrolidone
QF	-	Quality factor
RIGP	-	Radiation induced graft polymerization
SEM	-	Scanning electron microscope
SF	-	Silk fibroin
s-PP	-	Syndiotactic polypropylene
St	-	Styrene
TBO	-	Toluidine Blue O
TETA	-	Triethylenetetramine
TFC	-	Thin film composite
TGA	-	Thermogravimetric analysis

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THMAM -	Tri(hydroxymethyl) aminomethane
TMA -	Trimethylamine
UF -	Ultrafiltration
ULPA -	Ultra-Low Penetration Air Filter
VP -	Vinyl pyrrolidone
WK -	Wool Keratose

## LIST OF SYMBOLS

С	-	Concentration	-	%
C <sub>0</sub>	-	Feed concentration	-	%
DA	-	Degree of amination	-	%
DG	-	Degree of grafting	-	%
F	-	Flow rate	-	mmol/s
q	-	Adsorption capacity	-	Mmol/g
Т	-	Temperature	-	°C
tq	-	Stoichiometric time	-	second
$t_{q0}$	-	Blank stoichiometric time	-	second
$t_{qf}$	-	Final stoichiometric time	-	second
W	-	Sample weight	-	g
$\mathbf{W}_0$	-	Initial weight	-	g
Wa	-	Weight of the sample after amination	-	g
Wg	-	Weight of the sample after grafting	-	g

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### **CHAPTER 1**

#### **INTRODUCTION**

#### 1.1 Background

Global warming is one of the most crucial problems faced by human being for the past 50 years. This phenomenon is caused mainly by emission of greenhouse gases to the atmosphere. Carbon dioxide (CO<sub>2</sub>), sulfur hexafluoride (SF<sub>6</sub>), methane (CH<sub>4</sub>), hydrofluorocarbons (HFCs), water vapor, nitrous oxide (N<sub>2</sub>O), and perfluorocarbons (PFCs) are the most critical greenhouse gases which accumulate in the atmosphere, preventing the heat from reflecting back to the space, i.e. act like an "earth blanket" and result in an increase in the global temperature [1].

A certain level of these gases is naturally available in the atmosphere to keep the earth surface warm and inhabitable. Before industrial age in mid-17<sup>th</sup> century, there was a delicate balance between these gases in the atmosphere and the gases absorbed by natural waters (oceans, seas, etc.). However, the emergence of industrial era and increased need of human being to energy lead to the emission of large amounts of carbon dioxide into the atmosphere, disturbing this balance and increasing earth temperature; nowadays this phenomenon is known as "global warming".

Greenhouse gases can stay in the atmosphere for about a century. In the latest U.S. climate action report (2014), global warming is mentioned as "no longer a distant threat". According to this report, the average temperature of the United States

has increased by about 0.8°C since 1895 from which more than 80% is for the time period after 1980. If serious actions are not taken to reduce the increasing trend of CO<sub>2</sub> emission to the atmosphere, the average temperature of the earth is predicted to increase by 1.4-5.8°C until 2100. This temperature increase, either at the lower or at the higher end, will cause tremendous climate changes resulting in water expansion and sea level rise due to glacier melting. Intense tornados, hurricanes, floods, droughts, acidic oceans and spread of tropical diseases to new areas are just some of the examples of the effect of this climate change on earth. A recent study shows that 1°C rise in global temperature results in two to seven folds increase in the number of the events in the scale of Katrina [2]. In 2012 only, there were 11 climate disasters in the United States with estimated damage of more than 11 billion USD [3].

CO<sub>2</sub> is the most important greenhouse gas released into the atmosphere in large quantities. The effect of CO<sub>2</sub> on the earth temperature was first suggested by Svante Arrhenius in his landmark paper published in 1896 [4]. In his theory, earth receives energy from sunlight and re-emits some part of this energy as IR irradiation into the space. Greenhouse gases such as CO<sub>2</sub> accumulated in the atmosphere absorb this IR radiation and prevent it from re-emitting into the space and hence, help to increase the earth temperature. According to the U.S. climate action report 2014, carbon dioxide accounts for more than 80% of greenhouse gases (Figure 1.1) [3].



Figure 1.1 Greenhouse percentages based on teragram CO<sub>2</sub> equivalent (CO<sub>2</sub>e) [3]

Because of the growing concern on climate change driven by this man-made carbon emission, governments all over the world are looking at ways to reduce or stabilize their carbon footprint. United Kingdom has set a plan to reduce its carbon emission by 60 percent by 2050 and European Union has agreed to cut its emission by 20 percent until 2020. In 2009, the United States also committed to reduce its greenhouse gases emissions to the range of 17% below its level in 2005 by 2020 [3].

Burning of fossil fuels such as coal, natural gas and oil comprises 87% of all CO<sub>2</sub> emissions by human being. Deforestation, i.e. clearing the forests and other land use changes are responsible for 9% of CO<sub>2</sub> emission increase into the atmosphere. The remaining 4% is the result of industrial activities such as cement manufacturing [5]. Furthermore, production of electricity and heat represented 42% of global CO<sub>2</sub> emissions in 2013. Transportation, industry and residential use were placed in subsequent ranks with 23, 19 and 6% of global CO<sub>2</sub> emissions, respectively. The remaining 10% was for services and other sectors such as agriculture [6].

Generally, there are three methods for reducing CO<sub>2</sub> emissions into the atmosphere: 1) more efficient uses of energy, 2) using alternative energy resources such as renewable energy sources e.g. solar energy and wind energy, and 3) using CO<sub>2</sub> capture and sequestration (CCS) technologies. More efficient use of energy and using alternative energy resources are far from real-world applications. Therefore, CCS technologies currently are the most commonly used methods in large scales to diminish CO<sub>2</sub> emission.

Carbon sequestration which is defined as long-term storage of carbon dioxide or other forms of carbon to mitigate or delay global warming, is a useful technique of slowing down global warming without any necessary reduction in fossil fuels consumption. The first step in this process is capturing and separating carbon dioxide from waste gas. Four main methods have been developed for CO<sub>2</sub> separation and capture including cryogenics, membrane diffusion, solution absorption and solid adsorption.

Cryogenic distillation is widely used for the separation of other gases, but for CO<sub>2</sub> capturing from flue gas, this method is costly and not practical. Separation of CO<sub>2</sub> from a mixture of gases using membranes is very useful when the concentration

of  $CO_2$  is very high. In the case of capturing carbon dioxide from post-combustion flue gas, the content of  $CO_2$  is very dilute and this method is not very efficient. Liquid amine based process (also known as amine scrubbing) is the most commonly used method for commercial removal of  $CO_2$ . This method involves using monoethanolamine, diethanolamine, or methyldiethanolamine solutions and can remove carbon dioxide effectively [7].

Recently, there has been a great interest on solid adsorbents for CO<sub>2</sub> capturing. These materials can be categorized into physi-sorbents and chemisorbents. In physi-sorbents including activated carbon and zeolites, CO<sub>2</sub> is attached onto the surface of the adsorbent material through physical weak interactions. Even though the adsorption capacity of these materials is high and they can operate in near ambient temperatures, humidity which is usually available in CO<sub>2</sub> adsorption environments has negative effect on their performance and furthermore, their adsorption capacity decreases with temperature increase [8, 9].

In chemi-sorbents, usually amine functional groups are immobilized on organic or hybrid solid substrates using physical or chemical interactions. Impregnation of amines on organic substrates such as zeolites results in the formation of the first group of amine-containing solid adsorbents. In these materials adsorption capacity is high, but amine functional groups are washed away after a few cycle of adsorption/desorption [10]. Another group of chemi-sorbents can be synthesized by covalent bonding of amine-containing molecules onto silica base material. Adsorption capacity of the synthesized adsorbent is usually high, but amine efficiency is low and adsorption kinetics is slow.

#### **1.2 Problem Statement**

 $CO_2$  is the most critical greenhouse gas released into the atmosphere in large quantities. This large amount of  $CO_2$  in the atmosphere increases the earth temperature and prompts to tremendous problems that affect the existence of the human being such as intense tornados, hurricanes, floods, droughts and acidic rains. The main part of the  $CO_2$  emission comes from combustion of fossil fuels which are

the main source of energy used to meet energy demands of humanity for now and the near future. Approximately 85% of human energy consumption comes from fossil fuels. It was estimated that more than 32 billion tons of CO<sub>2</sub> was released into the air as a result of burning of fossil fuels in 2013 [6].

Currently, liquid amine absorption is the main commercial method used for CO<sub>2</sub> capturing. However, this process involves some challenges including high regeneration energy, large equipment size, solvent degradation, and equipment corrosion which limit its application in the future [11, 12].

Solid adsorption is an alternative technique attracting more attention recently. Among solid adsorbents, polymeric microfibers containing amine functional groups have shown some advantages over other adsorbents based on other kinds of substrates. Particularly, fibrous adsorbent have flexibility, low temperature function, humidity-aided adsorption mechanism and easy regeneration [13]. However, the adsorption capacity of these adsorbents is low because of incomplete access to amine functional groups. Furthermore, the work capacity of the adsorbent, pressure drop and production cost need to be improved.

One of the possible approached to improve the work capacity and the efficiency of microfibrous adsorbents is to decrease the size of the fibers and use nano-scale fibers i.e. nanofibers. Single nanofibers are one-dimensional structures made from various organic (polymers) and inorganic materials. Polymeric nanofibers usually are formed as non-woven mats, forming 3-D structures. Like microfibrous non-woven mats, nanofibrous mats have porous interconnected architecture formed due to the overlapping single fibers. Recently there has been an increasing interest on these structures because of their fascinating properties. Although there are many ways for producing nanofibers, such as phase separation [14], and template synthesis [15], electrospinning is the most versatile and commonly used method.

The nanofibrous mats or sheets have a 3-D porous structure and because of very small diameter of its fibers, the surface area is very high. Since adsorption occurs on the surface of materials, thus surface area is a very important factor in adsorption based technologies. On the other hand, because of the dominance of slip flow in nanofibrous structures, the pressure drop across filters made from nanofibers

is presumably lower than microfibrous counterparts. So, electrospun nanofibrous mats are very good candidate substrates for producing CO<sub>2</sub> polymeric adsorbent which is the main aim of this project. Several studies have already been conducted on using functionalized micro- and nano- fibers for removing different pollutants from solutions such as heavy metal ions and dyes [16-19]. The results showed that these ionically functionalized fibers are very promising chelating materials for adsorption and separation applications.

While nanofibers are very promising materials in different applications, they usually need to be modified via different techniques to impart functional or ionic groups and desired characteristics for a particular application. There are several methods for modifying polymeric nanofibers such as dip-coating, interfacial polymerization, and graft polymerization. Amongst these techniques, radiation induced graft polymerization (RIGP) or radiation induced grafting is very promising modification technique because of its potency to modify chemical and physical characteristics of polymers substrates in various physical forms (films, particles or fibers) without changing their inherent properties [20].

Combining these two fascinating techniques (electrospinning and RIGP) could provide a versatile and convenient way for producing polymeric nanofibrous mats for removing CO<sub>2</sub> from different environments. An intensive search in literature revealed that preparation of functionalized nanofibrous adsorbent for CO<sub>2</sub> capturing has not been reported yet.

#### 1.3 Objectives of the Study

The objective of this work is to develop a new nanofibrous amine bearing adsorbent for CO<sub>2</sub> separation from different environments at ambient conditions using electrospinning of s-PP followed by radiation induced graft polymerization of an acrylate monomer followed by functionalization with aminating agents.

The specific objective of the study is sub-divided into the following:

- 1. To prepare s-PP nanofibrous mats with controlled diameter by optimization of electrospinning parameters.
- To modify the obtained nanofibrous mats by radiation induced grafting of controlled amount of glycidyl methacrylate (GMA) under controlled parameters.
- 3. To functionalize the obtained ploy(GMA) grafted nanofibrous mats with appropriate amine agents.
- 4. To determine the properties of the obtained functional adsorbent using chemical and materials research aspects in correlation with the performed modification.
- 5. To evaluate the performance of the adsorbent for CO2 capturing in a fixed column under different operating conditions.

#### 1.4 Scope of the Study

The scope of the study involves 8 stages. Dissolving polymeric material (PP here) in an adequate solvent system to obtain a polymer solution suitable for electrospinning was the first step. Then, nanofibrous mats were produced with electrospinning using as prepared polymeric solution and the effect of different parameters including voltage (8-16 kV), flow rate (1-4 ml/h) and distance between needle tip and collector (10-20 cm) on fibers properties (diameter and morphology) was studied.

Characterization of electrospun nanofibers was carried out using various techniques including scanning electron microscope (SEM), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR), and Brunauer–Emmett–Teller porosity analysis (BET). In the next stage, electrospun nanofibers were modified using radiation induced graft polymerization of GMA onto s-PP nanofibers in order to introduce functional groups to the polymeric backbone. This includes irradiation of the fibers with electron beam

and investigation of the effect of the grafting parameters including monomer concentration (2.5-20 vol%), absorbed dose (40-200 kGy), time (20-120 min) and temperature (40-70°C) on the degree of grafting.

After grafting the obtained poly(GMA) grafted s-PP nanofibers also were characterized to identify their morphological (SEM), chemical (FTIR) and thermal (DSC and TGA) properties and evaluate their surface area and pore characteristics (BET).

Functionalization of poly(GMA) grafted s-PP nanofibers using three aminating agents such as ethanolamine, diethylamine or triethylamine was the next step to introduce amine groups for CO<sub>2</sub> adsorption. This includes conversion of the epoxy groups of GMA to various amine groups by treatment with the aminecontaining compounds under controlled conditions of amine concentration (20-100 vol%), temperature (30-80 °C) and time (7 min- 24 h). After Amination, the same Characterization techniques were used to identify their morphological (SEM), chemical (FTIR) and thermal (DSC and TGA) properties and evaluate their surface area and pore characteristics (BET);

Finally, CO<sub>2</sub> adsorption capacity of the modified nanofibers was evaluated in a fixed bed column and the effect of different operating parameters including degree of grafting (150-400%), amination agent (EA, DEA or TEA), initial concentration of CO<sub>2</sub> in the feed gas (5-15%) and temperature (30-50°C) on its adsorption capacity was studied. The breakthrough curves were also established for the three types of adsorbents. The adsorption and desorption cycles were established.

#### 1.5 Significance of the Study

This work provides a new amine-containing polymeric adsorbent for CO<sub>2</sub> capturing having nanofibrous structure for the first time using a unique combination of two fascinating methods involving electrospinning and radiation induced graft copolymerization. The newly obtained adsorbent is capable of capturing CO<sub>2</sub> from various environments in a relatively low temperature and pressure. Moreover, it

could be recovered very easily and using less energy without any need to complex and expensive processes. The adsorbent can be used in capturing CO<sub>2</sub> from atmosphere and help mitigate greenhouse effect.

The obtained adsorbent has smaller in fiber diameters and is lighter in weight than commercial products. This can be harnessed in the development of smaller adsorbent columns with larger surface area and higher operating capacity and certainly can lead to an improvement in the economy of the process. This could help industries to cut their CO<sub>2</sub> emission following stagnant regulation imposed by environmental authorities in various countries. Besides, the column filter that can be developed based on this adsorbent can be possibly used in improving in-door air quality in work places and homes. Such filters can be used in air-condition manufacturing and health and medical care industries.

The electrospinning of s-pp leading to the formation of substrate mats that was used for grafting of GMA is rarely reported in literature. Thus, the work reported herein is an interesting contribution for electrospinning of thermoplastic polymers such as PP. The RSM used for optimization of electrospinning parameters provide a statistical tool to design and predict the morphology of the nanofibers.

This work also provided an opportunity to optimize the parameters of radiation induced grafting of GMA onto s-PP to obtain graft copolymer capable of hosting various amine groups. This paves the way for introducing other functional groups that can further enhance the adsorption capacity of the obtained adsorbents.

#### **1.6 Contribution**

Contributions of the study are as follows:

• Optimization of electrospinning of s-PP in near room temperature was reported for the first time and a linear model was established for various electrospinning parameters.

- Radiation induced grafting of GMA on electrospun s-PP nanofibers using pre-irradiation technique is reported for the first time and the effect of various parameters is studied.
- Amination of grafted electrospun s-PP nanofibers is studied and the effect of various parameters on amination degree is researched.
- A new nanofibrous solid adsorbent containing various types of amine functional group was prepared capable of capturing CO<sub>2</sub> in room temperature with very high amine efficiency.
- The application of the adsorbent can be extended to remove various species from air using various functional groups during functionalization stage.

### **1.7 Thesis Outline**

The current thesis is presented in five chapters. Chapter 1 is an introduction that covers background of the study and problem statement and describes objectives, scope and significance of the study. In chapter 2, a comprehensive literature review including CO<sub>2</sub> removal techniques and their advantages and limitations, electrospinning and its parameters and applications, radiation induced grafting, and nanofiber characterization techniques is given. Chapter 3 contains the methodology used for fabrication, modification, characterization and testing of nanofibers for CO<sub>2</sub> adsorption. In Chapter 4 the results are presented and discussed with reference to previous works, obtained data are analyzed and interpreted. Chapter 5 presents the final conclusions and recommendations to improve the work in future studies. Finally, the references used in preparing this thesis are listed.

foggy, showing that some of the polymer molecules are solidifying in the solution. It leads to the formation of some small beads in all electrospun sample. To get better results, it is suggested to use a heating system such as infra-red illumination heater or syringe jacket heater to hold the temperature of the solution at 60°C all the time during electrospinning. Even though increasing the chamber temperature up to 45°C, as was done in this work, reduced the solidification effect of the s-PP in the solution, but it did not stop the process completely. It leads to the formation of some beads, decreasing the surface area and affecting final fibers properties.

The adsorption capacity of the synthesized materials was in the range of low to moderate. It was due to the high weight ratio of the carrier non-active polymer (s-PP) to the total weight of the final adsorbent. Any modification that can reduce this ratio and increase the active, amine containing portion of the material could result in an improvement in the adsorption capacity and put the material in the group of high adsorption capacity adsorbents. One of the recommended approaches is to use amination agents having more than one amine group in the molecule. For example, using diamines (e.g. ethylenediamine: EDA), triamines (Diethylenetriamine: DETA) Triethylenetetramine: tetramines (e.g. TETA) or even pentamines (Tetraethylenepentamine: TEPA) [13] could improve the adsorption capacity by increasing the ratio of the active part of the adsorbent.

Another approach for increasing adsorption capacity of the nanofibrous adsorbent is incorporation of physical enhancers such as carbon nanotubes, graphene, carbon nanoparticles, etc. into the electrospun nanofibers. Incorporation could be performed during electrospinning process by blending these carbon-containing particles into the electrospinning solution before nanofiber formation. These nanomaterials are known to adsorb carbon dioxide molecules through physical adsorption and it is expected to increase adsorption capacity of the synthesized material by having a synergic effect on the adsorption process by combining physisorption with chemisorption.

Finally, different types of grafting monomers such as vinyl benzyl chloride could be used in grafting stage as an alternative for GMA to see the effect of including aromatic species in the adsorbent capacity of the final adsorbent. It is expected to see improvement in the adsorption performance of the material through incorporation of aromatic rings into its molecular structure.

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