DEVELOPMENT OF FABRIC CLOTH ADSORBENT TO REDUCE CARBON DIOXIDE FROM AIR

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APPROVAL SHEET

This is to certify that the Research work described in this thesis is the original work of author(s) and has been carried out under my direct supervision. I have personally gone through all the data/results/materials reported in the manuscript and certify their correctness/authenticity. I further certify that the material included in this thesis is not plagiarized and has not been used in part or full in a manuscript already submitted or in the process of submission in partial/complete fulfillment of the award of any other degree from any institution. I also certify that the thesis has been prepared under my supervision according to the prescribed format and I endorse its evaluation for the award of Bachelor of Engineering in Environmental Engineering Degree through the official procedures of the Institute.

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Abstract

In this research, biochar was thermally derived from poultry litter. Biochar based PVA bound nanofibers are synthesized through electrospinning and its CO_2 adsorption capacity is analyzed under different operational conditions.

Biochar and fibers were characterized by Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS), Thermogravimetric Analysis (TGA), Fourier Transform Infrared (FT-IR) and X- Ray Diffraction (XRD). Biochar prepared at 500ºC showed rich micro-porosity. The average diameter of the nanofibers was found out to be 579nm and were thermally stable up to 300ºC. Presence of amine groups on surface of biochar was confirmed through FT-IR analysis.

Various operational conditions like temperature, contact time, amine treatment and effect of CO_2 concentration was studied. An increasing trend is noted in adsorption capacity with increasing contact time between the fabric and the gas and a reverse trend was prominent with increasing temperature. Keeping all other parameters constant, at 20ºC the adsorption capacity reached its maximum value of 365 mg/g. Similarly, at the contact time of 20 minutes, adsorption capacity reached 426mg/g. It is also noted that amine treated biochar-based fibers has enhanced adsorption capacity from 426 to 462 mg/g.

A comparative study concluded that a 10x10 ft. biochar-based fiber impregnated panaflex could adsorb 242g CO_2 while comparing for equivalent adsorption time a 40-year-old tree adsorbs only 6g CO_2. This research also has future implications in the field of water treatment, air quality improvement, soil amendment and fire health hazard management.

Acknowledgements

To start with, we are grateful to the Almighty Allah, for had His Supremacy not willed, this project could not have achieved success or recognition.

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Abbreviations

CO_2	Carbon Dioxide
GHG	Green House Gases
PL	Poultry Litter
FT- IR	Fourier-transform infrared spectroscopy
XRD	X-ray powder diffraction
TGA	Thermogravimetric Analysis
SEM	Scanning Electron Microscopy
EDS	Energy Dispersive Spectroscopy
PVA	Poly Vinyl Alcohol

Chapter 1

Introduction

1.1 Background

It is now generally accepted that mitigating climate change is the only way to secure an otherwise bleak future of the earth. The industrial revolution that began a century ago has neither slowed momentum nor paid nearly as much attention to its effects on the environment. With increased amount of Green House Gases (GHG) having anthropogenic origin now prevalent in our atmosphere, the induced anomalies in radiative forcing have become dominant factors in governing climate change. Many climate models and simulations developed over the years, to access the highest positive radiative forcing when compared to the other drivers of climate change. However very few attempts have been made to develop CO2 capture techniques from the atmosphere.

Growing CO_2 levels can evidently be blamed on the severe use of fossil fuels in internal combustion engines, burning down of forests and other human activities. CO_2 emissions having anthropogenic sources may take a century to leave the atmosphere, longer than any other heat-trapping gas. A cut back of as much as 80% in CO_2 emissions has become necessary to avoid a major climatic shift. Proposing a massive switch to non-fossil energy sources may get the job done, but requires time, money, political and social support. Nevertheless, there are other methods that may be employed in order to moderate out CO_2 emissions. One such method that has gained substantial attention in the past years is using adsorption techniques to capture CO_2 and thereby reduce its concentration in the atmosphere.

1.2 Problem Statement

Pakistan makes a tiny share in the total global greenhouse gas (GHG) emissions, but it is the 7th most vulnerable country to climate change. Due to the ongoing global warming, the climate of Pakistan has become increasingly volatile over the past decade experiencing disasters like cyclones, droughts and floods. In comparison to other heat-trapping gases, CO_2 puts us at the greatest risk of irreversible change if it continues to accumulate unabated in the atmosphere. Specifically, in Pakistan the trend of increasing carbon dioxide emissions is quite evident in recent reports. At such a speeding rate, we can only expect that such adversities will come back stronger and deadlier than before.

1.3 Proposed Solution

Various course of actions has been employed to counter the aforementioned problem. An example of such a measure is using adsorbents like silica and porous polymers to reduce CO_2 concentration. Biochar is a carbon (C)-rich byproduct, which has gained attention over the last decade due to its potential adsorption capacity and economical use. Biochar can be derived from sewage sludge, wood shavings, agricultural residues and poultry litter. For our project we are using poultry litter as a source for biochar production.

1.3.1. Poultry litter

Poultry litter is organic waste produced from chickens and turkeys like feathers, poultry excreta, spilled feed and bedding materials. The reason we chose this as a source of biochar synthesis, is because poultry litter has high carbon content, is accessible, cheap and abundant.

Poultry is one of the vibrant segments of livestock sector. It has been providing a significant portion of daily proteins to the Pakistani population ever since. According to 2017-18 statistics, domestic poultry accounts for 87.16 million birds while commercial poultry accounts for 64.6 million birds (Pakistan Economic Survey 2017-18). The quantity of poultry litter produced in a broiler unit depends on litter management, feed intake and its digestibility. For domestic poultry the total litter production is 319,399.2 tons while for commercial poultry it is 225,432 ton. Due to the improper management of poultry litter, it is usually disposed of at curbside or in landfills where it pollutes the surroundings.

1.3.2. Introduction to Nanofibers

The idea that we developed our project on, is to morph the biochar synthesized from poultry litter into nanofibers, that have the ability to adsorb CO_2 from the atmosphere. Before explaining the mechanism by which we will achieve this, here are a few facts about nanofibers in general.

- A human hair has a pore -diameter of around 80 micrometers and is about 200 times bigger than an average nanofiber.

- They possess a high specific surface area; low pore size; high porosity and are highly interconnected.
- Several methods have been established to produce Nano fibers such as template leaching, self-assembly, phase separation, melt blown and electrospinning.
- It is one of the known methods to produce fibers using electrostatic force to draw charged threads of polymers in the range to micrometer to nanometer.
- Also, electrospinning is relatively easy and fast process to produce nanofibers. Its advantage over the other processes is that it has low energy consumption.

1.3.2.1. Application of nanofibers

The unique properties of nanofibers make them applicable for numerous applications:

- In defense and security – nanofibers showed sensitivity towards war agents as they sense interfaces for chemical and biological toxins.
- It has been widely used in human healthcare for tissue/organ repair and regeneration.
- Electro spun fibers exhibited high porosity and a large surface area, due to this they are being chosen for polymer batteries, PV cells, and polymer electrolyte membrane fuel cells.
- High porosity, interconnectivity, electro spun nanofiber meshes are an excellent material for membrane preparation as well as adsorbents due to their large surface to volume ratio. Our project is also based on this application.

1.4. Application on Billboards

By developing Carbon Dioxide adsorbing fibers from biochar, we can effectively address the crux of the issue. The synthesized fibers can be applied to Pena flexes that display advertisements on billboards. Billboards are used all around the city for marketing, they can also be used as breathing trees. Such advertising structures are both an aesthetic and a space consuming issue, and many undermine the toll they take on the environment.

Rounding up our defense on why we chose to target billboards in particular, the reason that stands out the most is how they will be doing the job of several trees, not to mention how important it has become for Pakistan to save up on its water resources – an obvious necessity for growing vegetations. A startling discovery in recent studies indicate that we simply can't grow enough trees to capture the necessary amount of CO_2 simply because there isn't enough space.

Moreover, in our project we utilized equipment that is already present on an industrial level and a source that has little to no cost, lowering the capital necessary to be invested. Lastly, no separate framework needs to be constructed, as they can be easily applied to existing advertising structures.

1.5. Objectives

The objectives of the project were:

- Synthesis of Biochar from poultry litter
- Development of biochar nanofibers
- Adsorption of CO_2 onto the fibers

Chapter 2

Literature Review

2.1. Introduction

The increase in carbon dioxide concentration from the combustion of fossil fuel and many anthropogenic activities has become the most substantial issue. Carbon dioxide is the key culprit, responsible for global warming and worldwide climate change. The World Energy Outlook predicts that by 2030 carbon dioxide emissions from the burning of fossil fuel will be increased to 40.2 giga tons of carbon dioxide (Nguyen et al., 2016). Many studies have been done to reduce carbon dioxide emissions to the atmosphere and for post-combustion carbon dioxide capture technologies. The techniques used are efficient enough to capture carbon dioxide, but many problems are associated (1) Large energy requirement for solvent regeneration, and chemical stripping (2) Sorbents are expensive for large-scale application (3) High regeneration cost (Creamer et al., 2014). Biochar, solid renewable fuel has the potential solution to all these problem (Gąsior et al., 2017).

The biochar has the ability for CO_2 adsorption because it had rich microporous structure. The capacity and uptake rate of CO_2 adsorption increases with increasing adsorption temperature. (Guo et al., 2018).

Agricultural waste, food waste, and forestry are the primary source of feedstock in the biochar production. Other than these, sewage sludge, poultry litter, dairy manure, human and animals waste are considered as the biomass for low-cost adsorbent (Shakya et al.,2017). The Carbonization of biomass produces biochar. Song et al., said that to produce biosolid from poultry litter biochar 300^{o}C should be selected, and for char production 500^{o}C is recommended.

Many studies have been done on surface activation methodologies to enhance the surface affinity of biochar to capture carbon dioxide. Adsorbent modified with the amine is the most promising method to capture carbon dioxide from the flue gases. Nguyen and Lee reported clearly that biochar showed high selectivity of adsorbing carbon dioxide over nitrogen in the CO_2/N_2 mixture.

2.2. Case Studies

Following table 2.1, shows the literature review on different studies done on adsorption, nanofibers and adsorbent material.

Table 2. 1 – Literature Review

Research	Name	Year	Findings
Characteristics of CO_2 adsorption on biochar derived from biomass pyrolysis in molten salt	Guo et al.,	**2018**	• The biochar has a rich microporous structure and can exhibit a good performance of CO_2 adsorption. • There is inverse relation between the CO_2 adsorption and the adsorption temperature.
A novel removal of CO_2 using nitrogen doped biochar beads as a green adsorbent	Nguyen and Lee	**2016**	• The biochar beads have high selectivity of adsorbing CO_2 over N_2 in a CO_2/N_2 mixture.

Research	Name	Year	Findings
Development of adsorptive membranes by confinement of activated biochar into Electrospun nanofibers	Mehrdad et al.,	**2016**	• The average diameter of fibers increases as the concentration of particles increases. This is due to the increased viscosity of the solution.
Carbon Dioxide Adsorption on Sawdust Biochar	Hazimah et al.,	**2016**	• Treatment with amine increases the nitrogen contents of the biochar sample and hence further improve the CO_2 adsorption.
Quality variations of poultry litter biochar generated at different pyrolysis temperatures	Song et al.,	**2011**	• To produce biosolid from poultry litter biochar 300ºC should be selected, and for char production 500ºC is recommended.

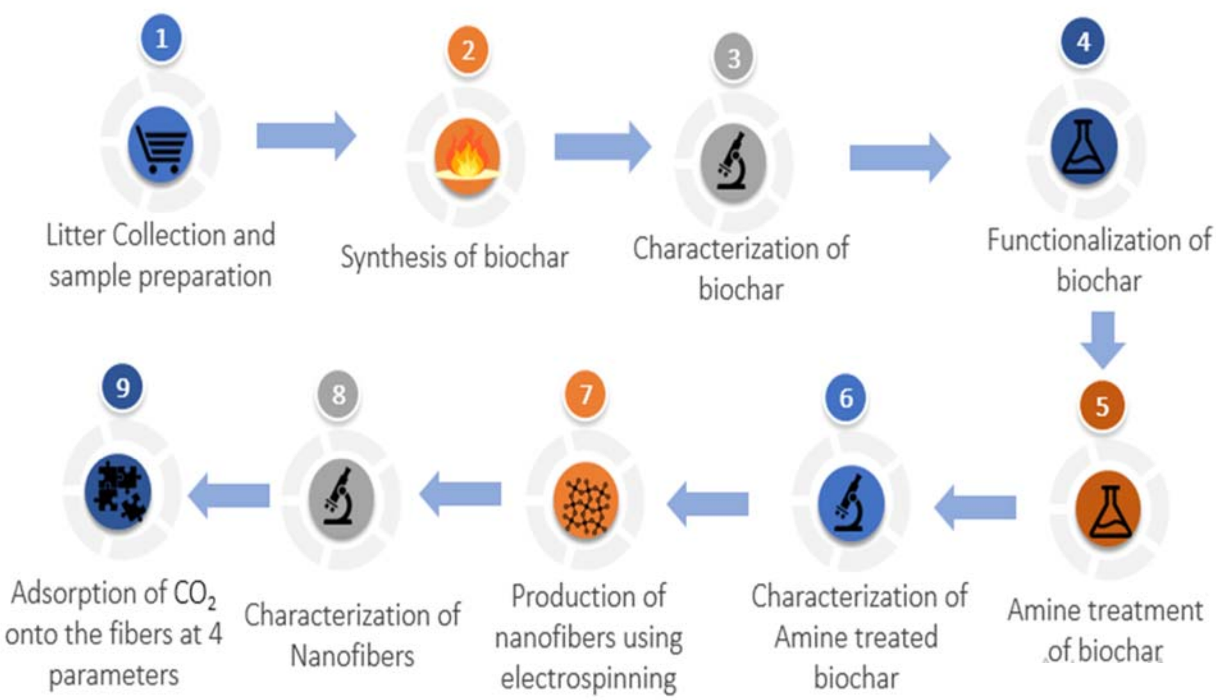
Chapter 3

Methodology

3.1. Material

- Poultry litter
- Nitric acid (HNO_3)
- Di Ethanol Amine (DEA)
- Poly vinyl alcohol (PVA)
- Distilled water
- CO_2 cylinder

3.2. Process steps



3.2.1. Sample Collection and Preparation

Poultry litter was collected from poultry farms located in I- 10 Islamabad. The litter was than cleaned to remove any unnecessary material that may interfere with the purity of the desired product. The sample was then taken in a china dish and weighed. It was placed in an oven at 105^{o}C for 18 to 24 hours to remove moisture. The dried sample was then taken out and grinded. It was weighed again. The moisture content of the sample was calculated. Sample was then ready to be converted into biochar.

3.2.1.1. Characterization of Poultry litter

Elemental composition of PL was determined using Energy dispersive Spectroscopy (EDS).

3.2.2. Synthesis of Biochar

A known amount of ground litter was placed in muffle furnace to be converted into biochar. It was placed in furnace at three different temperatures 400, 500- and 600-degrees C for 1 hour. The prepared biochar was than cooled down to room temperature for some time, it was weighed and stored in desiccator to prevent any contamination.

3.2.3. Characterization of Biochar

Biochar characterization was done using SEM-EDS, FT-IR AND XRD. SEM was used to observe the porous structure of biochar and to identify the pore diameter. Biochar prepared at three temperatures 400, 500- and 600^{O}C was subjected to SEM to see which temperature produced the best porous structure.

The biochar yield was also calculated at these temperatures using the formula

$$\textbf{Biochar Yield (\%)} = \frac{mass\ of\ biochar\ produced}{dry\ mass\ of\ raw\ material}\ X\ 100$$

Energy Dispersive Spectroscopy (EDS) of biochar was also done for the sake of elemental analysis. FT-IR was done to identify functional groups and X-ray powder diffraction was performed for phase identification of the crystalline material and cell dimensions.

3.2.4. Functionalization of biochar

Functionalization of biochar is necessary to create active sites on the surface of biochar particles so that the amine groups may attach on these sites.

The functionalization of biochar was achieved by applying the reflux method using nitric acid.

3.2.4.1. Reflux

It is a technique in which the vapors are condensed and returned to the system from which they originated. It is used in industrial and laboratory distillations shown in figure 3.1.

The major steps followed were;

1.A solution of 100ml of 65% nitric acid (HNO_3) was prepared by adding 40ml of nitric acid into 60 ml of distilled water and 4g of biochar was mixed with it in a round bottom flask.

2.Magnetic stirring of dispersion was done for 4-hour period under nitric acid reflux and the temperature was maintained to be 110^{o}C. The solution was then cooled down to room temperature.

3.The solution was then filtered out using a vacuum filtration assembly to separate the functionalized biochar from the solution. Distilled water was used to neutralize the particles and the washing process continued until pH of filtrate became neutral. The residue was then dried for further analysis.

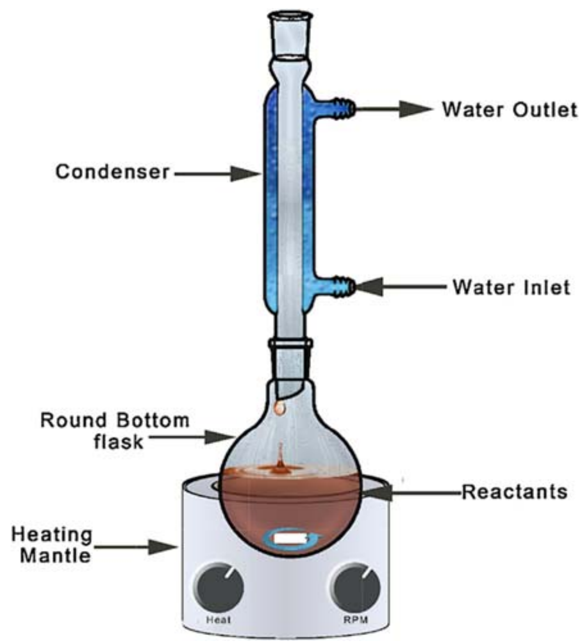


Figure 3.1 - Reflux setup

3.2.5. Amine treatment

Amine treatment of biochar was done using grafting method. Grafting is a process in which the amine group is attached on the surface of biochar particles. DEA was used for this purpose. Diethanolamine is polyfunctional, being a secondary amine and a diol with the formula $HN(CH_2CH_2OH)_2$. 10 ml of DEA was taken in a flask and 2g of biochar was dipped in it. The prepared solution was than heated at 50^{0}C for 1 hour along with continuous stirring with a magnetic bar. The prepared solution was then placed in oven at 100^{O}C for 24 hours to evaporate the solvent. After evaporation amine treated biochar was obtained. The biochar was then placed in desiccator.

3.2.6. Characterization of amine treated biochar

The amine treated biochar was analyzed under Fourier Transform Infrared Spectroscopy. Fourier-transform infrared spectroscopy (FT-IR) is a technique used to obtain an infrared spectrum of absorption or emission of a solid, liquid or gas. An FTIR spectrometer simultaneously collects high-spectral-resolution data over a wide spectral range. The presence of Functional groups was identified using this test.

3.2.7. Biochar nanofibers production using Electrospinning

The biochar was converted into nanofibers using electrospinning. The smaller the diameter of the fibers the larger is the surface area for adsorption so to produce nanofibers electrospinning was done.

3.2.7.1. Electrospinning

It is one of the known methods to produce fibers using electrostatic force to draw charged threads of polymers in the range to micrometer to nanometer.

3.2.7.2. Process

A sufficiently high voltage is applied to a liquid droplet. The body of the droplet is charged, and the electrostatic repulsion counteracts the surface tension causing the stretching of droplet and at a specific time the stream of fluid erupts from the surface. A well-known Taylor cone is formed. Due to high viscosity of the liquid, the stream does not breakup leading to the formation of a charged jet.

After the formation of Tylor cone, the charged jet moves toward the collector. There are various types of collectors like stationary flat plates, rotating drums, mandrels, and disks. In our case we used the rotating drum. Solid fibers will be formed as the solvent evaporates during its motion towards the collector. This results in a nanofiber that are being deposited on the collector.

In figure 3.2, experimental setup of electrospinning is as shown.

3.2.7.3. Setup for Electrospinning

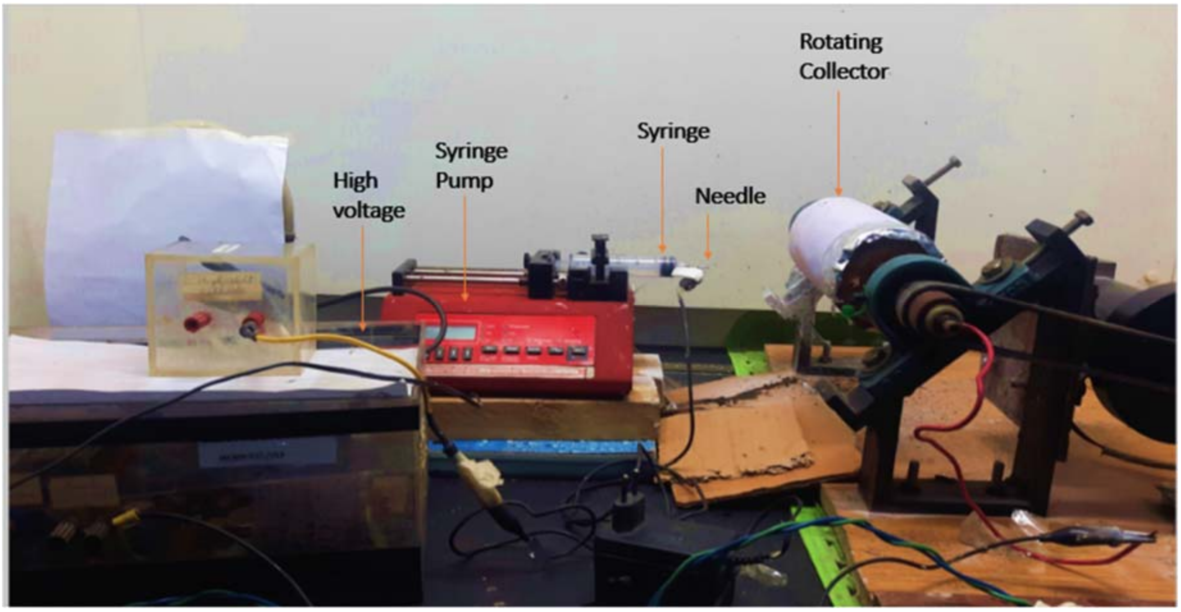


Figure 3.2 - Experimental Setup of Electrospinning

3.2.7.4. Sample preparation for electrospinning

- **Without amine treated biochar:** In the initial phase sample was prepared. 10% weight by volume of PVA was dissolved in distilled water and stirred at room temperature for 12hours. Then 2% weight by volume of biochar was dissolved in the prepared solution and stirred with a magnetic bar. The prepared solution was then inserted in the syringe pump to initiate electrospinning.

- **With amine treated biochar:** 10% weight by volume of PVA was dissolved in distilled water and stirred at room temperature for 12hours. Then 2% weight by volume of amine treated biochar was dissolved in the prepared solution and stirred with a magnetic bar. The prepared solution was then inserted in the syringe pump to initiate electrospinning.

3.2.7.5. Operational Parameters for electrospinning

In table 3.1., the operational parameter are mentioned which was adjusted after many trials.

Table 3.1 - Operational parameters of electrospinning

Factors	Value
Flow rate	0.25ml/hr
Voltage	16kV
Distance b/w needle and collector	12cm
Collector diameter	5cm
Collector length	12cm

3.2.8. Characterization of Nanofibers

The nanofibers were subjected to SEM analysis to check the biochar particles embedded in the fibers and TGA was also done to determine the mass loss and the structural strength of the nanofibers. The mass loss was determined using temperature changes.

3.2.9. Laboratory setup

Figure 3.3 shows the experimental setup used in laboratory for the adsorption of carbon dioxide.

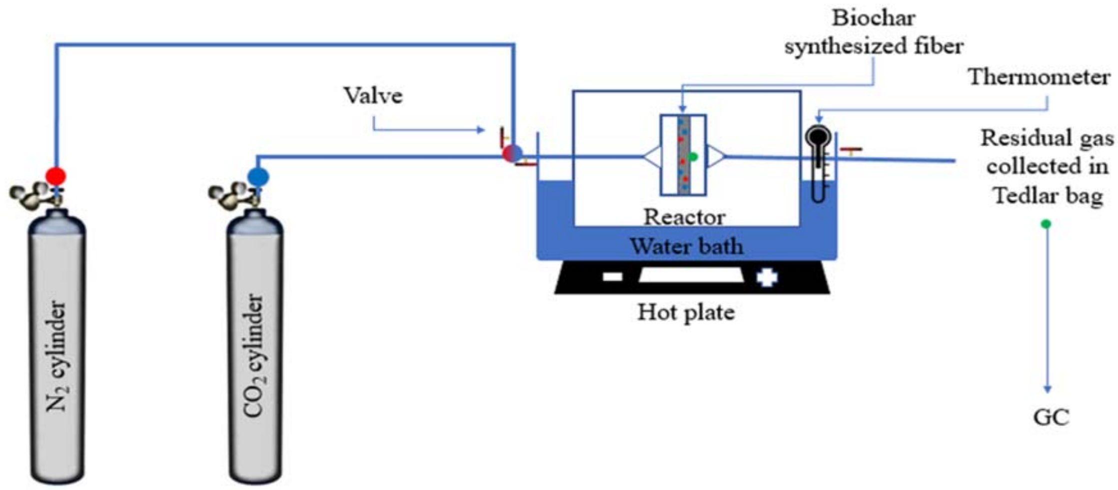


Figure 3.3 - Experimental Setup

One 10by10 inch and other 5by5 inch acrylic rectangular containers were designed. Water was filled in the outer container and heated with a heating rod. A thermocouple was used to observe the maintained temperature. Fabric cloth adsorbent was placed in the inner container connected with pipes attached to the cylinders containing CO_2 and N_2. The cylinders were attached with gauges to maintain the flow of gases. The flow rate was maintained to be 0.4 liters/min. The gas was allowed to pass through the chamber containing the fabric cloth adsorbent. Tedlar bag was connected to the end of pipe for the collection of residual gas.

3.3. Adsorption parameters

Adsorption of carbon dioxide is dependent on many factors. After consulting many literatures, we check adsorption on four different parameters.

- Temperature
- Contact Time
- Concentration of CO_2
- With and without Amine treatment

3.3.1. Temperature

Temperature is an important parameter while studying the adsorption of carbon dioxide. Adsorption was checked on four different temperatures i.e., 20^{O}C, 30^{O}C, 40^{O}C and 50^{O}C. These temperatures were chosen keeping in view the temperature trend of Pakistan. The gas was allowed to pass when these temperatures were maintained inside the reactor for same time. Once the gas was adsorbed, the residue gas was collected in the tedlar bag and the amount of carbon dioxide adsorbed was calculated using volumetric weight method.

3.3.2. Contact Time

Contact time is also an important parameter which tell us about the maximum capacity of fabric and estimates time of regeneration. Four different times (5,10,15,20 min) were selected to observe the effect of adsorption with time. Gas was passed through the adsorbent at selected temperature and the contact time was maintained with the help of valves.

3.3.3. Concentration of CO_2

Adsorption was observed for two different concentrations of gas(CO_2) 50% and 100% . At 100 % concentration pure CO_2 was passed through the adsorbent at selected time and temperature. For 50% concentration equal amounts of CO_2 and N_2 were passed through the reactor. The residue gas was collected in tedlar bag was then subjected to GC analysis to find the concentration of CO_2 in the residue gas.

3.3.4. Amine treatment

To observe the effect of amine treatment on adsorption, the fabric cloth adsorbent was replaced with the adsorbent prepared from amine treated biochar. The effect of amine treatment on biochar for adsorption of CO_2 was observed. The setup was run for selected temperatures and times and adsorption capacity was determined.

Chapter 4

Results and Discussion

In this chapter we will be discussing the elemental composition of poultry litter and biochar made from PL. Other than that, morphology of synthesized biochar and nanofibers would also be discussed. A comparison of the amine treated and without treated adsorbent is also performed. In the end we have the results of carbon dioxide adsorption on different parameters as discussed above in methodology section.

4.1. Biomass (Poultry Litter)

4.1.1. Moisture content

The table 4.1 shows the result of moisture content which was calculated using below mentioned formula:

$$MC(\%) = \frac{Weight\ of\ poultry\ litter\ before\ drying\ (w1) - Weight\ of\ poultry\ litter\ after\ drying (W2)}{\text{Weight of poultry litter before drying (W1)}} \times 100$$

Three different samples of poultry litter were collected and moisture content of all three samples are not showing noticeable variation; samples are representative. Samples were dried so that moisture content may not interfere with the time taken by muffle furnace to synthesize biochar at different temperatures.

Table 4.1 - Moisture Content of PL

Sr No.	W1 (g)	W2 (g)	Moisture Content (%)
1	200	94	53
2	200	92	54
3	200	98	51

4.1.2. Elemental composition

Table 4.2 and Figure 4.1 shows the elemental composition of poultry litter. It is clearly seen that carbon has the highest weight % than any other elements present in poultry litter. More the carbon content, more the carbon material made from biomass.

Table 4.2 - EDS of PL

Element	Weight %
C	**54.30**
N	7.52
O	30.12
Mg	0.48
Al	0.94
Si	2.82
S	0.67
Ch	0.32
K	1.62
Ca	1.20
Total	100

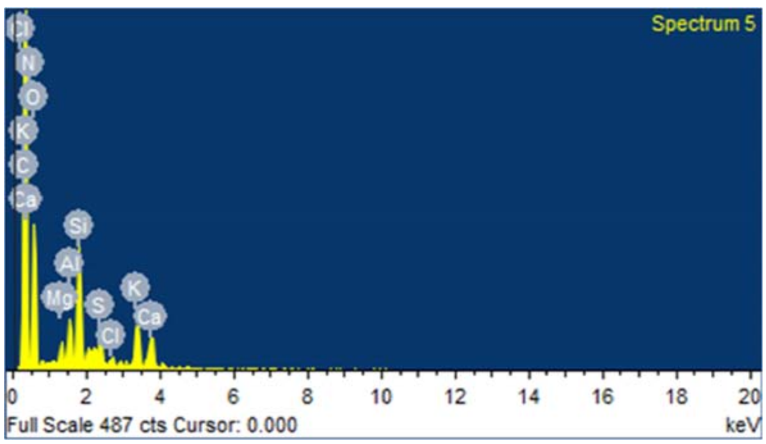


Figure 4.1 - EDS of PL

4.2. Adsorbent (Biochar)

4.2.1. Biochar yield

In figure 4.2, the common trend shows that with increasing temperature biochar yield decreases as carbon tends to stabilize at higher temperature. Biochar was prepared at three different temperatures; 400,500 and 600ºC to optimize temperature where maximum yield and structure was developed.

Biochar yield was calculated by formula:

$$\textbf{Biochar Yield (\%)} = \frac{mass\ of\ biochar\ produced}{dry\ mass\ of\ raw\ material}\ X\ 100$$

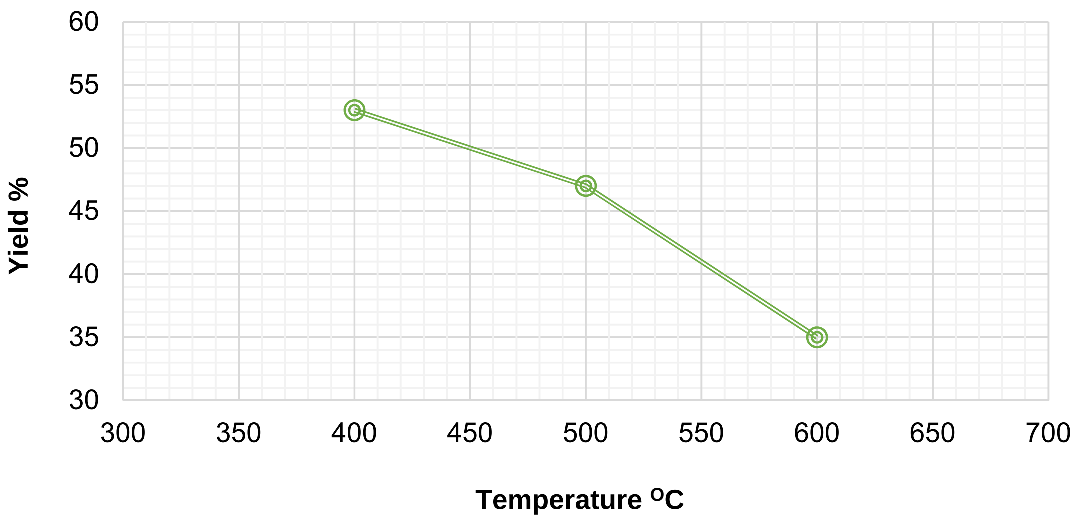


Figure 4.2 - Biochar yield at different temperatures

4.2.2. Morphology of biochar

The Figure 4.3 represents the morphology of biochar prepared at 500ºC. Biochar was analyzed using Scanning Electron Microscopy (SEM) having magnification of 500X and 2kX. Biochar prepared at 500ºC has well developed structure and definite pores while biochar synthesized at 400ºC does not have definite pores and well-defined structure. *Song et al., (2011)* also reported that for environmental application i.e. carbon dioxide sequestration, 500oC is recommended temperature for char production.

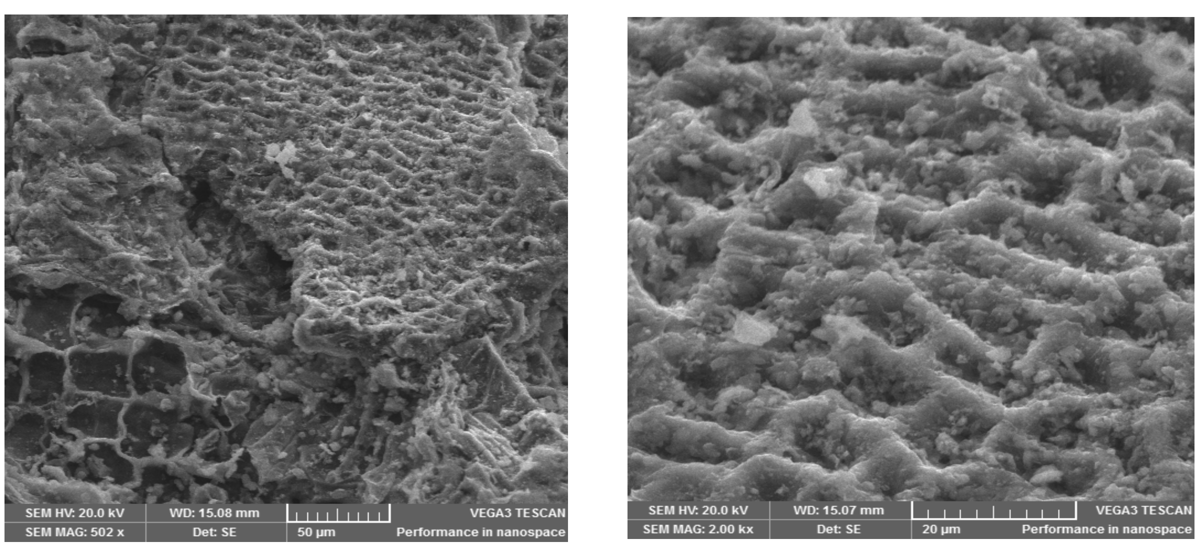


Figure 4.3 - SEM micrographs of biochar (500ºC)

4.2.3. Elemental Composition of biochar

The table 4.3 shows the elemental composition of biochar which shows that biochar prepared at 500°C has 72.64 wt % carbon which is highest among other elements present in it. Poultry litter was thermally treated, volatiles and other elements are not stable at higher temperature while carbon starts to stabilize at higher temperatures.

Table 4.3 - Elemental composition of Biochar

Element	Weight %
Carbon	72.64
Oxygen	17.66
Sodium	1.02
Magnesium	0.79
Phosphorus	2.40

4.3. Functionalization of Biochar

4.3.1. SEM analysis of functionalized biochar

Figure 4.4 shows the morphology of functionalized biochar. This was analyzed using SEM having magnification of 2kX. Biochar has been modified with nitric acid chemically. Functionalization process creates defects on the opening of ends and side walls of biochar which allow functional group to get attached with it. The SEM analysis shows that it has more clear pores and less amorphous carbon than biochar without chemical treatment. *Nguyen and Lee* reported that functionalization of biochar would increase the chances of functional groups attached on its surface and thus enhance its adsorption capacity.

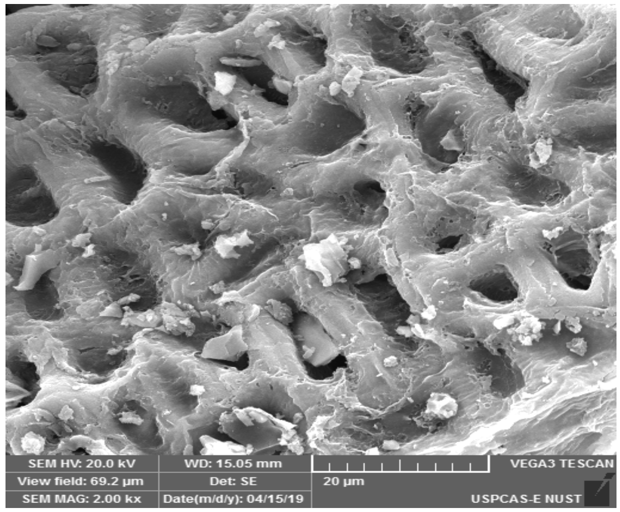


Figure 4. 4 - SEM of Functionalized Biochar

4.3.2. X-ray powder diffraction (XRD)

Figure 4.5 shows the XRD result of biochar and functionalized biochar. They have crystalline structure which can be clearly seen by narrowness of the peak.

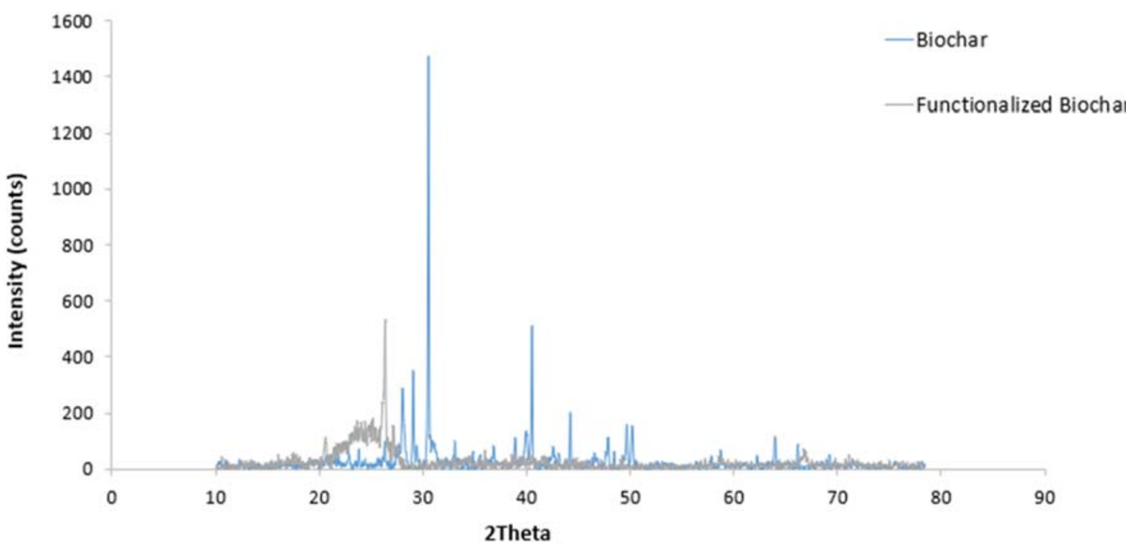


Figure 4. 5 - XRD of biochar and functionalized biochar

4.4. Amine Treatment of Biochar

4.4.1. Fourier-transform infrared spectroscopy (FTIR)

Figure 4.6 shows the result of FT-IR analysis. In the region of 4000-500 cm^{-1}, different peaks were observed to identify the amine functional group onto the surface of adsorbent (biochar).

In comparison with non-treated biochar, several new bands appeared on the Amine treated biochar. N-H bending showed peaks at 1650cm^{-1}, which shows the presence of amine group. The peak having wave number of 1073 cm^{-1}corresponds to vibration of C-N (stretching) of the amine treated biochar. Another band appeared at 2927 cm^{-1}, which was attributed to C-H stretching. It is clearly seen that the amine groups had been generated onto the surface of biochar, which would create more active sites for the CO_2 adsorption.

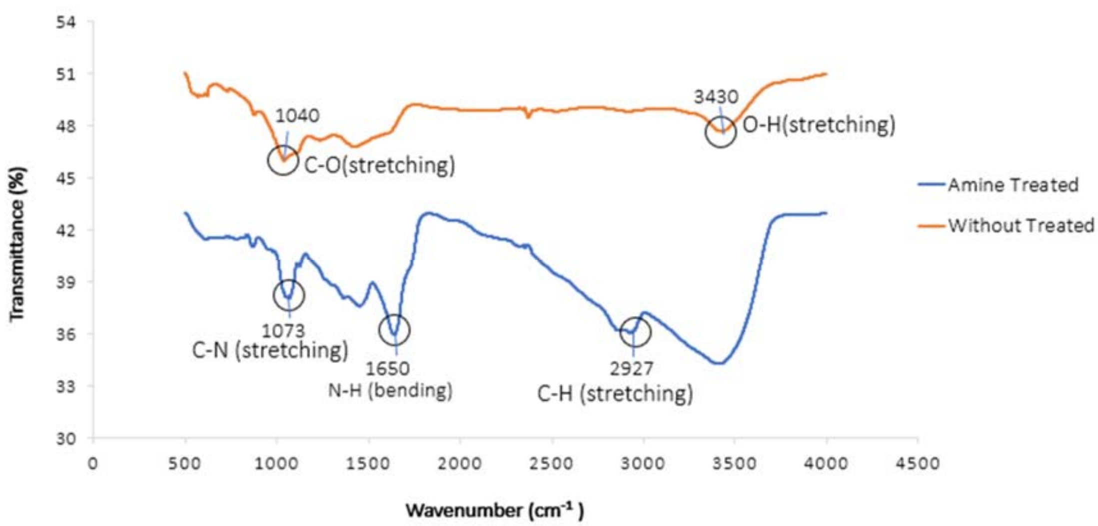


Figure 4.6 - FT-IR of Amine treated, and w/o treated Biochar

4.5. Biochar Nanofibers

4.5.1. Morphology of Nanofibers

Figure 4.7 represent the SEM micrograph of PVA based biochar nanofibers. Nanofibers were analyzed on the magnification of 5kX and 25kX. PVA based biochar fibers are uniform in shape and are almost in same size. The moderate speed of the rotational drum controlled the formation of randomly oriented fibers. The biochar particles are entrapped among fibers and are clearly seen from the figure 4.8.

The average diameter of PVA fibers was 231.5 ± 80 nm *(Mehrdad Taheran, 2016).* Image-J software was used to analyze fibers diameter and was found to be 579nm. The fiber diameter increased due to the addition of biochar which increased viscosity of the solution. When the viscosity of solution increases, resistance against being stretched also increases resulting the increase of fiber diameter.

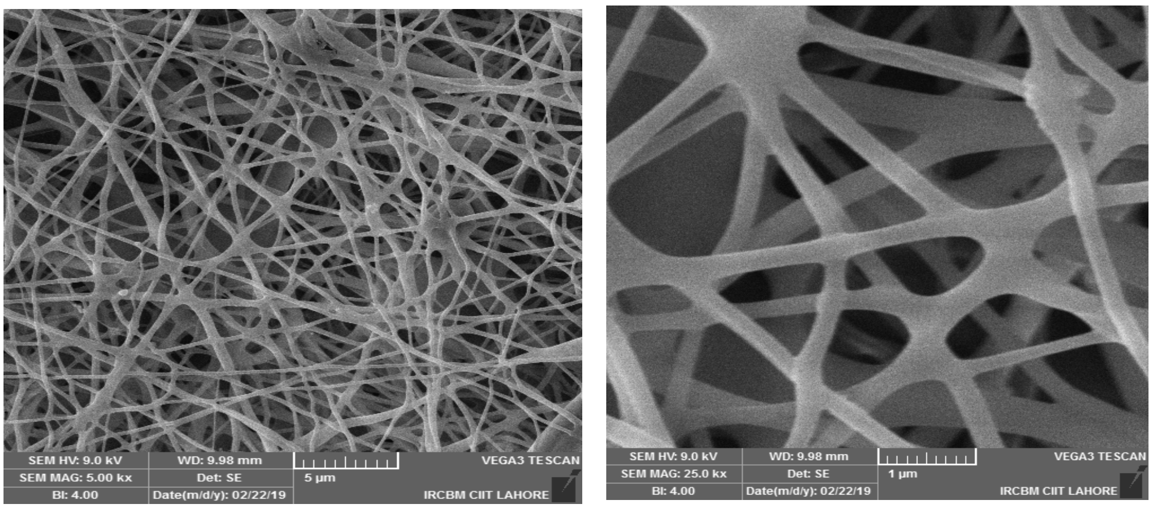


Figure 4.7 - SEM micrographs of nanofibers

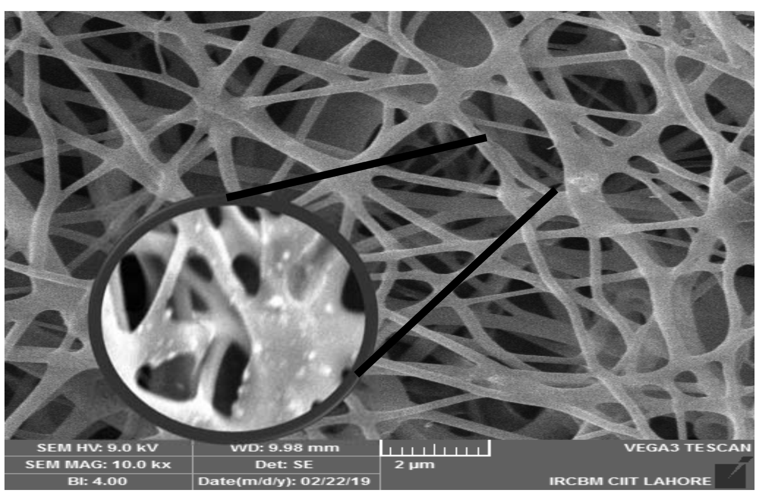


Figure 4.8 - Biochar particles entrapment

4.5.2. Thermogravimetric Analysis (TGA)

Figure 4.9 gives data on the thermal stability of the PVA based biochar fibers. Two plots are shown against temperature. Mass loss curve is represented in black which tells us about mass loss at different temperatures. Other curve tells us about the structure breakage.

Weight loss was observed for PVA based biochar fibers below 100°C. At this temperature, water and other small molecules are removed. The biochar fibers showed higher thermal stability in this temperature range, since the hydrophilic groups (OH) were reduced and resulting in less adsorbed water. At 220°C mass loss curve start decreasing, which showed the start of the decomposition and were thermally unstable over 300°C. In the temperature range of 500 to 1000°C, it is converted into ash.

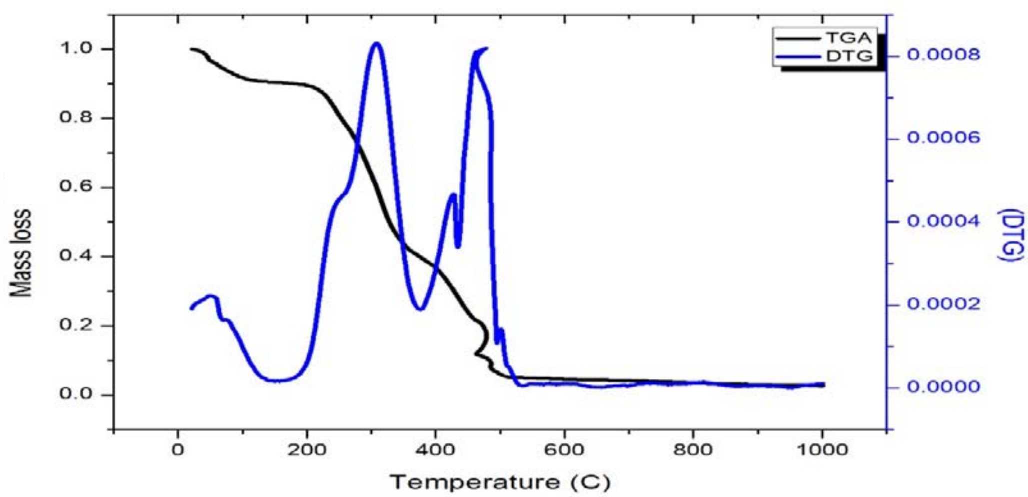


Figure 4.9 - TGA of nanofibers

4.6. Adsorption of CO_2

4.6.1. Effect of Temperature

The figure 4.10 indicated the effect of temperature on the adsorption of carbon dioxide. Temperature is an important parameter while studying the CO_2 adsorption as it is temperature dependent because of its exothermic nature. It is shown from the graph that at 20°C PVA based biochar fibers have maximum adsorption capacity which was 365mg/g. There is inverse relation between the adsorption temperature and adsorption capacity. Increasing temperature, decreasing adsorption capacity of CO_2.

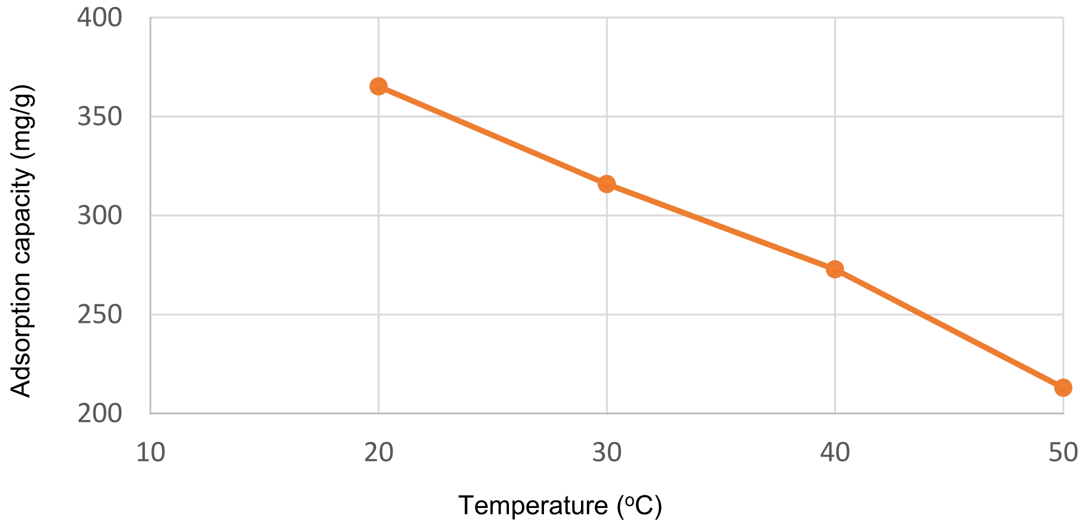


Figure 4.10 - Effect of temperature on CO_2 adsorption

4.6.2. Effect of Contact time

In figure 4.11, effect of contact time on adsorption capacity is shown. This trend shows that adsorption capacity has a direct relation with contact time. This is due to the fact the more the contact between gas and the adsorbent, higher the affinity of gas towards adsorbent.

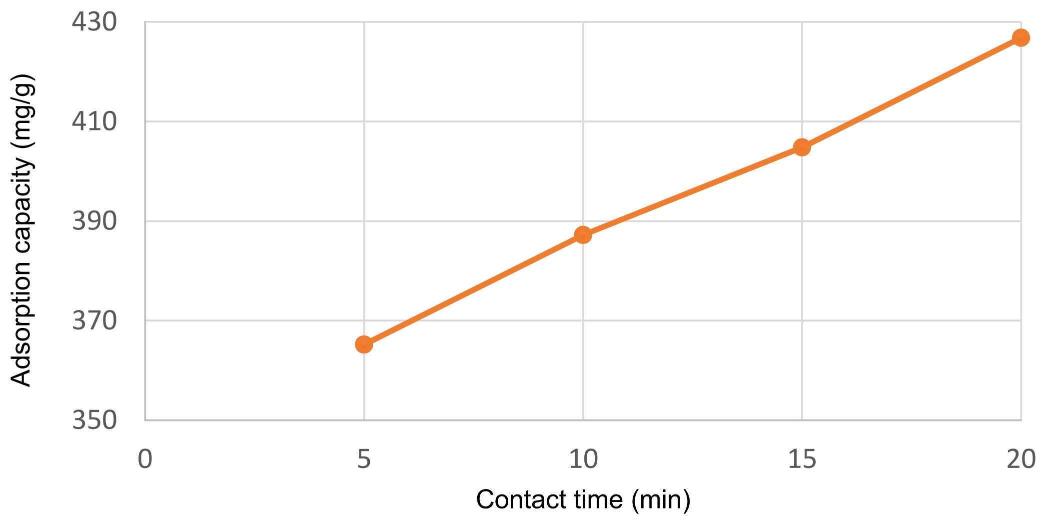


Figure 4.11- Effect of contact time on CO_2 adsorption

4.6.3. Effect of Amine treatment

Effect of amine treatment on adsorption capacity is shown in figure 4.12. It is clearly seen from the bar graph that amine treatment increases adsorption capacity. The maximum adsorption capacity at 20ºC and 20 min was 462mg/g. This is due to the increasing activation sites for adsorption. Primary reason behind this is that carbon dioxide is acidic gas and amine used is basic in nature, which increases affinity of carbon dioxide towards amine.

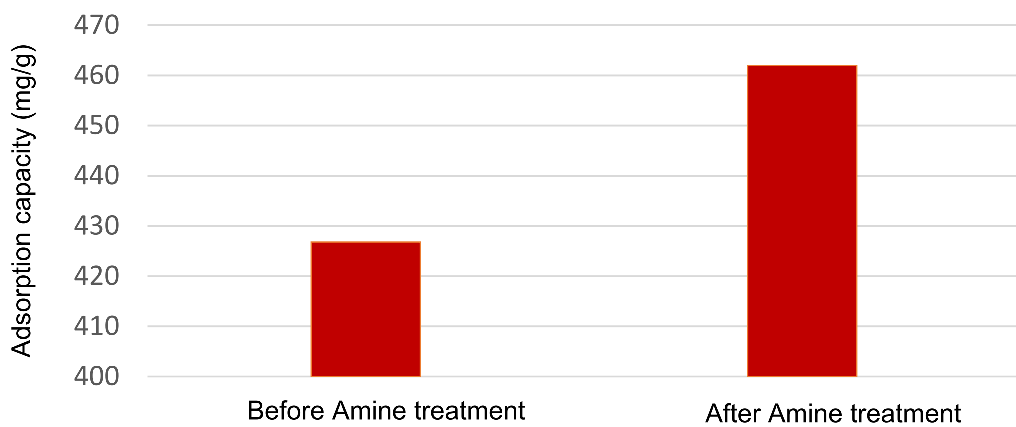


Figure 4.12 - Effect of Amine treatment on CO_2 adsorption

4.6.4. Effect of CO_2 concentration

Figure 4.13 shows the effect of CO_2 concentration on the adsorption capacity of biochar nanofibers. In this case mixture of CO_2/nitrogen is used. Concentration of carbon dioxide was set 50% and the remaining gas was nitrogen. After the contact between two gas mixtures and the adsorbent, the remaining gas that was not adsorbent was analyzed using GC to find out the concentration of carbon dioxide.

The graph bar shows that by decreasing carbon dioxide concentration, adsorption capacity decreases. The trend shows that adsorption capacity decreases upto 25%.

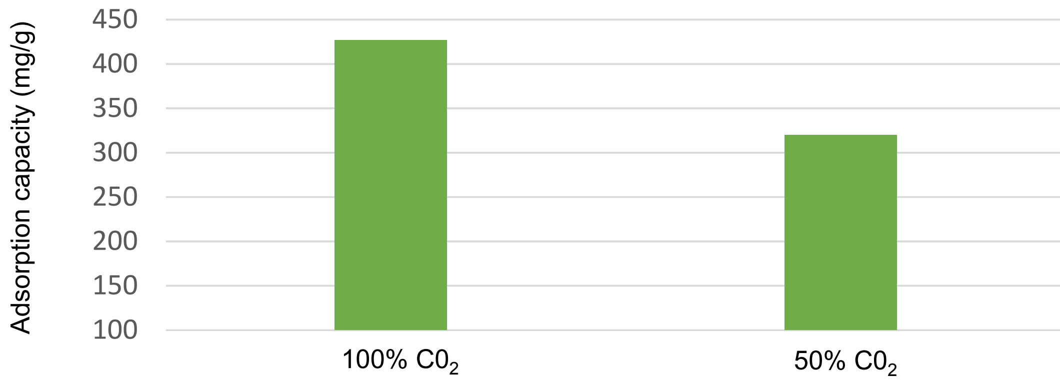


Figure 4.13 - Effect of CO_2 concentration on CO_2 adsorption

Chapter 5

Cost Estimation

5.1. Cost for 10*10 feet flex

In our project we utilized equipment that is already present on an industrial level (Electrospinning equipment) and a source (Poultry litter) that has no cost, lowering the amount necessary to be invested.

In table 5.1, cost was estimated for a **10*10 feet** flex with nano fibers. Binder used contributes the maximum amount to the total cost (58.9%) whereas electrospinning constitutes 29.4%. The total cost comes out to be 680/-Rs.

Table 5.1 - Estimated cost of all items

Item	Cost
Poultry waste	0%
Collection Cost	7.3 %
Thermal Treatment	4.4 %
Binder	58.9 %
Electro-spinning	29.4 %
Total	**Rs. 680/-**

Chapter 6

CO_2 Sequestration of Billboards vs Trees

6.1. Carbon dioxide Sequestration

In the U.S Department of Energy Report titled Methods for Calculating Carbon Sequestration by Trees in Urban and Suburban Settings, tree species were categorized into two types; hardwood and conifer. Further 3 divisions made on the basis of growth rate are slow, moderate and fast. The average age of a tree is reported to be 60 years and the sequestration rate varies with age.

In table 6.1, CO_2 sequestration rate for conifers and hardwood at 6 months and 40 years were used and this time was equalized to our adsorption time. The amount of CO_2 adsorbed on our proposed biochar-based fiber impregnated, 10 by 10ft panaflex is found to be much greater than the average CO_2 sequestrated by the trees.

Table 6.1 - Sequestration rate for conifer and hardwood

Factors	**Conifer***		**Hardwood***	
	6 months	**40 years**	**6 months**	**40 years**
Sequestration rate (g CO_2)	5.1	286.3	9.9	342.1
Equal time operations (g CO_2)	0.09	4.9	0.17	5.9

Amount of CO_2 adsorbed on billboard (10ft x 10ft) = **242 g** CO_2

Chapter 7

Applications

Apart from billboards, our project has the potential to be used in a number of other applications as well:

7.1. Water Treatment

Bio-Char is an efficient, environment friendly and low-cost adsorbent which can be used in water treatment because of its ability to adsorb organic pollutants and heavy metals. It is low cost adsorbent having potential of treating water.

7.2. Air Quality improvement

Biochar also has the tendency of improving air quality. It has the potential to adsorb NO_X and SO_X gases.

7.3. Safety Mask

Biochar has large surface area and high porosity because of these characteristics it shows high tendency to adsorb gases in case of fire. Safety mask can be modified using above mentioned adsorbent.

Chapter 8

Conclusion & Recommendations

8.1. Conclusion

Based on our research work, it is concluded that:

- Biochar prepared at **500ºC** showed better structure for CO_2 adsorption.
- Amine treatment increases the adsorption capacity from **426** to **462 mg/g**.
- Temperature and adsorption capacity have an inverse relation while there is a direct relation present between contact time and adsorption capacity.
- Produced fibers have shown structural strength up to **300ºC**.

8.2. Recommendations

In the future, further research can be conducted. Some of the recommendations are:

- Alternate technologies for fiber production should also be looked into like melt-spinning and solid filaments by cooling.
- Organic waste management for biochar production needs much more attention for potential CO_2 adsorption benefits.
- Surface regeneration of biochar should be explored.
- Adsorption should be done for longer time periods to determine the time in which it reaches its maximum adsorption capacity.

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