

Biochar for Carbon Dioxide (CO₂) Capture & Sequestration

A

Seminar Report

Submitted in partial fulfillment of the requirements for the award of the degree

of

MASTER OF SCIENCE

in

Department of Biotechnology and Bio Informatics

With specialization in

BIOTECHNOLOGY

Under the supervision

Of

Dr. ASHOK NADDA

(Assistant Professor)

By

RUPALI BHARDWAJ (197807)

To



JAYPEE UNIVERSITY OF INFORMATION TECHNOLOGY

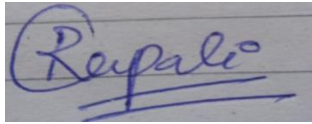
WAKNAGHAT, SOLAN – 173234

HIMACHAL PRADESH, INDIA

May-2021

STUDENT'S DECLARATION

I hereby declare that the work presented in the Seminar report entitled “**Biochar for Carbon Dioxide Capture & Sequestration**” submitted for partial fulfillment of the requirements for the degree of Master of Science in Biotechnology and Bio Informatics at **Jaypee University of Information Technology, Wakhnaghat** is an authentic record of my work carried out under the supervision of **Dr. ASHOK NADDA, Assistant Professor**. This work has not been submitted elsewhere for the reward of any other degree/diploma. I am fully responsible for the contents of my seminar report.



Signature of Student

Rupali Bhardwaj

197807

Department of Biotechnology and Bio Informatics

Jaypee University of Information Technology, Wakhnaghat, India

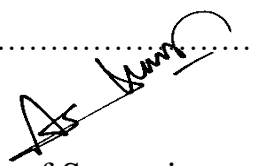
May-2021

CERTIFICATE

This is to certify that the work which is being presented in the project report titled “**Biochar for Carbon Dioxide Capture & Sequestration**” in partial fulfillment of the requirements for the award of the degree of Master of Science in Biotechnology and submitted to the Department of Biotechnology and Bio Informatics, **Jaypee University of Information Technology, Wakhnaghat** is an authentic record of work carried out by **RUPALI BHARDWAJ (197807)** during a period from January, 2021 to May, 2021 under the supervision of **Dr. ASHOK NADDA**, Department of Biotechnology and Bioinformatics, Jaypee University of Information Technology, Wakhnaghat.

The above statement made is correct to the best of my knowledge.

Date: -



Signature of Supervisor

Dr. ASHOK NADDA
Kumar

Assistant Professor
Department of BT& BI

JUIT Wakhnaghat



Signature of HOD

Prof. Dr. Sudhir

Professor & Head
Department of BT& BI

JUIT Wakhnaghat

ACKNOWLEDGEMENT

The completion of any project depends upon cooperation, coordination, and combined efforts of several sources of knowledge. I am grateful to my project guide **Dr. ASHOK NADDA, Assistant Professor**, for his even willing to give me valuable advice and direction whenever I approached him with any problem. I am thankful to him for providing immense guidance for this project.

I am also thankful to **Prof. Dr. Sudhir Kumar, Professor & Head** Department of Biotechnology and Bio Informatics, and all the faculty members for their immense cooperation and motivation for the research of my project.

RUPALI BHARDWAJ
(197807)

TABLE OF CONTENT

| Captions | Page No. |
|---|-----------------|
| STUDENT'S DECLARATION | 2 |
| CERTIFICATE | 3 |
| ACKNOWLEDGEMENT | 4 |
| LIST OF TABLES | 6 |
| LIST OF FIGURES | 7 |
| Abstract | 8 |
| Introduction | 9 |
| Use of biochar for biochar carbon dioxide sequestration | 12 |
| Use of potassium for increasing biochar carbon sequestration | 12 |
| Role of phosphoric acid | 14 |
| Adsorbents for CO ₂ capture on biochar | 16 |
| Use of metals for biochar modification | 19 |
| Chemical methods used to increase CO ₂ adsorption | 20 |
| Role of biochar enriched with nutrients for increasing soil fertility | 22 |
| Effect of biochar on sustainable agriculture | 24 |
| Solvents for CO ₂ capture | 28 |
| Diverse micro organism capable of utilizing CO ₂ | 32 |
| Conclusion | 35 |
| References | 36 |

LIST OF TABLES

| Table no. | Caption | Page no. |
|------------------|---|-----------------|
| 1. | Classification of membrane based on pore size | 20 |
| 2. | CO ₂ selectivity of different membranes at different temperature | 21 |
| 3. | CO ₂ adsorption capacity of modified biochar | 21 |
| 4. | Recovery of nutrients for experiment | 24 |
| 5. | Results observed after addition of biochar in field of Different crops | 25 |
| 6. | Different solvents used for carbon capture with its advantages And disadvantages | 30 |

LIST OF FIGURES

| Fig No. | Title | Page No |
|----------------|---|----------------|
| 1. | CO ₂ present in environment used to convert into Bioenergy using biochar | 11 |
| 2. | Comparison between untreated and potassium treated biochar | 14 |
| 3. | Carbon remaining in biochar after pyrolysis under different Production temperature and impregnation ratio | 16 |

Abstract

As we all know that global warming is increasing at an alarming rate and the contribution of Carbon dioxide (CO₂) is involved at large scale. Thus many scientists are working on how we can reduce CO₂ release that is effecting our environment as well as health of a mankind. We already know that the plants are capable of absorbing CO₂ but looking in the current scenario CO₂ released in environment is much higher than CO₂ absorbed by the plants. Thus one of the way on which scientists are paying attention is Biochar. Biochar is obtained from the waste materials that include plant wastes and other degradable waste. Pyrolysis is a process through which biochar can be obtained and it has various positive effects. Use of biochar is one of the effective ways that can entrap CO₂ and convert it into value added products. Therefore certain modification can be done in a biochar that would ultimately increase the CO₂ absorption and ultimately reduces global warming. Pretreatment of biochar with phosphoric acid has improved carbon retention and sorption ability of biochar. The results by adding phosphoric acid even shows that specific surface area of treated biochar was also increased that would ultimately increase the carbon absorption. Furthermore incorporation of metals such as magnesium chloride, magnesium acetate, and magnesium nitrate and magnesium sulphate in the biochar has lead to enhancement of CO₂ adsorption capacity. Different studies have found that biochar is an effective and eco friendly way to reduce global warming. Various modifications in biochar by adding different chemicals and metals into it has proven to be more effective by increasing CO₂ adsorption to the greater extent. Thus here we will see how effective biochar has proven to be beneficial for our environment and what certain medication can be performed on biochar by adding enzymes or chemicals that would ultimately increase CO₂ adsorption and we can ultimately reduce the presence of CO₂ in our environment.

Keywords: Biochar, Pyrolysis, Metals incorporation,

INTRODUCTION

Release of various gases such as CO₂, CH₄ and N₂O is a major environment issues that ultimately leads to global warming (Liu et al., 2019). Various studies have shown that CO₂ is major contributor for increasing global warming (Marescaux et al., 2018). Hence it has become essential to discover such methods which are environmental friendly and will reduce the CO₂ effect leading to increased pollution (Dutcher et al., 2013). Adsorption is one of the techniques that could be effectively used to reduce CO₂ present in atmosphere (Shafeeyan et al., 2010). There are different adsorbents that can be used to absorb CO₂ present in atmosphere which are Zeolites, mesoporous carbon, nonmaterial carbon and activated carbon. Biochar is a charcoal produced by pyrolysis that has potential for absorbing CO₂ present in atmosphere for a greater extent (Ok et al., 2018). As biochar is obtained from different waste such as crop waste, wood waste, food waste, decaying plants, animal manure and sewage waste it is considered eco friendly and also entraps CO₂ to a greater extent (Rajapaksha et al., 2019). As scientists have found that biochar has greater CO₂ adsorption property thus certain modification in biochar can enhance its adsorption property even more (Rajapaksha et al., 2016). By adding different chemicals into biochar it would increase its surface area thus greater carbon retention capacity (Wang et al., 2017). Phosphoric acid can be used as an activating agent in biochar that would lead to greater specific surface area. Incorporation of phosphoric acid to the biochar by total ratio at particular temperature has lead to opening of the pores to the greater extent thus greater capture of CO₂. The pretreatment of biochar with phosphoric acid has various benefits such as greater carbon retention, increase in pore size of biochar and greater specific surface area (Huang et al., 2014). Various methods have been developed for entrapment of CO₂ and technology that is widely preferred is adsorption by amine solutions. Different porous adsorbents that include Zeolites micro porous silica and activated carbons can be used to incorporate into biochar for enhancing its adsorption capacity. Rise in the concentration of stable carbon present biochar is another method that can increase capturing of CO₂. Incorporation of potassium in a biochar has revealed in greater yield of stable carbon (Masek et al., 2019). The structure of biochar incorporated with potassium shows enhanced cross linkage that would ultimately leads to stability (Le Brech et al., 2016). Modification in biochar has proven to provide great benefits for entrapment of CO₂. Phosphoric acid was added in a biochar that increases specific surface area and size and volume of pore (Wang et al., 2017). Biochar pretreated with phosphoric acid shows

greater carbon retention and greater carbon yield than the untreated one (Xu et al., 2014). Despite of all these advantages biochar has even proven to be a great medium for amendment of the soil (You et al., 2017). Biochar has helped to improve the soil fertility and added various nutrients (Woolf et al., 2010). These days, the interest for vitality is quickly expanding a direct result of the monetary development around the world. So as to fulfill this developing need, a bounteous measure of non-renewable energy source is required. Non-renewable energy source burning is frequently considered as one of the fundamental dangers to nature in light of the CO₂ discharge in the climate. In this manner, using CO₂ and changing over it into fills and synthetic substances, known as carbon capture and reuse (CCR) process, is a functioning alternative utilized worldwide to change over usable items into important items, and it is utilized to relieve CO₂ emanations which is progressively ideal contrasted with CSS choice. During the most recent years, transformation of CO₂ into value added synthetic compounds utilizing various methods for an incredible consideration from the specialists as it tends to be viewed as an answer for diminish the dangerous atmospheric deviation vitality emergency and the capacity of vitality issues. Methanol is a sustainable power source that can be delivered from any crude material containing carbon (fundamentally CO₂), just as it is a perfect wellspring of vitality that can be utilized as transportation fuel. When all is said in done, for a fuel to fulfill the market request, it must be manageable material, clean, and ready to be combined from accessible assets. These days, indeed, the greater part of the creation organizations around the globe use methanol as a crude material to deliver various items. Methanol is utilized in delivering solvents like the acidic corrosive, which speaks to 10% of the worldwide interest. Methanol can likewise be utilized in direct methanol power devices (DMFC), which is utilized for the transformation of substance vitality in methanol straightforwardly to electrical force under surrounding conditions. Methanol is viewed as one of the most significant natural feedstock that can be utilized in the businesses with a yearly creation of 65 million tons around the world

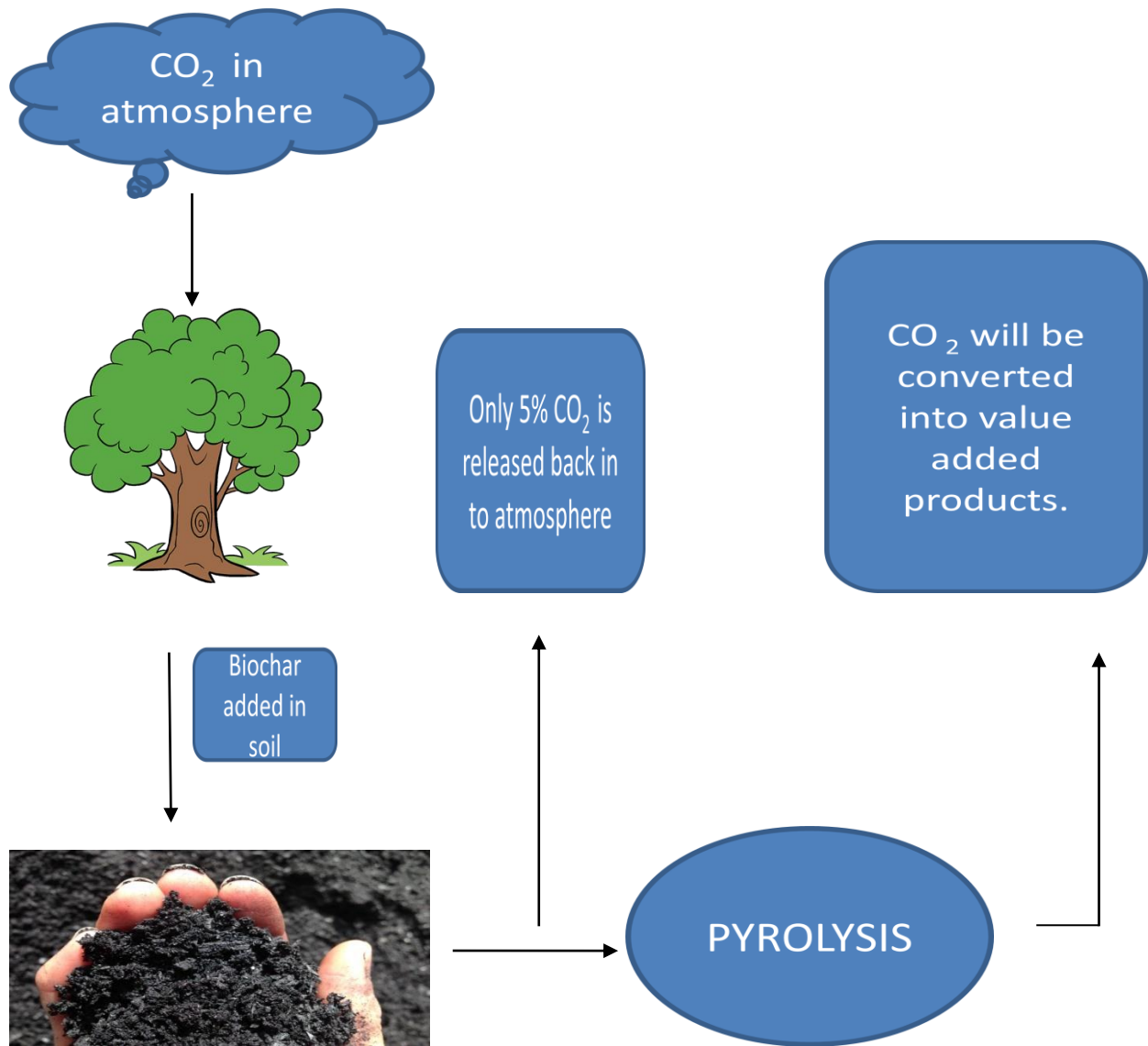


Fig1. CO₂ present in environment used to convert into Bioenergy using biochar

1. Use of biochar for CO₂ sequestration

CO₂ sequestration can also be referred as capture of CO₂ from the environment where various technologies help to capture CO₂ and store it that can further help in making environment friendly products that can be ethanol or methanol. It is beneficial for environment as it reduces the carbon dioxide content in environment and in addition from this carbon dioxide we can get various important fuels that can be helpful in long term. Thus biochar is an effective way for CO₂ capture and its sequestration.

Soil is the major source that stores greater amount of carbon that is even greater than CO₂ present in environment. Plants through the process of photosynthesis absorb the CO₂ thus getting captured in the soil but ultimately it is further added back into the environment with the help of biological processes performed by microorganisms. Therefore here CO₂ sequestration comes into role. As we can add biochar into the soil that has a potential for capturing greater amount of CO₂ in the soil that would ultimately reduce the release of CO₂ into the environment.

2. Use of Potassium for increasing the efficiency of biochar for CO₂ sequestration

Several studies and experiments performed by scientists show the results that various alkali metals including K, Na, Ca, Mg have shown the positive results for increasing biochar yield for CO₂ sequestration. Therefore use of such metals can be beneficial as it would enhance the absorption capacity of CO₂ in the biochar. In addition these metals are easily available and economically feasible.

2.1. Potassium doping in biochar

According to the experiment performed by Masek et al., 2019 on *Miscanthus* the biomass shows the positive results by adding alkali metals. Their results show that when doping of potassium was done the yield of biochar came out to be increased by 10.5% to 21.1% as compared to untreated biomass. According to then two other main criteria also include stable carbon yield. Therefore they use hydrogen peroxide for determining the stable carbon content thus showing the positive effect. Thus all alkali metal treatment results increase in stable carbon yield (Nowakowski et al., 2007).

The steps followed in potassium doping for biochar are as follow:

- Alkali metal loaded Miscanthus with 1% and 2% w/w content potassium was added by spraying potassium acetate on oven dried Miscanthus. [Fuentes et al., 2008]
- The potassium was added and moisture of biomass has been resorted.
- 1% potassium doped Miscanthus was pyrolysis at 350 to 750 degree Celsius.
- Hence, at last biochar structure was examined through Raman spectroscopy and X-ray diffraction.

Therefore the comparison was done between Potassium doped biochar versus untreated biochar the results that were observed were very positive. The potassium doped biochar has greater CO₂ adsorption capacity and the volume of pores was also increased as compared to untreated biochar. Thus doping of potassium found to appropriate can be used as a modification for biochar that would give us better CO₂ adsorption.

2.3 Affect of potassium doping on microstructure and carbon stability of biochar

The increased stability was determined by enhanced cross linking reaction (Le Brech et al., 2016). Structure was observed through Raman spectroscopy that can help to easily differentiate between Potassium doped and untreated biochar. The results that were observed includes that potassium doped biochar shows greater cross linkage which means greater absorption of CO₂ as well as increase in volume and size of pores were observed as compared to that of untreated biochar (Liu et al., 2015).

2.4. Potassium doping increases carbon sequestration

Earlier it was observed that biochar can store 0.7-1.8 Gt CO₂ but after performing the experiment of doping biochar with potassium it was found that biochar can store 45% more CO₂ (Smith et al., 2016). Another benefit that was added is majority of potassium treated biochar is that it also helps in soil amendment that means increasing the soil fertility through CaCl₂ extraction (Peter et al., 2015). Thus it was concluded that potassium doping has increased CO₂ sequestration as well as better slow release potassium fertilizer.

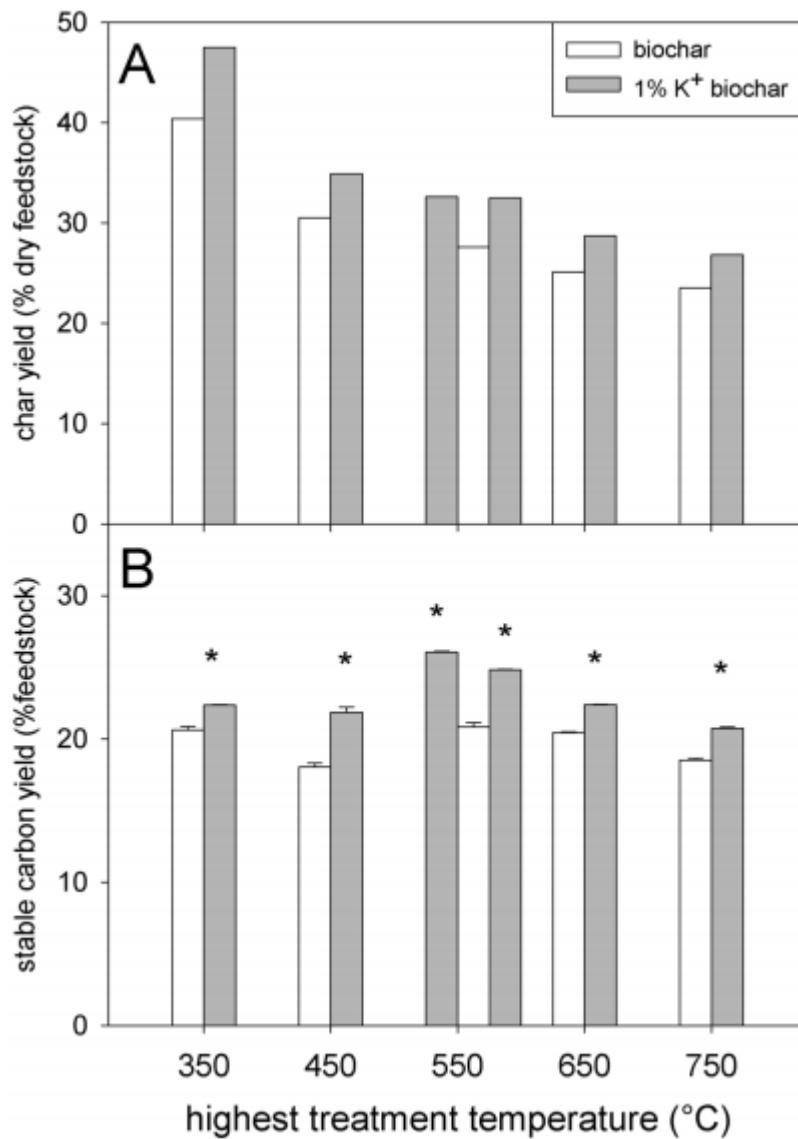


Fig 2: Comparison between untreated & potassium treated biochar [Masek et al., 2019]

3. Role of phosphoric acid

As previously studied biochar has given lots of beneficial aspects that are helpful to our environment but several of studies show that biochar has generally low specific surface area therefore scientists are working on the methods through which this specific surface area can be increased so as to get greater CO₂ sorption (Keiluweit et al., 2010). Therefore experiments performed by Zhao et al., 2017 shows that phosphoric acid can be used to pretreated biochar that would result in increased specific surface area.

This experiment was performed to get the results of various questions that were:

- To examine the pyrolysis temperature and inducing ratio of phosphoric acid on biochar so as to get appropriate pore structure.
- To check Carbon structure during co pyrolysis with phosphoric acid.
- To check sorption ability of phosphoric acid (Hungal et al., 2014).

3.1. Biochar production with Phosphoric acid

- Pine tree saw dust were collected
- Dried at 60 degree Celsius till particle size become greater than 1mm
- Then this sawdust was treated with diluted phosphoric acid
- 85% of phosphoric acid was diluted to 8.5 and then mixed with 50g of sawdust
- Thus inducing ratio were 0.359:1 and 0.718:1

Therefore the values were decreased as compared to those that were used to produce activated carbon (Le Blance et al., 2016).

3.2. Results of Biochar yield and CO₂ retention

Biochar yield can be calculated by weight of biochar subtracted by phosphoric acid upon weight of biomass. Thus Zhao et al 2016 found that there was a change in the weight of phosphoric acid thus actual yield came out to be much higher. CO₂ retention can be calculated by total carbon contents of biochar. Therefore it was concluded that the yield of biochar treated with phosphoric acid was quit high and the retention or absorption of CO₂ was also increased as compared to the untreated one.

3.3. Changes in pore formation by adding phosphoric acid

The surface area and pore volume show that they were much higher in biochar inducing with phosphoric acid. The experiment was performed at three different level and results show that the untreated biochar was having lesser specific surface area. There observation finally concluded that phosphoric acid induced biochar has shown better results than that of untreated one where there was increase in the surface area and increase in the pore size and its pore volume (Wang et al., 2017).

3.4 Enhancement of CO₂ Retention by adding phosphoric acid

The biochar that was pretreated with phosphoric acid results in better CO₂ retention and greater carbon yield that has increased from 46.5% to 78.5%. In addition it also increases the aroma that is due to decrease in hydrogen. The carbon retention was observed at three different temperatures that are 300,500,600 degree Celsius and the results that were observed were positive they concluded the biochar treated with phosphoric acid shows better carbon retention capacity than that of untreated biochar (Xu et al., 2014).

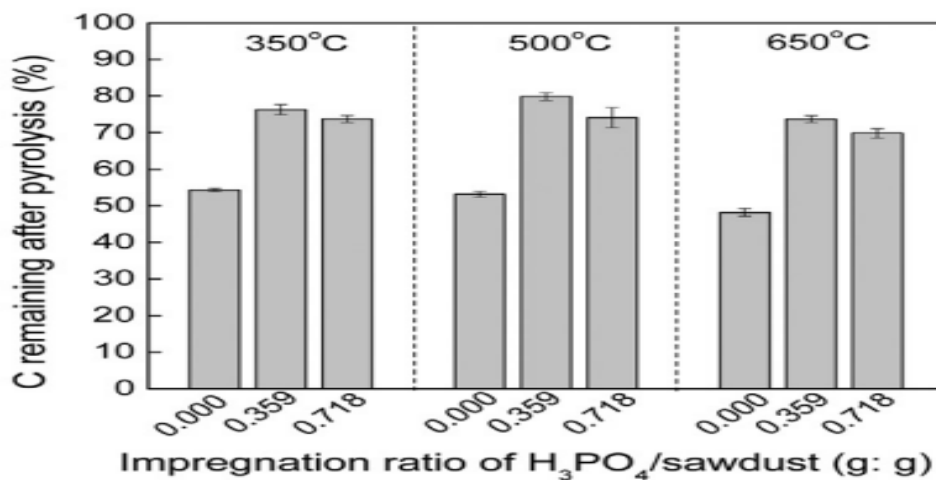


Fig 3: CO₂ remaining in biochars after pyrolysis under different production temperatures and impregnation ratios (Ling et al., 2017).

4. Adsorbents for CO₂ capture on biochar

Biochar has been proven to be environmental friendly and has proven its benefits in various aspect but one of the important is use of biochar as carbon dioxide adsorbent it is because biochar is 10 times more cheaper than other adsorbents thus it becomes economically feasible (Chatterjee et al., 2018). Studies show that raw biochar has low adsorption capacity but if this raw biochar is modified we can get enhanced biochar for great CO₂ adsorption.

4.1. Properties of biochar that influences CO₂ adsorption

4.1.1. Physical properties

Vander Waals forces are involved in CO₂ adsorption between biochar and gas molecules that are mainly related with specific surface area and pore size (Sun et al., 2014).

(a) Specific Surface area

Specific surface area of biochar is determined as the ratio between total surface area and total mass of biochar (You et al., 2017). The effect of Specific surface area of biochar has a greater impact on CO₂ adsorption (Xu et al., 2016). Greater the surface area greater the active site for CO₂ adsorption (Creamer et al., 2016). According to some studies high mineral content leads to reduction of specific surface area and blocking its pores on biochar surface. Furthermore if we increase the temperature during pyrolysis the surface area has also increased that may be due to increase in volatile matter that increases the volume of pore (Ahmad et al., 2014).

(b) Pore size and pore volume

Micro pores having diameter less than 1mm plays a vital role because CO₂ capture capacity is dependent on them (Zhang et al., 2013). An experiment as resulted that effect of pyrolysis temperature on pore volume leads to increase in micro pore volume (Angin et al., 2013).

4.1.2. Chemical properties

Alkalinity, mineral composition, functional groups are certain chemical properties that adversely affect the biochar (Huang et al., 2015).

(a) Basic functional groups

The adsorption of CO₂ on the surface of biochar is very essential thus surface basicity has a greater contribution on it because ultimately it enhances the affinity of biochar for CO₂ (Shafeeyan et al., 2010). Functional groups containing nitrogen (amide, imides, pyridium) and oxygen (ketones, pyrones, chromens) have a major role in surface basicity (Chiang et al., 2017).

(b) Alkaline and alkaline earth metals

The presence of alkaline metals such as Sodium, potassium, Calcium and magnesium has proven to increase the adsorption capacity of carbon dioxide on the biochar surface that may be due to formation of basic sites (Xu et al., 2016).

(c) Hydrophobicity, polarity, aromaticity

Biochar having characteristics of Hydrophobicity, non polarity mainly contributes to greater CO₂ adsorption capacity, low hydrogen and carbon ratio has found to have higher degree of aromaticity (You et al., 2017).

4.2 Modification of Biochar for greater CO₂ adsorption

4.2.1 Alkali based modification

Various studies have shown the use of KOH or NaOH as the activating agent for biochar that helps to increase the O content that initially increase the surface basicity of biochar. They also help to create greater surface area (Li et al., 2014) there were different experiments performed where KOH was induced in biochar and it has shown positive results that includes high surface area and greater micro pores thus exhibiting higher capacity for carbon dioxide adsorption.

4.2.2. Amino based modification

Introduction of ammonia or nitrogen containing functional groups has proven to increase surface area and enhance carbon dioxide adsorption (Palansooriya et al., 2019).

4.2.3. CO₂ activation of biochar

Biochar can be treated with certain activated CO₂ that leads to enhancement of micro pores that helps increasing CO₂ adsorption (Rashidi et al., 2016).

5. Use of metals for biochar modification:

Modification of biochar in order to increase CO₂ adsorption has become a necessary aspect. There are various techniques that are being discovered but with various shortcomings and those is not much environment friendly. Thus it is the necessity to develop such technologies that are environmental friendly too. In this situation use of solid adsorbents are being preferred (Madzaki et al., 2016).

The experiment performed by Guo et al that notices that use of MgO is beneficial because of various characteristics that are non toxicity and basic nature (Guo et al., 2020). In their studies they concluded that presence of MgO has basic sites of biochar surface leads to adsorption of acidic CO₂ with basic O²⁻ in the O²⁻-Mg²⁺ bonds to form carbonate (Lahijani et al., 2018).

Secondly in the presence of MgO the adsorption of CO₂ is more even at low temperature that can be done by the process called carbonation (Elvira et al., 2017).

5.1 Experiment performed by Guo et al was

- Rambutan peel (*Naphelium lappaceum*) was used for making biochar.
- Rambutan peel were washed, cut and dried in oven at 105 degree Celsius for 24 hrs
- Rambutan peel biomass was heated in tube furnace under N₂ for pyrolysis temperature ranging from 500-900 degree Celsius
- Samples were allowed to cool down for 90 minutes
- The biochar yield obtained were: 27.18% at 500 degree Celsius
21.47% at 700 degree Celsius
13.25% at 900 degree Celsius
- Samples were set for grinding and then stored

5.2 Preparation of metalized biochar

- To obtain metal oxide biochar different magnesium salts were introduced through wet impregnation method. The Mg salts used were:
 - Magnesium nitrate hexahydrate
 - Magnesium sulphate heptahydrate
 - Magnesium chloride hexahydrate
 - Magnesium acetate tetra hydrate
- 5% Mg solution has to be achieved
- Thus, metal precursor was dissolved in 60ml of deionized water.
- 0.5g biochar was added in the solutions
- Mixture was kept for stirring for 6hrs
- Then was kept in oven at 105 degree Celsius for 24hrs

- Afterwards dry metalized biochar was obtained and heated under Nitrogen flow at 500 degree Celsius for 15 minutes.
- Then obtained metalized biochar were stored in sealed container

5.3 Results of metal loading on biochar

- The biochar pyrolyzed at 900 degree Celsius shows highest CO₂ adsorption
- The biochar loaded with magnesium nitrate shows the highest CO₂ adsorption that is 76.78 mg g⁻¹ that has been increased by 11.7% then the untreated one.
- The biochar loaded with magnesium acetate shows the lowest adsorption capacity that was 68.15 mg g⁻¹

Thus, scientists study shows that loading of metal ion on the surface of biochar leads to increase in surface basicity that leads to higher adsorption of CO₂ (Xu et al., 2016).

6. 1. Chemical Methods used to increase CO₂ adsorption

Membranes are used as a method of CO₂ capture in various fields because of its advantage that is low price and easy availability. Membranes act as a filter various gas molecules get filtered through it and thus the desired molecules of gas are achieved.

Advantages of membranes:

- Cost effective
- Low capital & operational cost
- Simplicity & Reliability
- Adaptability
- Design efficiency

Table 1: Classification of membrane based on pore size

| Pore Classification | Pore size (nm) |
|---------------------|----------------|
| Micro pore | <2 |
| Meso pore | 2-50 |
| Macro pore | >50 |

6.1 Membrane separation mechanism

- Size sieving: The gas molecules can be filtered based on their size. The size of membrane is based on the size of desired gas.
- Surface diffusion: It is generally based on the affinity of desired gas molecule that diffuses the desired gas. Diffusion rate of Carbon dioxide is 0.33nm
- Ion transport: Ions of desired gas is used in the membrane filtration process

6.1.1 Membranes used for CO₂ adsorption

Table 2: CO₂ selectivity of different membranes at different temperature

| Membrane | Permeability (mol/s/m Pa) | CO ₂ selectivity (%) | Temperature (degree Celsius) | References |
|---------------------|------------------------------|------------------------------------|---------------------------------|---------------------|
| Palladium | 9×10^{-9} | 27 | 227 | Khatib et al., 2011 |
| Silica (Si400) | 2.01×10^{-6} | 7 | 200 | Tong et al., 2004 |
| Poly vinyl chloride | 5.36×10^{-12} | 11 | 35 | Choi et al., 2008 |
| Zeolites-A | 9.45×10^{-10a} | 10 | 35 | Gu et al., 2008 |
| MOF-5 | 2.80×10^{-6} | 4.3 | 25 | Cao et al., 2012 |
| Cellulose acetate | 2.48×10^{-7a} | 40.17 | 37 | Ahmad et al., 2014 |

6.1.2. Modified biochar used for CO₂ capture:

Table 3: CO₂ adsorption capacity of modified biochar

| Modified biochar | CO ₂ adsorption (%) | Temperature (degree Celsius) | References |
|------------------------------------|--------------------------------|---------------------------------|--------------------|
| Potassium based biochar | 31.8 | 300-600 | Masek et al., 2019 |
| Phosphoric acid based biochar | 73.9-78.5 | 350-500 | Zaho et al., 2017 |
| Magnesium nitrate based biochar | 76.75 | 400-700 | Guo et al., 2020 |

7. Role of Biochar enriched with nutrients for increasing soil fertility

As we know that India is counted amongst the highest agriculture cultivating countries in the world and is found that the traditional agricultural system are the major contributor for environmental pollution. According to various studies and survey it is found that agricultural waste is always left untreated thus contributing to the pollution. Hence this waste can be converted into Bioenergy or biofertilizer that can help to enhance the fertility of soil (Geissdoerfer et al., 2017).

Anaerobic digestion has been considered as a greater technology that can produce Bioenergy from the agricultural waste from past few decades (Angelidaki et al., 2018). The anaerobic digestate generally includes various nutrients such as Ca, Mg, K, Zn, Cu, Fe, Mn in added to organic matter thus it concludes to be greater source of agricultural nutrients (Risberg et al., 2017).

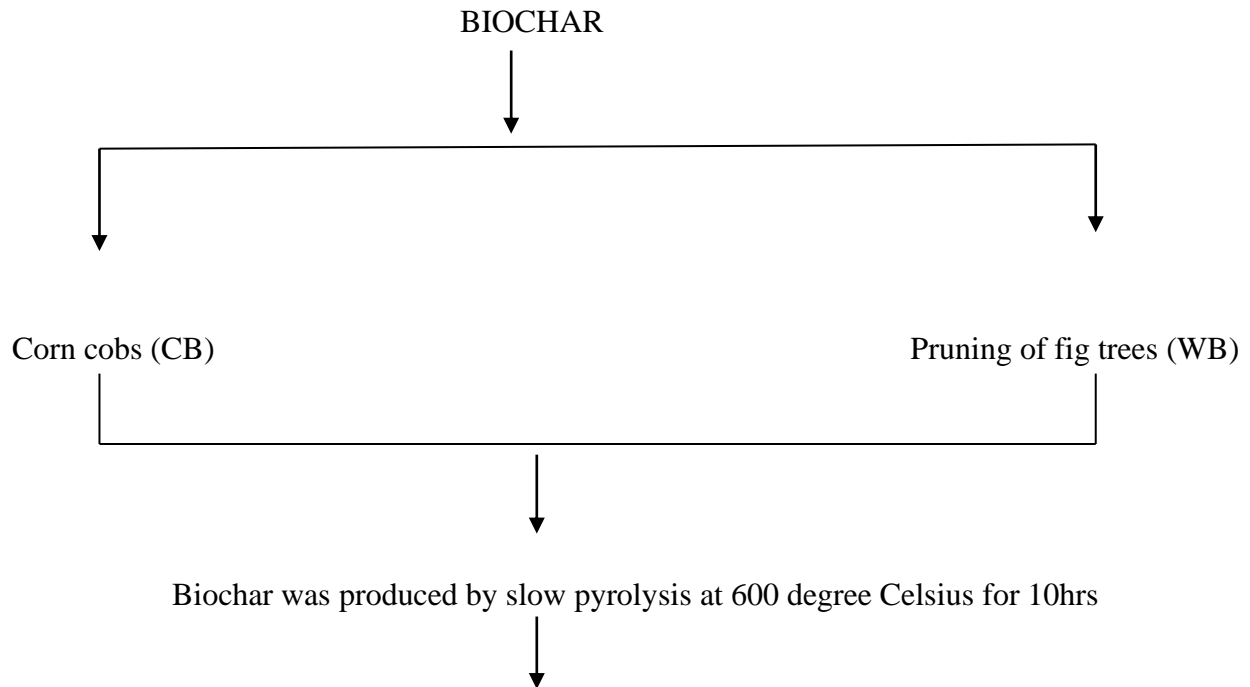
But the present scenario is facing certain challenges which are as follow:

- Increase in the number of industrialized livestock and biogas plant the production of anaerobic digestate is higher than the agricultural potential (Torrijos et al., 2016).
- Due to guidelines of agricultural councils only small amount of anaerobic digestate can be used in the land and use of anaerobic digestate is totally restricted in non cropping season (Chen et al., 2013).
- It requires large storage area and transportation to the distance parts are also difficult (Chadwick et al., 2015).

Therefore, for dealing with such difficulties one alternative that could be considered is anaerobic digestion treatment integrated with pyrolysis. Thus resultant biochar can help in adsorption of nutrients and helps to increase the soil fertility. Various studies show that biochar adsorbs Nitrogen, Phosphorus, Potassium and various organic matters from different areas (Takaya et al., 2016). Thus this biochar will help to improve soil texture and nutrients (Novak et al., 2018).

7.1 Experimentation

Experiment by Simon Kizito et al., 2019 was as follow



Biochar surface area was determined by N₂ adsorption and structural composition was determined by XRD technology

7.2. Procedure to concentrate anaerobic digestate nutrients on biochar

- Raw biochar (CB & WB) were dried at 85 degree Celsius overnight to stabilize moisture content
- Biochar was added to digestate with the ratio of 1:5 (wt/wt)
- Mixture was stirred for 48 hrs
- pH was adjusted at 6
- Thus, amount of nutrients adsorbed on biochar were calculated based on initial or final concentration.
- At the end liquid and solid phase were separated by manual sieving (0.25)
-

7.3 Results

Table 4: Recovery of nutrients from the experiment

| Nutrients | Corn cobs (CB) (mg/g) | Pruning of fig trees (mg/g) |
|-----------------------------------|--------------------------|--------------------------------|
| NH ₄ ⁺ --N | 15.3 | 23.6 |
| PO ₄ ³⁻ --P | 23 | 19 |
| K ⁺ | 27.2 | 21 |

8. Effects of biochar on sustainable agriculture

Various greenhouse gases are released through agriculture that leads to their contribution in global warming (Burney et al., 2010 ; Robertson, 2000; Smith et al., 2008). Contribution of agriculture for the release of greenhouse gases is approximately 24% (Smith et al., 2007) and contribution for release of methane and nitrous oxide is 54% and 84% (Smith et al., 2008). Therefore use of biochar has come on a positive note that would lower the greenhouse gas emission (Spokas and Reicosky, 2009; Zhang et al., 2012b; Zimmerman et al., 2008). The release of CO₂ is mainly observed by burning of the agricultural waste (Smith et al., 2008). CO₂ released through agricultural process is naturally sequestered through photosynthesis but in a long term for greater CO₂ entrapment it is not an effective way therefore biochar can be added that would increase the efficiency for CO₂ sequestration (Lee et al., 2010). In addition to increase CO₂ sequestration through biochar it has also decrease the release of methane and nitrous oxide (Liu et al., 2011).

8.1 Effect of biochar for soil amendment

Different scientists conclude that addition of biochar into the soil has come up with not only increase CO₂ sequestration but also it has helped in amendment of soil that includes increased soil quality and soil fertility and additionally improved the nutrient cycle in the soil. The properties of biochar are depended on the type of waste material that is being used and different temperature at which pyrolysis takes place (Lehmann et al., 2011; Barrow 2012; Albuquerque et

al., 2014). Various properties of biochar affect the soil quality and in addition their chemical and physical characteristics can be affected in a same way (Downie et al., 2009). When biochar is added into the soil it directly affects on the different properties of soil that includes its surface area, porous activity, water holding capacity, penetration power and many more (De la Rosa et al., 2018; Downie et al., 2009; Mukherjee and Lal, 2013).

8.1.1. Physical effects

Soil consists of different characteristics that are important role not only in the growth of plants but also in the reduced release of harmful gases because of its functions that includes water and nutrient holding capacity (Batool et al., 2015; Downie et al., 2009; Waters et al., 2011) but soil generally does not possess greater water and nutrient holding capacity that may be due to presence of clay in greater amount or smaller surface area (Troeh et al., 2005). Therefore here biochar is added as biochar possesses greater surface area that would generally retain more amount of water and minerals (Downie et al., 2009). Studies have shown that addition of biochar into the soil has given 4.8 times better results as compared to the untreated one (Liang et al., 2006). Many scientists have concluded that combine use of soil and clay with addition of biochar has increased number of pore as well as its size (Brodowski et al., 2006; Cheng et al., 2006).

Table 5: Results observed after addition of biochar in a field of different crops

| Culture System | Crop used | Biochar added | Results | References |
|----------------|-----------|---------------------|---|------------------------|
| Open fields | Rice | Teak wood residues | <ul style="list-style-type: none"> ➤ High grain yield ➤ Improved response to Nitrogen treatment | (Asai et al., 2009) |
| Open fields | Maize | Wheat straw | <ul style="list-style-type: none"> ➤ Maize yield increased by 15.8% ➤ GHG emission was also reduced | (Zhang et al., 2012b) |
| Open fields | Grape | varied hardwood and | <ul style="list-style-type: none"> ➤ No effects on plant growth | (Schmidt et al., 2014) |

| | | | | |
|-------------|--------|-------------------------------|--|-------------------------|
| | | varied coniferous wood chips | ➤ No specific difference was observed in the quality | |
| Open fields | Apple | Acacia whole tree green waste | ➤ Positive impacts were observed including greater water retention | (Eyles et al., 2015) |
| Open fields | Cotton | Cotton stalk | ➤ Water content in leaf increases | (Kannan et al., 2017) |
| Open fields | Maize | Pine wood | ➤ Addition of biochar have significant effect in biomass | (Pressler et al., 2017) |

8.1.2. Chemical effects

As we know that biochar has larger surface area and greater permeability due to presence of porous, these characteristics may offer a chance to hold and adsorb plant nutrients and thus improve soil fertility (Lehmann, 2007b). Numerous new studies have recorded various advantages with biochar addition to soil, including Cation exchange capacity (CEC), decreased N leaching, upgraded microbial addition, liming, and different benefits (Cornelissen et al., 2013; Kloss et al., 2014; Lehmann et al., 2011b; Mia et al., 2014; Ventura et al., 2012). Soil cation exchange capacity (CEC) is a proportion of its capacity to hold positively charged particles (i.e., Ca^{2+} , K^{+}), while anion exchange capacity (AEC) holds negatively charged particles (i.e., NO_3^{-}) (Joseph et al., 2010). Nonetheless, this capacity of cations and anions of biochars are likely subject to their cation exchange capacity and anion exchange capacity (Lehmann and Joseph, 2015).

8.1.3. Soil biological activity

There are varieties of complex organism present in soil, like microbes, parasites, nematodes, protozoa, and different spineless creatures. The presence of these microbes are constantly changing because of soil qualities and the various factors, especially concerning the addition of biochar (Thies et al., 2009). The studies done till date shows that the addition of biochar to soils

can establish a medium that increases soil microbial activity, and hence influencing soil microbiological properties. For example, (Lehmann et al., 2011b; Rutigliano et al., 2014; Tong et al., 2014; and Gul et al., 2015) increase in the biological activity of microbes when biochar was incorporated into soil. Additionally types of feedstock added in the soils could have a poisonous impact on soil microorganisms due to bio-oils and natural mixtures adsorbed on the surfaces of some biochar (McClellan et al., 2007). Biochar's high surface area and its capacity to absorb nutrients, give a positive effect to microorganisms like microscopic organisms, actinomycetes and arbuscular mycorrhizal parasites to colonize, develop and duplicate (Kookana et al., 2011; Thies et al., 2009).

9. Use of different solvents for CO₂ capture

9.1 Chemical absorption solvents

9.1.1. Conventional amine-based solvents

This process is mainly amine based that can be used for removal of CO₂ and hydrogen sulfide. CO₂ is retained normally utilizing amines to frame a dissolvable carbonate salt. The safeguard works underneath 60°C and surrounding pressure (Kohl et al., 1997). These days, amine-based concentration retention came up as a potential innovation that can be applied to capture CO₂ outflows in mechanical procedures such as non-renewable energy sources power plants, concrete creation and iron and steel fabricating. Post-burning is the closest near market and modernly created carbon catch and capacity innovation. In particular, the alkanolamines are unstable, modest and safe to deal with mixes and are usually grouped by the level of substitution on the focal nitrogen; a solitary substitution meaning an essential amine; a twofold substitution, an auxiliary amine; and a triple substitution, a tertiary amine.

9.1.2. Sterically hindered amine solvents

These are viewed as a sort of amines which can enhance CO₂ capture rates in correlation with the normal essential and second amines, typically amino alcohols. A Sterically hindered amine is framed by an essential or auxiliary amine in which the amino acids are formed to a tertiary carbon particle in the main case or an optional or tertiary carbon molecule in the second. This strong bond form high free-amine fixation in arrangement, so the vitality utilization to discharge CO₂ is bring down that the basic essential and second amines decline up to 15% can be accomplished utilizing ruined amines (Hüser et al., 2017).

9.1.3 Non-amine-based solvents

These are called to those concoction solvents which don't incorporate an amine group in their structure sub-atomic. The most pertinent dissolvable proposed as an option in contrast to the traditional amine-based solvents is the sodium carbonate (Na_2CO_3). About 30% p/p sodium carbonate slurry is utilized to give a fundamental situation in which CO_2 is ingested as bicarbonate followed by sodium bicarbonate arrangement. The NaHCO_3 precipitation upgrades the bicarbonate development and, subsequently, the CO_2 catch limit of the dissolvable is improved (Spigarelli et al., 2013).

9.1.4. Ionic liquid

Scientists have found through their studies that amine-based solvents, specifically ionic fluids (ILs) have a positive effect. These mixes are natural salts with raised heating points and in this way low fume pressure, which can specifically ingest corrosive gases, for example, CO_2 and SO_2 , including moderately low recovery vitality prerequisites (Zeng et al., 2017) has a specific molecular structures specifically designed for each application, in particular for low CO_2 concentrated flue gas treatment (Luo et al., 2017).

9.2. Physical Absorption Solvents:

Physical absorption forms are energetically prescribed to isolate CO_2 in pre-combustion processes that usually work at lift CO_2 incomplete weight. Physical solvents can specifically catch CO_2 in contact with a gas stream without a synthetic response happening. As it was shown in the presentation area, the high fractional weights of CO_2 and low temperatures are alluring to acquire an improved exhibition of the physical ingestion process as far as assimilation rates and dissolvability harmony of CO_2 . At that point, the rich dissolvable is recovered.

Physical Absorption Solvents are as follow:

9.2.1. Selexol

Selexol is a process for acid gas removal solvent that separates acid gases and is being used from long period of time (Kohl et al., 1997). In this process flue gas is dehydrated and then send to absorption column at 30 atm and 0-5 degree Celsius and then there is selectivity of acid gas in

the column. A pre treatment column is used for separation of carbon dioxide and thus at the last stage CO₂ is recovered (Hammond et al., 2014).

9.2.2. Rectisol

Rectisol is another process that helps in removal of gas which includes H₂S and CO₂ from different mixtures of gases. The CO₂ obtained has various advantages that can be used in the production of certain value added products including methanol, ethanol, urea, ammonia and many more. This process is highly selective towards carbon dioxide and thus it can be easily separated from the mixture of gases. In Rectisol syngas needs to be cooled before its introduction to the column. Firstly sulphur compounds are removed and at the end CO₂ can be captured.

9.2.3. Ifpexol

Ifpexol gas is used for natural gas application. It is two steps process these firstly removal of condensable hydrocarbons and water. Secondly removes acid gas (Lecomte et al., 2010). In this process absorber works in low temperature that is at -29 degree Celsius so that methanol loss can be reduced. This process helps to capture carbon dioxide and methanol at low temperature.

9.2.4. Fluor

Among all the different process for carbon dioxide capture solvents fluor is considered one of the appropriate processes (Reddy et al., 2008). In this process moderate to high temperature is required. Similarly flue gas needs to be dehydrated first before it enters into the column. Hence carbon dioxide absorption takes place through carbon dioxide loaded solvents and thus high purity of carbon dioxide is recovered

9.2.5. Purisol

This process is mainly performed to treat at high temperature because it has high selectivity for H₂S. In this process for obtaining carbon dioxide the removal of H₂S is not needed. This process takes place at 50 bar and -15 degree Celsius and thus we can obtain the required gas (Yu et al., 2012).

Table 6: Different solvents used for CO₂ capture with their advantages and disadvantages

| PROCESS | ADVANTAGES | DISADVANTAGES |
|----------|--|---|
| SELEXOL | <p>Non-thermal solvent regeneration</p> <p>Non-corrosive solvent</p> <p>Dry gas leaves from the absorber</p> | <ul style="list-style-type: none"> • Most efficient at elevated pressures |
| RECTISOL | <ul style="list-style-type: none"> • Non-foaming solvent | <ul style="list-style-type: none"> • High refrigeration costs |
| IPEXOL | <ul style="list-style-type: none"> • High chemical and thermal stability • Non-corrosive solvent | <ul style="list-style-type: none"> • High capital costs • Amalgams formation at low Temperature |
| FLUOR | <p>High CO₂ solubility</p> <ul style="list-style-type: none"> • Non-thermal regeneration • Simple operation • Non-corrosive solvent | <ul style="list-style-type: none"> • High solvent circulation rates • Expensive solvent |
| PURISOL | <ul style="list-style-type: none"> • Non-foaming solvent • High chemical and thermal stability • Non-corrosive solvent | <ul style="list-style-type: none"> • High compression cost • Most efficient at high-pressure |
| SULFINOL | <ul style="list-style-type: none"> • High capacity • Low solvent circulation rate | <ul style="list-style-type: none"> • Foaming issues • Corrosive solvent • Thermal regeneration |

Conclusion

Biochar has proven to be environmental friendly and economical for adsorption of carbon dioxide because of its characteristic properties. Major characteristics of biochar include greater specific surface area, pore size and pore volume. Therefore modified biochar by addition of chemical or physical solvents has proven more effective as it would increase surface area and pore size. Therefore further studies should focus on modification of biochar that would increase the capture of carbon dioxide that could be further used for sequestration of carbon dioxide. In the above work biochar was prepared from the waste material through the process of pyrolysis. Various metals were incorporated into biochar that would modify the biochar and enhance its characteristics for carbon dioxide adsorption. Therefore different metals show different results with respect to different temperature. Various chemicals such as potassium, phosphoric acid. Magnesium nitrate, magnesium acetate and many more other chemicals were incorporated into biochar that has shown positive results such as enlarged specific surface area, increase in pore size and volume, increase in carbon retention and many more. Therefore future studies and experiment should focus on engineering of biochar and development of new technologies for capture of carbon dioxide and its sequestration.

REFERENCES:

- [1] Ahmad M, Rajapaksha AU, Lim JE, Zhang M, Bolan N, Mohan D., 2014. Biochar as a sorbent for contaminant management in soil and water: a review. *Chemosphere* 99:19–33.
- [2] Ahmad, A. L.; Jawad, Z. A.; Low, S. C., 2014. A cellulose acetate/multi-walled carbon nanotube mixed matrix membrane for CO₂/N₂ separation. *Journal of Membrane Science*, 451 (1), 55–66.
- [3] Alburquerque, J.A., Calero, J.M., Barron, V., Torrent, J., del Campillo, M.C., Gallardo, A., Villar, R., 2014. Effects of biochars produced from different feedstocks on soil properties and sunflower growth. *Journal of Plant Nutrition and Soil Science* 177, 16– 25.
- [4] Angelidaki, I.; Treu, L.; Tsapekos, P.; Luo, G.; Campanaro, S.; Wenzel, H.; Kougias, P.G 2018. Biogas upgrading and utilization: Current status and perspectives. *Biotechnol. Adv.* 452–466.
- [5] Angin D 2013. Effect of pyrolysis temperature and heating rate on biochar obtained from pyrolysis of safflower seed press cake. *Bioresour Technol.* 128:593–7.
- [6] Asai, H., Samson, B.K., Stephan, H.M., Songyikhangsuthor, K., Homma, K., Kiyono, Y., Inoue, Y., Shiraiwa, T., Horie, T., 2009. Biochar amendment techniques for upland rice production in Northern Laos. 1. Soil physical properties, leaf SPAD and grain yield. *Field Crops Research* 111, 81–84.
- [7] Barrow, C.J., 2012. Biochar : potential for countering land degradation and for improving agriculture. *Applied Geography* 34, 21–28.
- [8] Batool, A., Taj, S., Rashid, A., Khalid, A., Qadeer, S., Saleem, A.R., Ghufuran, M.a., 2015. Potential of soil amendments (Biochar and gypsum) in increasing water use efficiency of *abelmoschus esculentus* L. Moench. *Frontiers in Plant Science* 6, 1–13.
- [9] Brodowski, S., John, B., Flessa, H., Amelung, W., 2006. Aggregate-occluded black carbon in soil. *European Journal of Soil Science* 57, 539–546.

- [10] Burney, J.A., Davis, S.J., Lobell, D.B., 2010. Greenhouse gas mitigation by agricultural intensification. *PNAS* 107, 12052–12057.
- [11] Cao, F.; Zhang, C.; Xiao, Y., et al., Helium recovery by a Cu-BTC metal–organic-framework membrane. *Industrial & Engineering Chemistry Research* 2012,51 (34), 11274–11278.
- [12] Chadwick, D.; Wei, J.; Yan'an, T.; Guanghui, Y.; Qirong, S.; Qing, C 2015. Improving manure nutrient management towards sustainable agricultural intensification in china. *Agric. Ecosyst. Environ.* 209, 34–46.
- [13] Chatterjee R, Sajjadi B, Mattern DL, Chen WY, Zubatiuk T, Leszczynska D, 2018. Ultrasound cavitation intensified amine functionalization: a feasible strategy for enhancing CO₂ capture capacity of biochar. *Fuel* 225:287–98.
- [14] Chen, B.; Chen, S 2013. Life cycle assessment of coupling household biogas production to agricultural industry: A case study of biogas-linked persimmon cultivation and processing system. *Energy Policy* 62, 707–716.
- [15] Cheng, C.H., Lehmann, J., Thies, J.E., Burton, S.D., Engelhard, M.H., 2006. Oxidation of black carbon by biotic and abiotic processes. *Organic Geochemistry* 37, 1477–1488
- [16] Choi, S.; Coronas, J.; Lai, Z., 2008 Fabrication and gas separation properties of polybenzimidazole (PBI)/nanoporous silicates hybrid membranes. *Journal of Membrane Science*, 316 (1–2), 145–152.
- [17] Chiang Y, Juang R. 2017 *Journal of the Taiwan Institute of Chemical Engineers* Surface modifications of carbonaceous materials for carbon dioxide adsorption : a review. *J Taiwan Inst Chem Eng* ;71:214–34.
- [18] Cornelissen, G., Martinsen, V., Shitumbanuma, V., Alling, V., Breedveld, G., Rutherford, D., Sparrevik, M., Hale, S., Obia, A., Mulder, J., 2013. Biochar effect on maize yield and soil characteristics in five conservation farming sites in Zambia. *Agronomy* 3, 256–274.
- [19] Creamer AE, Gao B 2016. Carbon-based adsorbents for postcombustion CO₂ capture: a critical review. *Environ Sci Technology* 50:7276–89.

- [20] D. Woolf, J.E. Amonette, F.A. Street-Perrott, J. Lehmann, S. Joseph 2010. Sustainable biochar to mitigate global climate change, *Nat. Commun.* 1 -56.
- [21] De la Rosa, J.M., Rosado, M., Paneque, M., Miller, A.Z., Knicker, H., 2018. Effects of aging under field conditions on biochar structure and composition: implications for biochar stability in soils. *The Science of the Total Environment* 613614, 969–976.
- [22] Downie, A., Crosky, A., Munroe, P., 2009. Physical properties of biochar. *Biochar for Environmental Management. Science and Technology*, p. 416.
- [23] Dutcher B, Fan M, Russell AG 2015. Amine-based CO₂ capture technology development from the beginning of 2013-A review. *ACS Appl Mater Interfaces*; 7: 2137–48.
- [24] Elvira GB, Francisco GC, Víctor SM, Alberto MLR 2017. MgO-based adsorbents for CO₂ adsorption: influence of structural and textural properties on the CO₂ adsorption performance. *J Environ Sci (China)* 57:418–428.
- [25] Ewering C, Heuser F, Benölken JK, Brämer CO, Steinbüchel A 2006. Metabolic engineering of strains of *Ralstonia eutropha* and *Pseudomonas putida* for biotechnological production of 2-methylcitric acid. *Metab Eng* 8: 587-602.
- [26] Eyles, A., Bound, S.A., Oliver, G., Corkrey, R., Hardie, M., Green, S., Close, D.C., 2015. Impact of biochar amendment on the growth, physiology and fruit of a young commercial apple orchard. *Trees - Structure and Function* 29, 1817–1826
- [27] Fuentes, M. E. 2008. A survey of the influence of biomass mineral matter in the thermochemical conversion of short rotation willow coppice. *J. energy Inst.* 81, 234–241.
- [28] Geissdoerfer, M.; Savaget, P.; Bocken, N.M.P.; Hultink, E.J 2017. The circular economy—A new sustainability paradigm? *J. Clean. Prod.* 143, 757–768.
- [29] Gu, X.; Tang, Z.; Dong, J., 2008. On-stream modification of MFI zeolite membranes for enhancing hydrogen separation at high temperature. *Microporous and Mesoporous Materials*, 111 (1), 441–448.

- [30] Gul, S., Whalen, J.K., Thomas, B.W., Sachdeva, V., Deng, H., 2015. Physico-chemical properties and microbial responses in biochar-amended soils: mechanisms and future directions. *Agriculture Ecosystems and Environment* 206, 46–59.
- [31] Guo Y, Tan C, Sun J 2020. Biomass ash stabilized MgO adsorbents for CO₂ capture application. *Fuel* 259:116298.
- [32] Hammond GP, Spargo J 2014. The prospects for coal-fired power plants with carbon capture and storage: A UK perspective. *Energy Conversion and Management*.;86:476-489
- [33] Huang, Y., S.X. Li, J.H. Chen, X.L. Zhang, and Y.P. Chen. 2014. Adsorption of Pb(II) on mesoporous activated carbons fabricated from water hyacinth using H₃ PO₄ activation: Adsorption capacity, kinetic and isotherm studies. *Appl. Surf. Sci.* 293:160–168.
- [34] Huang YF, Chiueh PT, Shih CH, Lo SL, Sun L, Zhong Y, 2015. Microwave pyrolysis of rice straw to produce biochar as an adsorbent for CO₂ capture. *Energy*;84: 75–82.
- [35] Hüser N, Schmitz O, Kenig EY 2017. A comparative study of different amine-based solvents for CO₂ -capture using the rate-based approach. *Chemical Engineering Science* ;157: 221-231
- [36] Kannan, V., Srinivasan, G., Babu, R., Thiyageshwari, S., Sivakumar, T., 2017. Effect of biochar, mulch and PPFM spray on leaf relative water content, leaf proline, chlorophyll stability index and yield of cotton under moisture stress condition. *International Journal of Current Microbiology and Applied Sciences* 6, 604–611.
- [37] Keiluweit, M., P.S. Nico, M.G. Johnson, and M. Kleber. 2010. Dynamic molecular structure of plant biomass-derived black carbon (biochar). *Environ. Sci. Technol.* 44:1247–1253.
- [38] Khatib, S. J.; Oyama, S. T.; Souza, K. R. D., 2011. Review of silica membranes for hydrogen separation prepared by chemical vapor deposition. *Journal of Membrane Science & Technology* 14 (25), 25–60.
- [39] Kohl L, Nielsen RB 1997. Alkanolamines for Hydrogen Sulfide and Carbon Dioxide Removal. *Gas Purif.* 5th ed. Houston, Texas: Gulf Publication. 900 p

- [40] Kloss, S., Zehetner, F., Wimmer, B., Buecker, J., Rempt, F., Soja, G., 2014. Biochar application to temperate soils : effects on soil fertility and crop growth under greenhouse conditions. *Journal of Plant Nutrition and Soil Science* 177, 3–15.
- [41] Kookana, R.S., Sarmah, a.K., Van Zwieten, L., Krull, E., Singh, B., 2011. Biochar application to soil. agronomic and environmental benefits and unintended consequences. *Advances in Agronomy*. Academic Press, pp. 103–143.
- [42] Lahijani P, Mohammadi M, Rahman A 2018. Metal incorporated biochar as a potential adsorbent for high capacity CO₂ capture at Environ Sci Pollut Res ambient condition. *J CO₂ Utilization* 26:281–293.
- [43] LeBlanc, J., M. Uchimiya, G. Ramakrishnan, M.J. Castaldi, and A. Orlov. 2016. Across-phase biomass pyrolysis stoichiometry, energy balance, and product formation kinetics. *Energy Fuels* 30:6537–6546.
- [44] Le Brech, Y. 2016. Effect of Potassium on the Mechanisms of Biomass Pyrolysis Studied using Complementary Analytical Techniques. *ChemSusChem* 9, 863–872.
- [45] Lecomte F, Broutin P, Lebas E, Appert O, Jones T 2010. CO₂ capture: Technologies to Reduce Greenhouse Gas Emissions. 176 p
- [46] Lee, J.W., Hawkins, B., Day, D.M., Reicosky, D.C., 2010. Sustainability: the capacity of smokeless biomass pyrolysis for energy production, global carbon capture and sequestration. *Energy & Environmental Science* 3, 1695–1705.
- [47] Lehmann, J., 2007b. Bio-energy in the black. *Frontiers in Ecology and the Environment* 5, 381–387.
- [48] Lehmann, J., Rajkovich, S., Enders, A., Hanley, K., Hyland, C., Zimmerman, A.R., Lehmann, J., 2011a. Corn growth and nitrogen nutrition after additions of biochars with varying properties to a temperate soil Corn growth and nitrogen nutrition after additions of biochars with varying properties to a temperate soil. *Biology and Fertility of Soils* 48, 271–284.
- [49] Lehmann, J., Rillig, M.C., Thies, J., Masiello, C.A., Hockaday, W.C., Crowley, D., 2011b. Biochar effects on soil biota - A review. *Soil Biology & Biochemistry* 43, 1812–1836.

- [50] Lehmann, J., Joseph, S., 2015. Biochar for environmental management. In: Lehmann, J., Joseph, S. (Eds.), Science and Technology. Earthscan, London, UK, p. 2015.
- [51] Li J, Lv G, Bai W, Liu Q, Zhang Y, Song J 2014. Modification and use of biochar from wheat straw (*Triticum aestivum* L.) for nitrate and phosphate removal from water. *Desalin Water Treat*; 57:1–13.
- [52] Liang, B., Lehmann, J., Solomon, D., Kinyangi, J., Grossman, J., O’Neill, B., Skjemstad, J.O., Thies, J., Luizao, F.J., Petersen, J., Neves, E.G., 2006. Black carbon increases cation ~ exchange capacity in soils. *Soil Science Society of America Journal* 70, 1719–1730.
- [53] Ling Zhao, Wei Zheng, Ondřej Mašek, Xiang Chen, Bowen Gu, Brajendra K. Sharma, and Xinde Cao 2017. Roles of Phosphoric Acid in Biochar Formation: Synchronously Improving Carbon Retention and Sorption Capacity.
- [54] Liu C, Yao Z, Wang K, Zheng X, Li B 2019. Net ecosystem carbon and greenhouse gas budgets in fiber and cereal cropping systems. *Science Total Environment*; 647: 895–904.
- [55] Liu, Y., Yang, M., Wu, Y., Wang, H., Chen, Y., Wu, W., 2011. Reducing CH₄ and CO₂ emissions from waterlogged paddy soil with biochar. *Journal of Soils and Sediments* 11, 930–939.
- [56] Liu, H. Jiang, H.-Q. Yu 2015. Development of biochar-based functional materials: toward a sustainable platform carbon material, *Chem. Rev.* 115 (22) 12251–12285.
- [57] Luo X, Wang C 2017. The development of carbon capture by functionalized ionic liquids. *Current Opinion in Green and Sustainable Chemistry.* 3:33-38
- [58] Madzaki H, KarimGhani WAWAB, NurZalikhRebitanim ABA 2016. Carbon dioxide adsorption on sawdust biochar. *Procedia Eng* 148: 718–725.
- [59] Marescaux A, Thieu V, Garnier J 2018. Carbon dioxide, methane and nitrous oxide emissions from the human-impacted Seine watershed in France. *Science Total Environment* ;643:247–59

- [60] Masek Ondrej, Wolfram Buss, Peter Brownsort, Massimo Rovere, Alberto Tagliaferro, LingZhao, XindeCao & GuangwenXu., 2019. Potassium doping increases biochar carbon sequestration potential by 45%, facilitating decoupling of carbon sequestration from soil improvement. 9:5514
- [61] McClellan, A.T., Deenik, J.G., Antal, M., 2007. Effects of Flash Carbonized Macadamia Nutshell Charcoal On Plant Growth and Soil Chemical Properties. American Society of Agronomy Abstracts, New Orleans, LA 37 November.
- [62] Mia, S., van Groenigen, J.W., van de Voorde, T.F.J., Oram, N.J., Bezemer, T.M., Mommer, L., Jeffery, S., 2014. Biochar application rate affects biological nitrogen fixation in red clover conditional on potassium availability. *Agriculture Ecosystems and Environment* 191, 83–91.
- [63] Mukherjee, A., Lal, R., 2013. Biochar impacts on soil physical properties and greenhouse gas emissions. *Agronomy* 3, 313–339.
- [64] Novak, J.M.; Johnson, M.G.; Spokas, K.A 2018. Concentration and release of phosphorus and potassium from lignocellulosic- and manure-based biochars for fertilizer reuse. *Front. Sustain. Food System*, 2, 54.
- [65] Nowakowski, D. J., Jones, J. M., Brydson, R. M. D. & Ross, A. B 2007. Potassium catalysis in the pyrolysis behaviour of short rotation willow coppice. *Fuel* 86, 2389–2402.
- [66] Ok YS, Tsang DC, Bolan N, Novak JM 2018. Biochar from biomass and waste: fundamentals and applications.
- [67] Palansooriya KN, Wong JTF, Hashimoto Y, Huang L, Rinklebe J, Chang SX, 2019. Response of microbial communities to biochar-amended soils: a critical review. *Biochar*; 1:3–22.
- [68] Peters, J., Iribarren, D. & Dufour, J 2015. Biomass pyrolysis for biochar or energy applications: A life cycle assessment. *Environ. Sci. Technol.*

[69] Pressler, Y., Foster, E.J., Moore, J.C., Cotrufo, M.F., 2017. Coupled biochar amendment and limited irrigation strategies do not affect a degraded soil food web in a maize agro ecosystem, compared to the native grassland. *GCB Bioenergy* 9, 1344–1355.

[70] Rajapaksha AU, Ok YS, El-Naggar A, Kim H, Song F, Kang S, 2019. Dissolved organic matter characterization of biochars produced from different feedstock materials. *J Environ Manag* ;233:393–9.

[71] Rajapaksha AU, Chen SS, Tsang DCW, Zhang M, Vithanage M, Mandal S, 2016. Engineered/designer biochar for contaminant removal/immobilization from soil and water: potential and implication of biochar modification. *Chemosphere*; 148:276–91

[72] Rashidi NA, Yusup S 2016. An overview of activated carbons utilization for the postcombustion carbon dioxide capture. *J CO₂ Utilizing* ;13:1–16.

[73] Reddy S, Johnson D, Gilmartin J 2008. Fluor’s Econamine FG Plus SM Technology For CO₂ Capture at Coal-fired Power Plants.

[74] Risberg, K.; Cederlund, H.; Pell, M.; Arthurson, V.; Schnurer, A 2017. Comparative characterization of digestate versus pig slurry and cow manure—Chemical composition and effects on soil microbial activity: *Waste Management*. 61, 529–538.

[75] Robertson, G.P., 2000. Greenhouse gases in intensive agriculture: contributions of individual gases to the radiative forcing of the atmosphere. *Science* 289 (80), 1922– 1925.

[76] Rutigliano, F.a., Romano, M., Marzaioli, R., Baglivo, I., Baronti, S., Miglietta, F., Castaldi, S., 2014. Effect of biochar addition on soil microbial community in a wheat crop. *European Journal of Soil Biology* 60, 9–15.

[77] Schmidt, H.P., Kammann, C., Niggli, C., Evangelou, M.W.H., Mackie, K.A., Abiven, S., 2014. Biochar and biochar-compost as soil amendments to a vineyard soil: influences on plant

growth, nutrient uptake, plant health and grape quality. *Agriculture Ecosystems and Environment* 191, 117–123

[78] Shafeeyan MS, Daud WMAW, Houshmand A, Shamiri A 2010. A review on surface modification of activated carbon for carbon dioxide adsorption. *J Anal Appl Pyrolysis*;89:143–51.

[79] Smith, P 2016. Soil carbon sequestration and biochar as negative emission technologies. *Glob Chang. Biol.* 22, 1315–1324.

[80] Smith, P., Martino, D., Cai, Z., Gwary, D., Janzen, H., Kumar, P., McCarl, B., Ogle, S., O'Mara, F., Rice, C., Scholes, B., Sirotenko, O., 2007. Agriculture, in: climate change: mitigation. Contribution of Working Group III to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press, pp. 497-540.

[81] Smith, P., Martino, D., Cai, Z., Gwary, D., Janzen, H., Kumar, P., McCarl, B., Ogle, S., O'Mara, F., Rice, C., Scholes, B., Sirotenko, O., Howden, M., McAllister, T., Pan, G., Romanenkov, V., Schneider, U., Towprayoon, S., Wattenbach, M., Smith, J., 2008. Greenhouse gas mitigation in agriculture. *Philosophical Transactions of the Royal Society B Biology Science* 363, 789–813.

[82] Spigarelli BP, Kawatra SK 2013. Opportunities and challenges in carbon dioxide capture. *Journal of CO2 Utilization.*;1:69-87

[83] Spokas, K.a.K.a, Reicosky, D.C.D.C., 2009. Impacts of sixteen different biochars on soil greenhouse gas production. *Annals of Environmental Science* 3, 179–193.

[84] Sun Y, Gao B, Yao Y, Fang J, Zhang M, Zhou Y, 2014. Effects of feedstock type, production method, and pyrolysis temperature on biochar and hydrochar properties. *Chem Eng J*;240:574–8.

- [85] S. You, Y.S. Ok, S.S. Chen, D.C.W. Tsang, E.E. Kwon, J. Lee, C.-H. Wang 2017. A critical review on sustainable biochar system through gasification: energy and environmental applications, *Bioresour. Technol.* 246, 242–253.
- [86] Takaya, C.A.; Fletcher, L.A.; Singh, S.; Anyikude, K.U.; Ross, A.B 2016. Phosphate and ammonium sorption capacity of biochar and hydrochar from different wastes. *Chemosphere*, 145, 518–527.
- [87] Thies, J.E., Rilling, M.C., 2009. Characteristics of biochar: biological properties. *Biochar for Environmental Management*.
- [88] Tong, H. D.; Gielens, F. C.; Gardeniers, J. G. E., 2004. Microfabricated palladium-silver alloy membranes and their application in hydrogen separation. *Industrial & Engineering Chemistry Research*,43 (15), 4182–4187.
- [89] Tong, H., Hu, M., Li, F.B., Liu, C.S., Chen, M.J., 2014. Biochar enhances the microbial and chemical transformation of pentachlorophenol in paddy soil. *Soil Biology & Biochemistry* 70, 142–150.
- [90] Troeh, F.R., Thompson, L.M., 2005. *Soils and Soil Fertility*. Blackwell Publishing, Iowa, US.
- [91] Torrijos, M 2016. State of development of biogas production in europe. *Procedia Environ. Sci.*, 35, 881–889.
- [92] Ventura, M., Sorrenti, G., Panzacchi, P., George, E., Tonon, G., 2012. Biochar reduces short-term nitrate leaching from a horizon in an apple orchard. *Journal of Environmental Quality* 42, 76–82
- [93] Wang, P., L. Tang, X. Wei, G.M. Zeng, Y.Y. Zhou, and Y.C. Deng. 2017. Synthesis and application of iron and zinc doped biochar for removal of pnitrophenol in wastewater and assessment of the influence of co-existed Pb(II). *Appl. Surf. Sci.* 392:391–401.

- [94] Waters, D., Van Zwieten, L., Singh, B.P., Downie, A., Cowie, A.L., Lehmann, J., 2011. Biochar in soil for climate change mitigation and adaptation. *Soil Health and Climate Change*. Springer, Berlin, Heidelberg, pp. 345–368.
- [95] Xu, J., L. Chen, H. Qu, Y. Jiao, J. Xie, and G. Xing. 2014. Preparation and characterization of activated carbon from reedy grass leaves by chemical activation with H₃ PO₄. *Appl. Surf. Sci.* 320:674–680.
- [96] Xu X, Kan Y, Zhao L, Cao X 2016. Chemical transformation of CO₂ during its capture by waste biomass derived biochars. *Environ Pollution*; 213:533–40.
- [97] Xu X, Kan Y, Zhao L, Cao X 2016. Chemical transformation of CO₂ during its capture by waste biomass derived biochars. *Environ Pollution* 213:533–540.
- [98] Yu CH, Huang CH, Tan CS 2012. A review of CO₂ capture by absorption and adsorption. *Aerosol and Air Quality Research.*;12(5):745-769
- [99] You S, Ok YS, Chen SS, Tsang DCW, Kwon EE, Lee J, 2017. A critical review on sustainable biochar system through gasification: energy and environmental applications. *Bioresource Technology*;246:242–53.
- [100] Zeng S, Zhang X, Bai L, Zhang X, Wang H, Wang J, 2017. Ionic-liquid-based CO₂ capture systems: Structure, interaction and process. *Chemical Reviews*; 117:9625-9673
- [101] Zhang Z, Zhou J, Xing W, Xue Q, Yan Z, Zhuo S, 2013. Critical role of small micro pores in high CO₂ uptake. *Phys Chem Chem Phys* ;15:2523.
- [102] Zhang, A., Liu, Y., Pan, G., Hussain, Q., Li, L., Zheng, J., Zhang, X., 2012b. Effect of biochar amendment on maize yield and greenhouse gas emissions from a soil organic carbon poor calcareous loamy soil from Central China Plain. *Plant and Soil* 351, 263– 275.

[103] Zhao Ling, Wei Zheng, Ondřej Mašek, Xiang Chen, Bowen Gu, Brajendra K. Sharma, and Xinde Cao., 2017 Roles of Phosphoric Acid in Biochar Formation: Synchronously Improving Carbon Retention and Sorption Capacity, 240-247.

[104] Zimmerman, A.R., Gao, B., Ahn, M.Y., 2011. Positive and negative carbon mineralization priming effects among a variety of biochar-amended soils. *Soil Biology & Biochemistry* 43, 1169–1179.