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Biochar characterization and its application for removal of pharmaceutical pollutants

Master's thesis in Chemical Engineering
Supervisor: Kristifer Gunnar Passo
Co-supervisor: Sachin Maruti Chavan (UiS)
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NTNU
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Universitetet
i Stavanger

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Abstract

Biochar is widely studied and applied for its beneficial effects in different fields. It has prominent characteristics to behave as efficient and cost-effective sorbent. This study investigates surface properties, porosity and adsorption properties of biochar and determine its applicability for removal of toxic pharmaceutical pollutant Tetracycline from waste streams. Four samples of biochar provided by SINTEF Energy were characterized by XRD, BET, TGA and its adsorption characteristics using UV spectroscopy and adsorption isotherm. The effect of different parameters on adsorption uptake was also studied and performed by varying pH of the solution. It was observed for biochar samples having chips form possess smaller pore size and larger overall pore volume. The biochar samples prepared under CO_2 atmosphere possess larger surface area. The biochar samples however seem to carry comparable properties. The adsorption isotherm indicates increase in adsorption capacity of biochar by increase in pH value of the solution. The adsorption was analyzed at 24hr, 72, 96 and 120 hours of interaction. The results from this study may facilitate investigations for removal of toxic pharmaceutical contaminants from water bodies and waste streams and optimizing removal process of such compounds.

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1. Introduction

Thinking of a substance made of organic fossil and contribute to climate change for positive, gives Biochar all the attention now a days. Biochar is made by burning waste from forest, agriculture or biomass, sewage sludge, algal biomass, and poultry manure via pyrolysis with reduced/no oxygen supply. Other methods include hydrothermal carbonization, and gasification. It forms charcoal like appearance but has no or little impurities thus most carbon content. The advantage of using least oxygen during pyrolysis is that the material burns with least release of secondary matter. The fossil is converted to primary content i.e. carbon in a stable form. It is a black, porous matter having approx. 70% carbon content and nitrogen, hydrogen and oxygen in the remaining 30%. The chemical composition depends upon the process of fabrication as well as the feedstock. It is light weight and provides high surface to volume ratio. In addition to acting as a fine adsorbent, it finds an abundant application in agriculture as soil amendment to enhance crop production and prevent pathogens to effect the plant roots. It also act as carbon sequestration regent for crops (1). Each type has its own distinct benefits. For example, biochar produced from manure has richer nutrient content than that formed from wood chips, whereas wood based biochar does not degrade as quickly, persisting over a longer period of time. The feedstock for biochar is used from manure carries rich nutrients and find it application as soil enrichment additive. Due to its high surface area, it is widely used as adsorbent for the removal of antibiotics, organic pollutants, microplastics, dyes, heavy metals, and phenols from waste water. Biochar carries advantages of convenient operation due to simple structure design (2) and have more economic benefits than reverse osmosis, ion exchange, and electrolysis due to simple procedures

General properties of biochars says that they are mineral rich materials with high porosity and large surface area and pH value lies in neutral to alkaline range. Wood based biochar has high total carbon content, low ash content and low total N, P, K, S, Ca, Mg, Al, Na, and Cu minerals. Higher temperatures often yield biochar that has a greater absorption capacity. This increases the potential for biochar to absorb and contain toxic substances like mercury. Biochar can take various forms, appearing as sticks, pellets, or ash. (3)

The increase in pyrolysis temperature increased the ash content, pH, and surface basicity and decreased the surface acidity [15]. In the case of fast pyrolysis, biomass is rapidly heated to 400–550 °C and the main product is bio-oil while in slow pyrolysis, the biomass is slowly heated to the desired peak temperature and the main products are biochar and syngas. (4) The stability of biochar to sustain hundreds to thousands of years in the soil endorses it to contain a higher proportion of aromatic structures. This makes it highly resistant against chemical and biological decomposition. The source of the materials collected for biochar preparation carries great importance on its properties. For example biochar prepared from different feed stocks have different properties i.e. pH, surface area and essential nutrients. Biochar derived from bamboo, hickory wood and eucalyptus, have large surface area, so there are some kind of biochar that are best suitable to enhance soil fertility and while others may have high potential of metal mobilization or immobilization.

Morphological studies of biochar revealed that carbon based coal, charcoal and coke often include local regions that exhibit crystalline structure. By contrast, x-ray diffraction studies have revealed that biochars are mostly amorphous in structure (5) International Union of Pure and Applied Chemistry (IUPAC) identifies pore sizes of less than 2 nm as micro-pores, 2-50 nm as meso-pores, and size greater than as macropore. (6)

1.1. Necessary pharmaceutical waste management

In waste water management technology, biochar has been in spot light during the recent years. Several advantages of its application in this field includes low cost preparation, higher yield, high surface to volume ratio, large pore volume, environmental friendly and high resource recovery potential. It is being widely utilized to treat livestock waste water because of its easy applicability and cost effectiveness. Or even it is treated under the facilities that are not designed for the specific purpose, it still means to get discharged in the environment untreated. Appropriate treatment of waste water is a need of today's world to incur less Waste water can be considered a resource if it is properly treated before disposal to water streams or landfill. The untreated

pharmaceutical waste disposed may carry Pharmaceuticals, and their decomposed derivatives that can be of the form unknown can become an easy source of long term health risks. A study in New Zealand was conducted by Sara M. Hanning et. al. (7) on communal waste stream for different types of pharmaceutical waste. The data was compared with 12 local pharmaceutical waste bins which indicated the common drugs that are identified in the stream were as hazardous to cause damages to nervous system, cardiovascular system and alimentary tract and also the metabolism. It is so common that the waste stream is dumped into primary stream which is then utilized for aquaculture, feed stock, and agriculture without prior treatment. It is required that all cytotoxic compounds should be disposed in a separate waste stream that must be incinerated before sending off to the environment. They encouraged to undertake broad range of data that will enable to classify pharmaceutical pollutants and take necessary primary or secondary waste treatment. National Return and Disposal of Unwanted Medicines (RUM) scheme in Australia set up a policy to return pharmaceutical waste or unused drugs to community pharmacies which are then disposed off according to the guidelines. (8)Such initiative are also in action in Sweden, UK and other countries as well.

Based on acute risk assessment according to environmental persistence, bioaccumulation and toxicity, pharmaceuticals in water bodies for aquatic environment were studied. The data was then utilize to introduce a 'Wise list' by Regional Drug And Therapeutics Committee Stockholm, Sweden. The list contains recommended pharmaceuticals for treatment of common diseases and minimize the environmental impact. Initiated in 2003 and until 2015 the Wise list is improvised gradually to develop environmentally classified pharmaceuticals with details of their environmental risk, precautionary principles and exemptions.

1.2.   Pharmaceutical pollutants Norway

Norwegian pollution control authority conducted risk assessment of pharmaceutical pollutant according to EMEA (European Medicines Evaluation Agency) guideline (9). Norwegian priority pharmaceuticals were selected for evaluation i.e. 11 pharmaceuticals which includes; Cefuroxime, tetracycline (TC), sulfamethoxazole, ciprofloxacin, paracetamol, ibuprofen,

cyclophosphamide, diclofenac, ethinylestradiol, trimethoprim and metoprolol. The assessment is done according to the Predicted environmental concentrations (PECs) by EMEA guidelines and compared with conventional model to estimate risk quotients. For calculation of risk quotients, the capacity of pharmaceutical compounds for physio-chemical adsorption and biodegradability were also given considerable attention. Acute toxicity data was also taken in consideration with regard to water bodies. The figure 1 to depict the relation of defined daily dose (DDD) and risk quotients to predict the participation of pharmaceutical compound in society. Cefuroxime and paracetamol are seen to be consumed in higher amounts then others. However its ecological parameters does not show much concerning values. The second highest consumption of drugs contains tetracycline (TC), ciprofloxacin and ibuprofen. The risk quotients for these drugs shows acute vulnerability against ciprofloxacin for the environment. The data shows high absorbance property and 0-2.5% biodegradability (9). Poor biodegradability depicts the accumulation of such compounds for longer time in the environment. The second pharmaceutical in this category i.e. tetracycline shows very high adsorption capacity and almost similar biodegradability when disposed. Studies indicate the adverse effect of TC on Aquatic environment which highlights ecotoxicity, production of antibiotic resistance genes and bacterial resistance (10). Due to its stability against biodegradation, the compound tends to exist in water bodies for longer. The respective risk quotient is calculated above the safe limit. Sulfamethoxazole shows a high value of risk quotient but the DDD is little.

Biochar carries advantages of being abundant raw material, cost effective production, rich surface and porous structure that complement adsorption process (11) (12). TC waste management has been addressed widely using biochar by direct surface adsorption or acting as catalyst to assist Persulphate oxidation (10). Biochar is being utilized as an effective facilitator for removal of pharmaceutical waste. Ziyang et al. studies removal of TC using biochar to by adsorption and advanced oxidation processes. (13).
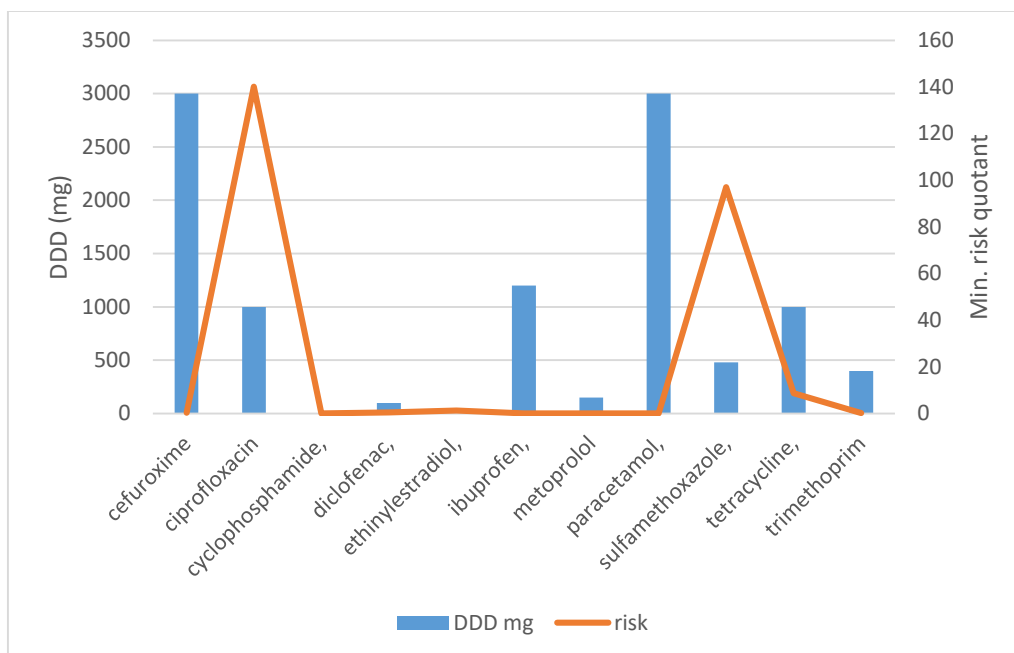
Figure 1 Risk quotients of pollutants in Norway in relation to their DDD

1.3. TC Toxicity study

Tetracycline (TC) having four benzene rings in its structure and molecular formula of $C_{22}H_{24}N_2O_8$ is a widely used antibiotic. It is the second highest antibiotic in production for human and veterinary disease treatments (14). It is a stable, non-biodegradable and water soluble compound that makes its presence in water bodies hazardous for aquatic life and a public health concern when it is exposed to surface or ground water (15). The antibacterial nature of TC makes it difficult to detoxify or destruct TC by biological methods. Several chemical processes were
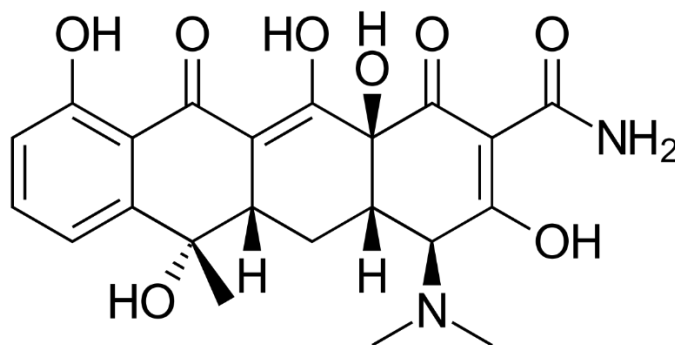
Figure 2 Tetracycline chemical structure

identified such as electrochemical, ultrasound and sonochemical oxidation. It has been observed that these processes tend to undertake set up of complex facilities, application of different transition metals/reagent and are overshadowing energy whereas using biochar as an adsorbant makes the cleaning process simpler and inexpensive (16). The overall risks that are expected because of disposal of TC every day in large amounts of waste, residues, and wastewater, breaks into various ecosystems i.e. via soil erosion, animal manure, and untreated effluent disposal. Jandira et. al. studied damages caused by TC pollution by investigating bone samples from an ancient population (350–550 CE) in Sudanese which showed taphonomic infiltration of bacteria and fungi, that indicated the TC percolation potential is much greater than expected. It has been observed to lead modifications and resistant mutations of bacteria and its genes (17)
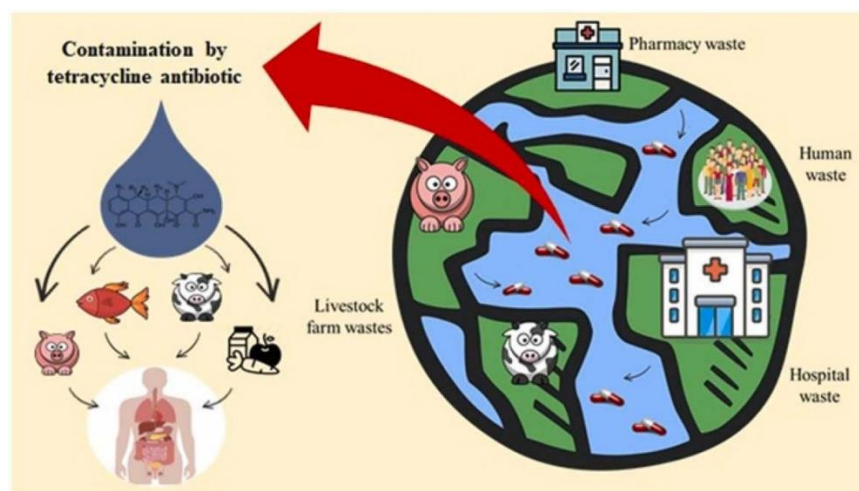
Figure 3 contamination by TC in ecological syatem (source:17)

2. Novelty of the thesis

In this study we intended to characterize four types of biochar provided by SINTEF Energy. The origin of biochar is Birch bark which is one of the most common trees in southern and northern Norway. Two of the samples have chip type conformation and the other have needles form. They are analyzed to find out their porosity, surface area and pore size distribution. It is furthermore analyzed for its adsorption capabilities for one of the prominent pharmaceutical compound

found in wastewater i.e. Tetracycline. It is investigated to evaluate application of biochar in pharmaceutical removal. The samples are identified with the following nomenclature thought out the report.

Table 1 Sample details

Name	Id	Production Heating Rate - Final Temp	Atmosphere	Morphology
Birch bark char	BBC 700N2	10K/min – 700 C	N2	Chips
Birch bark char	BBC 700CO2	10K/min – 700 C	CO2	Chips
Birch needles char	BBN 700N2	10K/min – 700 C	N2	Needles
Birch needles char	BBN 700CO2	10K/min – 700 C	CO2	Needles

The removal mechanism mainly involve adsorption as primary step however, it is observed in literature to be followed by Persulphate oxidation based degradation. The porous surface of biochar help to entrap more molecules than any other surface adsorption. The degradation step complements the complete removal of toxicity by breaking down the effluents into CO_2 and H_2O. In this study we will analyze surface area, porosity, pore size distribution and adsorption/desorption capability of biochar. The adsorption capacity will be evaluated by altering pH from 2 to 10.

3. Literature review

3.1. Adsorption

The mechanism of this procedure based on physical as well as chemical interaction. The adsorption mechanism consist of three steps; External diffusion, Particle diffusion, Surface reaction. The polarity of adsorbate molecules aids the interaction by pore filling, hydrophobic interaction, electrostatic attraction or π-π interaction. It can be generally considered to be derived by weak interactions. Chemical adsorption is carried out by electron sharing pairs that forms a chemical bond between adsorbent and the adsorbate. It is not exclusively defined to be

limited to one or both phenomenon but it is considered to occur simultaneously and complementing each other.

At first the adsorption takes place at faster pace. The porous structure of biochar helps the Tetracycline (TC) molecules to diffuse into the adsorption sites very rapidly in the initial phase. The aromatic ring of each TC molecule has a number of polar groups including –OH, –NH_2 as well as 8 –H bond donors and 11– H bond acceptors (18) The phenolic hydroxyl groups on TC molecule favors the hydrogen bond formation with C-H group on Biochar surface (13). TC binds with π electrons and thus enabling π- π interaction for chemical adsorption. Once all the available sites on Biochar surface are consumed i.e. saturation, the adsorption slows down and it is said to have achieved equilibrium. (19)

Table 2 Differences between physical and chemical adsorption (19)

Parameter	Chemical adsorption	Physical adsorption
Type of bonding	Chemical bond, electrostatic interaction, ion exchange	Van der Waals, hydrogen bond interaction
Heat of adsorption	20-400 kJ/mol	10-40 kJ/mol
Adsorption-desorption	Irreversible, adsorbed and desorbed compounds will be different.	Reversible,
Activation energy	High	Low
Adsorption temperature	High	Low
Layer formation	Monolayer	Mono or multilayer

Adsorption is generally exothermic defined by Gibbs free energy. Adsorption is observed to be spontaneous, the change in Gibbs free energy is negative ($\Delta G < 0$). In adsorption, the adsorbate is adsorbed on the surface and decreases entropy ($\Delta S < 0$). Thus, enthalpy must be negative to

have a spontaneous process. It is reasonable to assume that majority of adsorption processes are exothermic. Gibbs free energy is given by following expression

$$\Delta G = \Delta H - T\Delta S$$

G is Gibbs free energy, H is enthalpy, T is temperature and S is entropy.

3.2.   Effect of Parameters

A literature review of different parameters that might fall upon in a particular waste stream. It will be helpful to assess better results and see if it could be beneficial to undergo a pretreatment of the waste stream.

3.2.1. The pH value:

Solution pH greatly defines the adsorption capacities of the biochar. The pH value determines the reactive oxygen species and the surface charge at the biochar surface. Hua Wang et. Al. studied the pH increase increased adsorption capacity initially until pH5 but then fell (20) The pH of the solution changes the surface charges of tetracycline and biochar, and therefore shows an influence on the adsorption processes. In case of higher pH, the solution becomes higher in OH$^-$ species or OH• radicals. The solution is more in OH$^-$ ions so it is in weak acidic condition so it carries strong oxidative ability for electron rich organic compounds and therefore is able to degrade pollutants. When the pH is lower so the solution is in strong acidic environment, this lower pH than the zero potential of biochar surface carries strong affinity for anionic species. TC is an amphoteric molecule and we focus on the three forms of TC that could exist in respective pKa values (3.32, 7.78, and 9.58). it depicts four kinds of species where the most dominant presents when pH is less than 3.3 and it is cationic. above 3.3 and below 7.7 it is zwitterionic or dipolar. and anionic at pH> 7.7. (13)The biochar surface is electron deficient because the biochar was positively charged when the pH was 2-4. As a result there forms a relatively weak π-π interactions between biochar and tetracycline and a decreased adsorption capacity (20) When

the pH is greater than 8, anionic TC contributed more than 50% to adsorption. This can be said due to negative charge assisted H bond (–(CAHB)) that forms between the negative tetracycline species and surface carboxylate of the biochar (20) as observed in this adsorption study.

3.2.2. Concentration and biochar dosage:

The initial concentration of pharmaceutical in a solution an important factor to assist mass transfer. Concentration gradients reduces resistance in adsorption by providing a driving force. The effects on concentration also increases interactions between the surface and adsorbates. Several reports have shown that an increase in initial concentration has resulted in higher adsorption capacities until the adsorbent is saturated. Ziyang et al (13) used persulfate for pharmaceutical degradation and have observed increased efficiency with increase of biochar dosage. This is because of more adsorption sites on biochar surface so improving degradation. Xiong et al (21) utilized biochar for adsorption and peroxodisulfate as catalyst for TC degradation. Moreover they implemented magnetic biochar which further improved the degradation up to 88%.

3.2.3. Coexisting ions:

Ions effects how any pollutant molecule will be able to adsorb on biochar surface. Cations can have positive or negative effect on adsorption capacity, anion however have negligible effects. A study by Pan et al (22) reports the presence of Na+ and Ca+ ions tend to reduce the adsorption of TC on biochar surface. The presence of such ions hinders the adsorption sites and the surface functional groups on biochar sometimes react with these ions and reduce further adsorption capability. The presence of certain cations promotes the adsorption by reducing the solubility of the target pollutant and make it available to get captured by biochar surface (23)

3.2.4. Solution temperature:

The effect of temperature on adsorption capacity is summarized by, "(i) modify molecular activity at solid liquid interface, (ii) interrupt the interactions among the functional groups of solute and adsorbent species, and (iii) modify the nature of adsorbent" (24) Temperature can determines how the pollutant molecules will be able to interact with biochar surface. With the temperature rise, the diffusion efficiency increases and the mobility of target particles helps interaction with adsorbent surface. In physical adsorption, the kinetic energy received from the high temperatures gives the adsorbate molecules enough energy to break the weak interactive forces. For chemical adsorption, the initial increase in temperature shows higher adsorption capacity due to a required activation energy. The capacity declines as the temperature increases more due to kinetic energy overcoming the strong forces holding together the adsorbates on the surface (25). If the target pollutant has to be degraded further, it will be possible to improve the efficiency of degradation by selecting the right temperature. For instance, Ziyang et al (13) studied persulfate based degradation of TC using biochar and determined the optimum temperature rise that is beneficial for the process. In the meantime it is important to keep the process's economic concerns as well as keep the molecules adsorbed on the adsorbate.

4. Characterization techniques

4.1. XRD

XRD characterization is done using D8 Advance Eco diffractometer equipped with a Lynxeye detector available in Geology and reservoir lab UIS. It helps to determine the underlying crystal structure of a material; it enables verification of the crystallinity of structure. Crystals are regular arrays of atoms, whilst X-rays are waves of electromagnetic radiation. Crystal atoms scatter the incident X-rays is known as elastic scattering; the electron is known as the scatterer. A regular array of scatterers/atoms produces a regular array of spherical waves. In the majority of directions, these waves can cancel each other out i.e. destructive interference. But they still add constructively in a few specific directions, governed by Bragg's law:

$$2d\sin\theta = n\lambda$$

Where, d is the spacing between diffracting planes

θ is the incident angle,

n is an integer, and

λ is the beam wavelength

The specific directions appear as spots on the diffraction pattern called as reflections. It is therefore said that the X-ray diffraction patterns resulted from electromagnetic waves impinging on a regular array of scatterers. X-rays are effectively used to produce the diffraction pattern because their wavelength, λ, is often the same order of magnitude as the spacing d, between the crystal planes (1-100 angstroms).

4.2. TGA

Mettler Toledo TGA/DSC 3+ was used to carry out In thermogravimetric analysis (TGA). For the analysis, sample is continually weighted while heating and an inert gas is passed over it throughout the analysis. The atmosphere can be set as inert atmosphere, synthetic gas mixtures or vacuum. Thermogravimetric analysis (TGA) measures the property of mass related to temperature change. It is very helpful to determine the activation temperature for adsorbtion. Some solids undergo reactions upon heating and evolve gaseous byproducts. These gaseous byproducts are removed and changes in the mass of the sample are recorded. TGA generally employs three variations:

Dynamic TGA - Temperature continues to increase over time and mass is recorded. This gives simultaneous identification of how much gas is removed and the temperature at which it occurs.

Static TGA - Temperature is held constant and the mass is measured. This analysis is used to gain information about a decomposition that occurs at a certain temperature or to investigate the ability of material to withstand a given temperature.

Quasistatic TGA - Sample is heated in multiple temperature intervals, and held at the intervals until the mass stabilizes. This method is used to investigate substances that are known to decompose in various ways at different temperatures.

In this study we employed Dynamic TGA. The activation temperature point is chosen where moisture and content evaporates from the pores. This corresponds to the first flat plateau in the TGA curve. For biochar, the amount of moisture, organic carbon, carbonates, and ash content can be 40 determined through TGA.

4.3.   UV spectrometry

UV-vis spectroscopic data gives qualitative and quantitative information of a given compound. In case of both quantitative and qualitative analysis, it is important to use a reference cell to zero the instrument for the solvent the compound is in. In case of quantitative analysis, calibrating the instrument using known concentrations of the compound with the same solvent as the unknown sample, will be required. If just proof that a compound is in the sample being analyzed, a calibration curve will not be necessary. If a degradation study or reaction is being performed, and analysis of concentration of the compound in solution is required, a calibration curve will essentially be needed.

To make a calibration curve, at least three or five concentrations of the compound will be needed. The characterization technique works on absorbance of light energy or electromagnetic radiation, which excites electrons from the ground state to the first singlet excited state. The UV-Vis region of energy for the electromagnetic spectrum ranges from 1.5 to 6.2 eV and relates to a wavelength range of 800 - 200 nm. The instruments has a light source, a sample holder and a detector, but some have a filter for selecting one wavelength at a time. The Beer-Lambert Law, is the working principle of this absorbance spectroscopy, i.e.

$$A = \varepsilon bc$$

For a single wavelength, A is absorbance (unitless, or arbitrary units), ε is the molar absorptivity of the compound or molecule in solution ($M^{-1}cm^{-1}$), b is the path length of the cuvette (usually 1 cm), and c is the concentration of the solution (M).

4.4. BET

Brunauer-Emmett-Teller (BET) theory explains the physical adsorption of gas molecules on a solid surface and serves as a basis for an important analysis technique for the measurement of the specific surface area. Nitrogen is used as gaseous adsorbate for surface probing by BET methods. It is therefore important to keep the analysis temperature same as the boiling temperature of N2. (26) It is not always essential to use N2 as adsorbate, other adsorbates are also utilized like argon, carbon dioxide, and water. Specific surface area is a scale-dependent property and we imply that the quantities of specific surface area determined through BET theory depends on the adsorbate molecule and its adsorption cross section. Method is commonly applied to calculate the specific surface area on the basis of nitrogen adsorption isotherm measurements. The linear form of the BET equation is as follows

$$\frac{1}{v(\frac{p}{po}-1)} = \frac{C-1}{VmC}\frac{p}{po} + \frac{1}{VmC} \tag{4.1}$$

where p/p^0 is the relative pressure,
v is the specific amount adsorbed at relative pressure p/p0
Vm is the volume of monolayer adsorbed gas
C is a constant related to energy of monolayer adsorption

By plotting the linear BET equation, the monolayer adsorbed volume (Vm) is calculated with the formula

$$Vm = \frac{1}{a+b} \tag{4.2}$$

where a is the intercept ($a = \frac{1}{nmC}$)
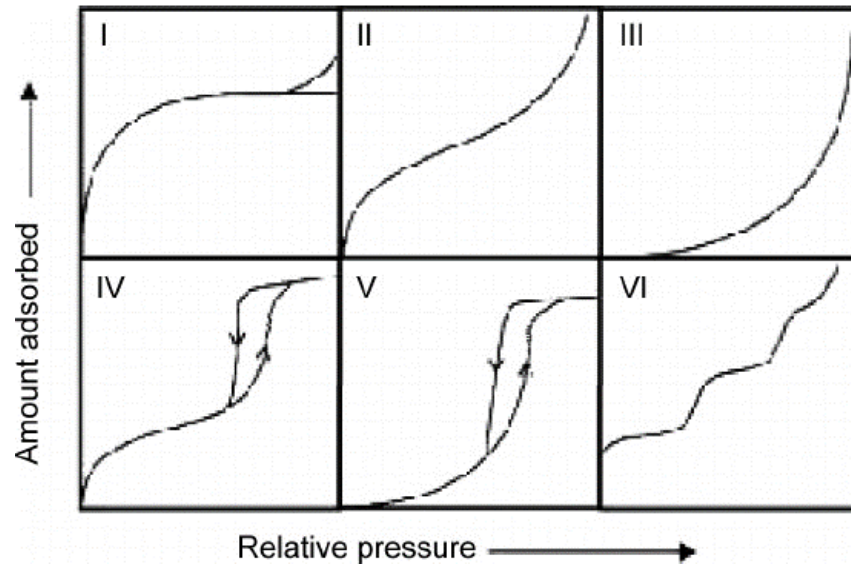b is the slope ($b = \frac{C-1}{nmC}$)

Figure 4 Types of Adsorption isotherm by IUPAC

Several types of adsorption isotherms for gas-solid equilibrium are defined that are expected to achived from BET analysis.

- Type (I) isotherm is used for describing adsorption on microporous adsorbents. This isotherm is used when the adsorption follows the Langmuir theory and is saturated when the surface is covered by a monolayer of adsorbate.

- Type (II) and (III) isotherms are used to describe macro-porous adsorption. In type (II) isotherm there is an initial formation of a monolayer. Subsequently, multilayer adsorption happens and the adsorption increases.

- Type (II) isotherm are dominated by strong adsorbate-adsorbent interactions. For type (III) adsorption, the adsorbate-adsorbate interactions are dominant. As more adsorbate attaches on the surface, the adsorbates interacts more frequently with the attached adsorbates increasing the adsorption.

- Type (IV) and (V) isotherms describes mono-, multi-layer adsorption and capillary condensation. The isotherms are used for mesoporous surfaces. In type (IV), monolayer adsorption occurs first and is followed by multilayer adsorption. At the saturated vapor pressure, the mesopores are filled with liquid inhibiting further adsorption. This is known as capillary condensation. Type (V) adsorption happens the same way as type (III), but the

capillary condensation prevents further adsorption. The curves for type (IV) and (V) shows hysteresis which are deviation in the adsorption- and desorption curves.

- Type (VI) isotherm shows adsorption that can happen with multiple steps. This data can be used to characterize the isotherm type for nitrogen sorption.

4.5. Adsorption experiment

In adsorption experiment (liquid-solid), the adsorbent is activated at a specific temperature to remove the solvent and moisture in the pores. A known initial concentration and volume of the aqueous phase containing the adsorbate is measured. The mass of the adsorbent is measured after activation. Adsorption occurs under isothermal conditions. The relation between the adsorption uptake is calculated with the mass balance equation 5.6. The equilibrium concentration is indirectly measured with UV-spectroscopy. A calibration curve is made with solutions of known concentrations. The calibration curve gives a linear relation between absorbance to the concentration. Equilibrium concentration is calculated using the equation:

$$Ce = \frac{Absorbance - b}{a}$$

where Ce is the equilibrium concentration of aqueous phase
b is the interception of the calibration curve
a is the slope of the calibration curve

4.6. Adsorption isotherm

The equilibrium adsorption uptake occures when the adsorbent has reached maximum capacity for a given equilibrium concentration of adsorbate. This information is often presented as adsorption isotherms. The different equilibrium uptakes of adsorbate is plotted against the equilibrium concentration for solid-liquid adsorption. The adsorption isotherms gives important information on the affinity between adsorbent and adsorbate. The adsorption capacity for a given equilibrium concentration can be described by the mass balance equation

$$qe = \frac{(Co - Ce)V}{M}$$

where qe is the adsorption capacity (mg/g)
Co is the initial concentration of adsorbate in the aqueous phase (mg/L)
Ce is the equilibrium concentration of adsorbate in the aqueous phase (mg/L)
V is the volume of aqueous phase (L)
M is the mass of activated adsorbent (g)

Many models for adsorption isotherms have been developed including Langmuir, Freundlich, Brunauer – Emmett – Teller (BET), and Dubinin-Radushkevich (D-R). For solid-liquid adsorption, Langmuir and Freundlich are the most applied isotherms. The Langmuir isotherm is based on a monolayer adsorption on the surface of the adsorbent. Additionally, there are no lateral interaction between the adsorbate molecules from weak dispersive forces, and the surface sites have equal affinity for the adsorbates (27) The Langmuir equation for solid-liquid adsorption is

$$qe = \frac{Q^o b \, Ce}{1 + bCe}$$

where qe is the equilibrium loading of adsorbent (mg adsorbate/g adsorbent)
Q^o is the monolayer adsorption capacity where the adsorbate cover the whole surface (mg/g)
Ce is the equilibrium concentration of adsorbate in aqueous phase (mg/L)
b is the a constant related to free adsorption energy

The Freundlich isotherm is another model that is based on empirical data. The model can describe adsorption on a heterogenous surface and multilayer adsorption. (27) The equation for Freundlich is given by

$$qe = K_F \, Ce^{1/n}$$

where qe is the equilibrium loading of adsorbent (mg adsorbate/g adsorbent)
Ce is the equilibrium concentration of adsorbate in aqueous phase (mg/L)
K_F is a constant related to adsorption capacity
1/n is the intensity of adsorption (larger value of 1/n indicates favorable adsorption)

5. Materials and methods

The focal material of interest i.e. biochar was supplied by SINTEF Energy. The biochar was made form Birch bark in the presence of different gaseous atmosphere. It was intended to give different pore sizes to the biochar at the end of pyrolysis. Pyrolysis was done at heating rate of 10K/min until 700 °C (~ 975K) as final temperature. The samples were made from the feedstock holding chips type and needles type morphology. The pharmaceutical compound that was selected from the list of High risk quotient pharmaceutical waste was Tetracycline. Tetracycline hydrochloride (95.0-102.0%) form Sigma Aldrich was used for the experiments. Table 4 enlists source of chemicals and other equipment used during the experiments.

Table 3 Chemicals and equipment

Chemicals Used		
name	Phase	Source
BBN 700 N2	solid	SINTEF
BBN 700 CO2	solid	SINTEF
BBC 700 N2	solid	SINTEF
BBC 700 CO2	solid	SINTEF
Tetracycline	solid	Sigma Aldrich
HCL 1M	aq	Sigma Aldrich
NaOH 1M	aq	Sigma Aldrich
Equipment		
- Ultra centrifuge - Digital orbital shaker - Ultrasonic water bath - Vortex mixer - Ph indicator - Hot air oven - Magnetic stirrer bars - Magnetic bar retriever - Micropipette - Finnpipette - Glass vials - Beakers - Pasteur pipette - Glass pipette - Mortal pestle		

- **Volumetric flasks**
- **Precision scales**
- **Centrifuge tubes**
- **Syringe filters**
- **Various other**

5.1. TGA

TGA analysis was done for all of the four biochar samples to collect information about volatile matters, moisture and ash content. About 10mg of each sample was placed in alumina oxide crucible. The samples were then heated from room temperature to 900°C at the rate of 10 °C /min in the presence of synthetic air. The experiment was run for 4 hours until the complete dehydration was achieved. The sample was cooled to room temperature and weight loss was determined to evaluate the volatile matter present initially. The data was exported as xy-files and plotted in excel

5.2. XRD

X-ray diffraction was done to identify presence of any crystallographic structure in the biochar lattice. The samples were finely grounded using mortar and pestle and placed on the sample holder (sample reception $\emptyset$ 25 mm). A flat glass plate was used to slightly compress the sample and smoothen the surface of the powder. The X-ray tube was energized at 40 kV with a current of 25 mA. The samples were scanned from 2° to 50° 2θ with step of 0.0103° and a scan speed of 5.85°/min. The data was exported as xy-files and plotted in excel.

5.3. BET Analysis

Nitrogen adsorption/desorption isotherms of biochar samples were determined using BET TriStar II 3020 3.02 available at department of energy and petroleum engineering UIS. Before the gas

adsorption measurements, the samples were degassed in a vacuum system and at a temperature of 120 °C for 24 h. The samples were then cooled down to 25 °C prior to the analysis. The samples were then weighted and transferred to the relevant ports at the BET equipment. The isotherm was measured at liquid nitrogen temperature (-196 °C or 77K) and nitrogen pressure ranging from 10^{-4} to 0.995 P/Ps (relative pressure of N).

The total pore volume was calculated from nitrogen adsorption data as volume of liquid nitrogen The surface areas were calculated using the BET equation. Average pore diameter were obtained through the Barrett-Joyner-Halenda (BJH) method. In addition to the objective, the BET analysis can be used to analyze the t-plots to further determine the percentage of micropore, mesopore and macropore. Do Thi et. al. (28) determined the percentages of pore sizes by using t-plot method, Micropore surface area was calculated from ratio between micropore area and total surface area. The micropore volume is calculated by its percentage with total surface volume. The micropore volume is subtracted from the total volume to get meso+macro pore volume.

5.4.   UV Spectroscopy

Different concentrations of TC was determined using UV vis spectrophotometer. 6 different concentrations were prepared and analyzed via UV spectrophotometer and a calibration curve was developed. Full spectrum scan in the wavelength range of 100-900 was carried out. Linear regression was obtained to standardize the concentration against absorbance.

5.5.   Absorption of TC on biochar

The adsorption capacity was evaluated in two ways. Biochar sample with highest surface area i.e. BBN700CO2 was selected. It is dried in oven at 100°C for 24 hours before suspending in the solution. Stock solution of TC with concentration 60mg/L was prepared in distilled water in a schott bottle. The concentration is then reduced to make 50mg/L, 40mg/L, 30mg/L 20mg/L and 10mg/L in five 50ml beakers. Predefined loading of biochar i.e. 50mg was added to 25ml of each

prepared solution. The beakers are kept at room temperature for 24 hours, 72 hours, 96 hours and 120 hours with constant stirring. The respective absorbance was tested at each stated number of hours to determine if the saturation was achieved.

The literature does not clearly state the concentration of TC that is exposed in waste streams. Therefore an intermediate capacity was chosen to determine the effect of reactive oxygen species on its adsorption capacity on biochar. The pH of TC i.e. 4 is reduced as well as increased by addition of 1M HCl and 1M NaOH solutions respectively. The solution with pH2, pH6, pH 8 and pH10 were prepared. 25ml of 20mg/L TC solutions are exposed to 50mg of biochar each for 120 hours with assistance of continuous stirring to ensure high contact. Biochar was kept in oven at 100°C for 24 hours prior the dispersion in solutions; to ensure removal of any entrapped moisture.

6. Results and discussion

6.1. XRD

The sharp peak observed around 29° (2θ) indicates inorganic compounds. It is mostly indicates the presence of Calcite or Mg-calcite crystalline phases. The observation of calcite can be expected from calcium oxalate present in various type of woods/bark during combustion. A large range of biochar prepared at high temperature of 700°C are known to carry Calcite which is formed by transformation of whewellite in biochars with increased pyrolysis temperature. (29) No sharp and high intensity crystalline peaks were observed and it can be expected because the biochar samples were made from bark. Crystalline peaks with high intensity in the sample would indicate mineral impurities such as inorganic oxides which indicates increased ash content. In case of BBC700N2 and BBN700N2 no such sharp peak has been observed. The table is given by Johnston & Balwant et. al. can be used to analyze the crystalline peaks. The considerably small peak around 35° (2θ) in each biochar type corresponds to Aluminum that is most possibly detected from sample holder.
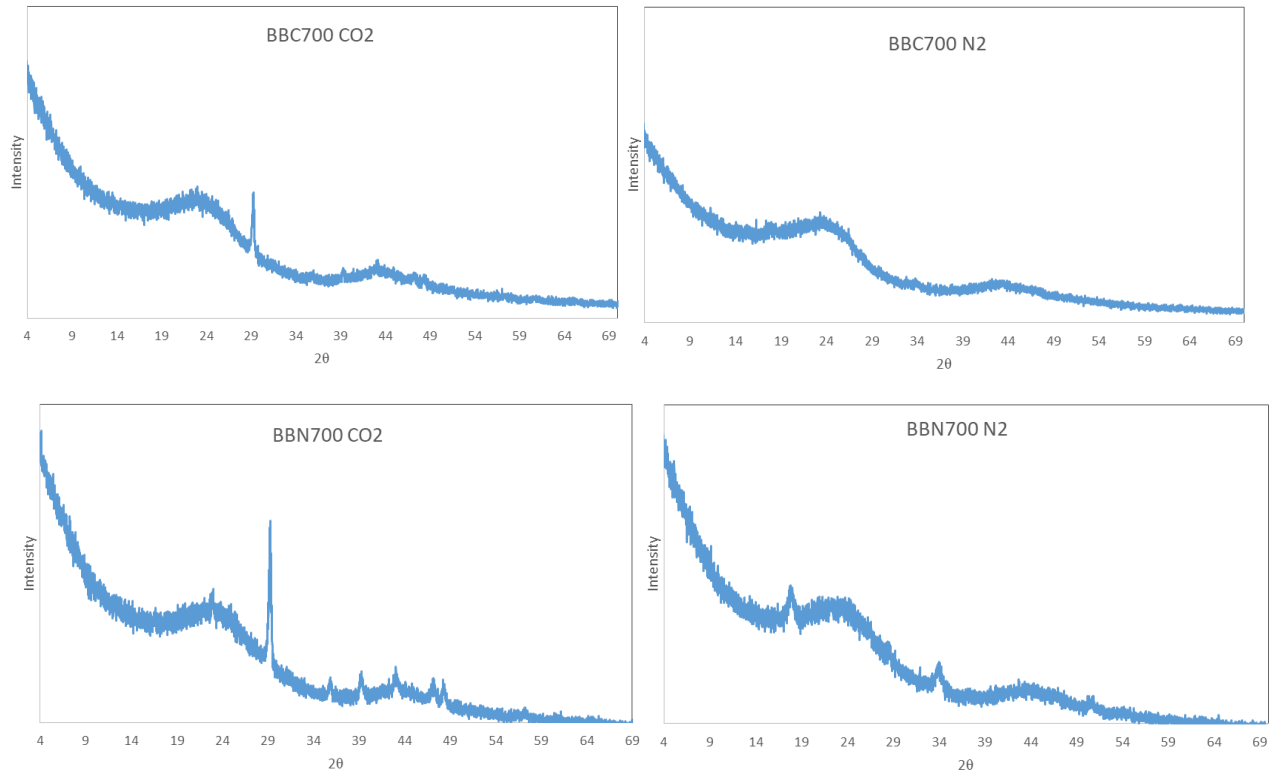
Figure 5 XRD plots of biochar samples

The broad peak observed in XRD plots of BBC700CO2, BBN700CO2 and BBN700N2 indicates amorphous carbon or silica. (30) This ranges from 20° to $26^{\circ}(2\theta)$ as shown in figure) is formed due to scattering of X-rays by amorphous carbon and sometimes amorphous silica. Such broad indication is present in case of BBN700N2 as well but it does not seem much prominent. It can be stated that the broad hump corresponds to the presence of interlaying graphite carbon. These carbonates can be suggested to present due to process followed for the preparation if biochar. The samples prepared in the presence of CO_2 i.e. BBC700CO2, BBN700CO2 can be
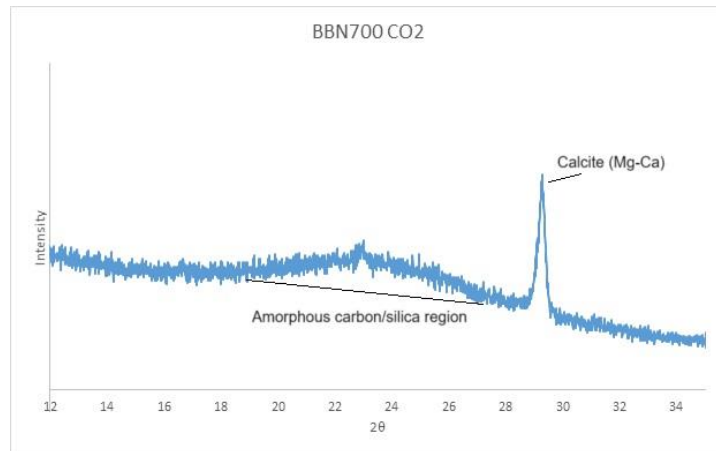
Figure 6 XRD measurement of biochar samples. Amorphous carbon is observed

perceived to have entrapped CO2 during the pyrolysis. This could be a possibility that is lacking in case of BBC700N2 and BBN700N2. Traces of quartz can be depicted at the small peak around 26º. Some carbonate containing elements can be the origin of this observation i.e. soil particles mixed with bark samples when collecting the biomass (31)

6.2.   TGA analysis

TGA data for biochar samples were evaluated for decomposition steps it follow. The first weight loss region formed by the loss of moisture content occurred in the temperature range of 25°C to 200°C. The weight loss was calculated as a percentage of the initial mass. All of the four samples followed almost similar pattern and loss percentages. The moisture content out of total mass was calculated to be 3.5% of the total mass. Additional loss of 2.5% of the organic carbon content occurred from 200–500°C. Loss of total 11% of mass was observed after complete decomposition at 900°C. Johannes et. al. indicated the removal of carbonates in the temperature range of 500–900°C.
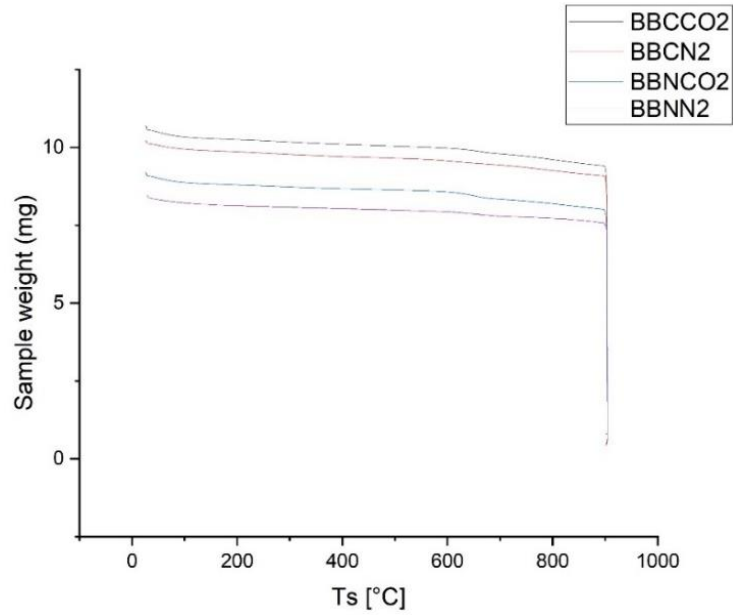
Figure 7 TGA plot of four biochar samples

As soon as the synthetic air is released inside the chamber, the weight loss due to burning is observed up to 85% of the initial mass. All of the four samples shows similar behavior and trend. The total loss of 96% of the sample mass shows 4% of ash content was present in the sample.
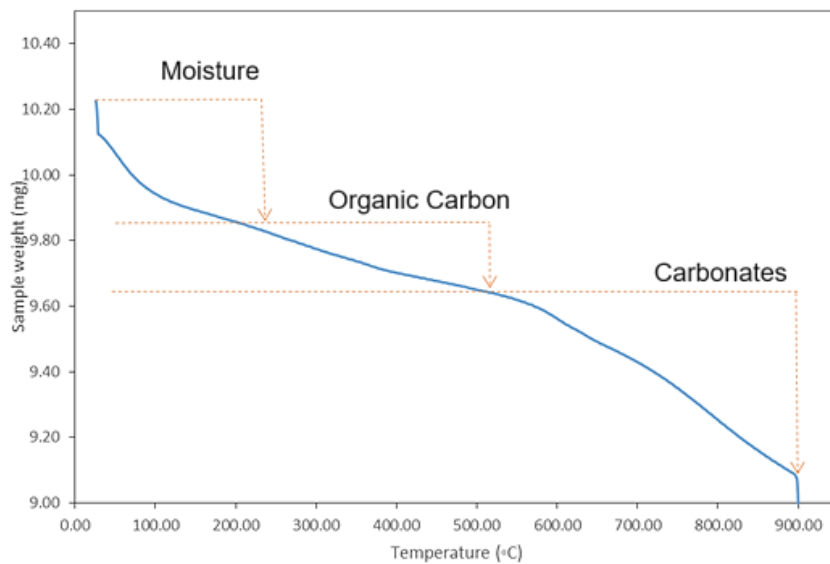

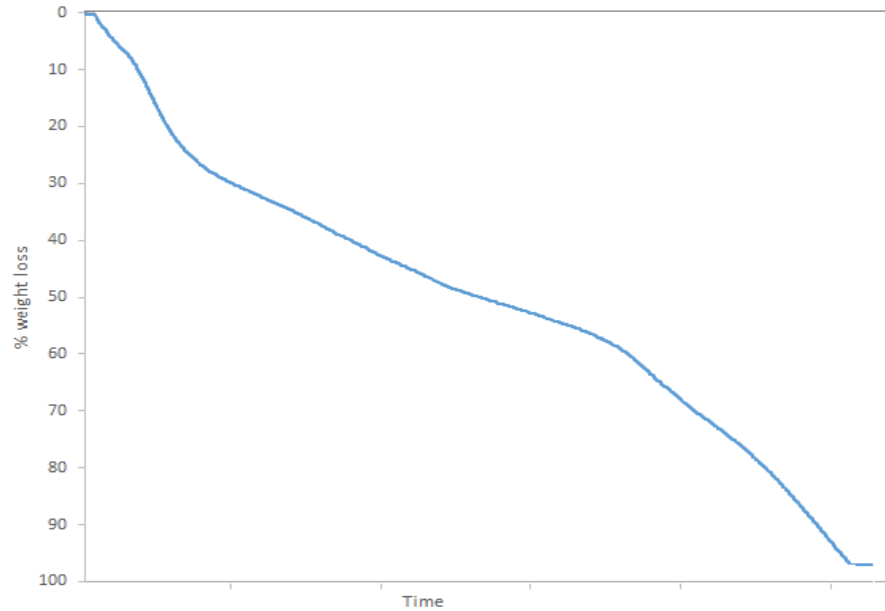*Figure 8 TGA of biochar in insert atmosphere with N2-flow*

Figure 9 . Weight loss measurement at 900 °C under synthetic air flow

6.3.   BET

The linear BET-plot is made from equation (4.1). Only selected few points in the BET graph were used to get a linear correlation. Table shows the results of nitrogen adsorption. The monolayer pore volume (Vm) was calculated using equation (4.2).

Table 4 BET analysis results summary

Sample	Surface area (m²/g)	Total pore volume (cm³/g)	Average pore size (nm)	V_m (cm³/g STP)	Correlation factor
BBC700CO2	394	0.154	1.37	90	0.9998
BBC700N2	235	0. 154	1.32	54	0.9999
BBN700CO2	358	0.142	7.37	82	0.9998
BBN700N2	278	0.117	7.06	64	0.9998

N2-sorption of biochar samples activated overnight at 250 °C under vacuum. The curve resembles a type (I) isotherm for all for the four samples.
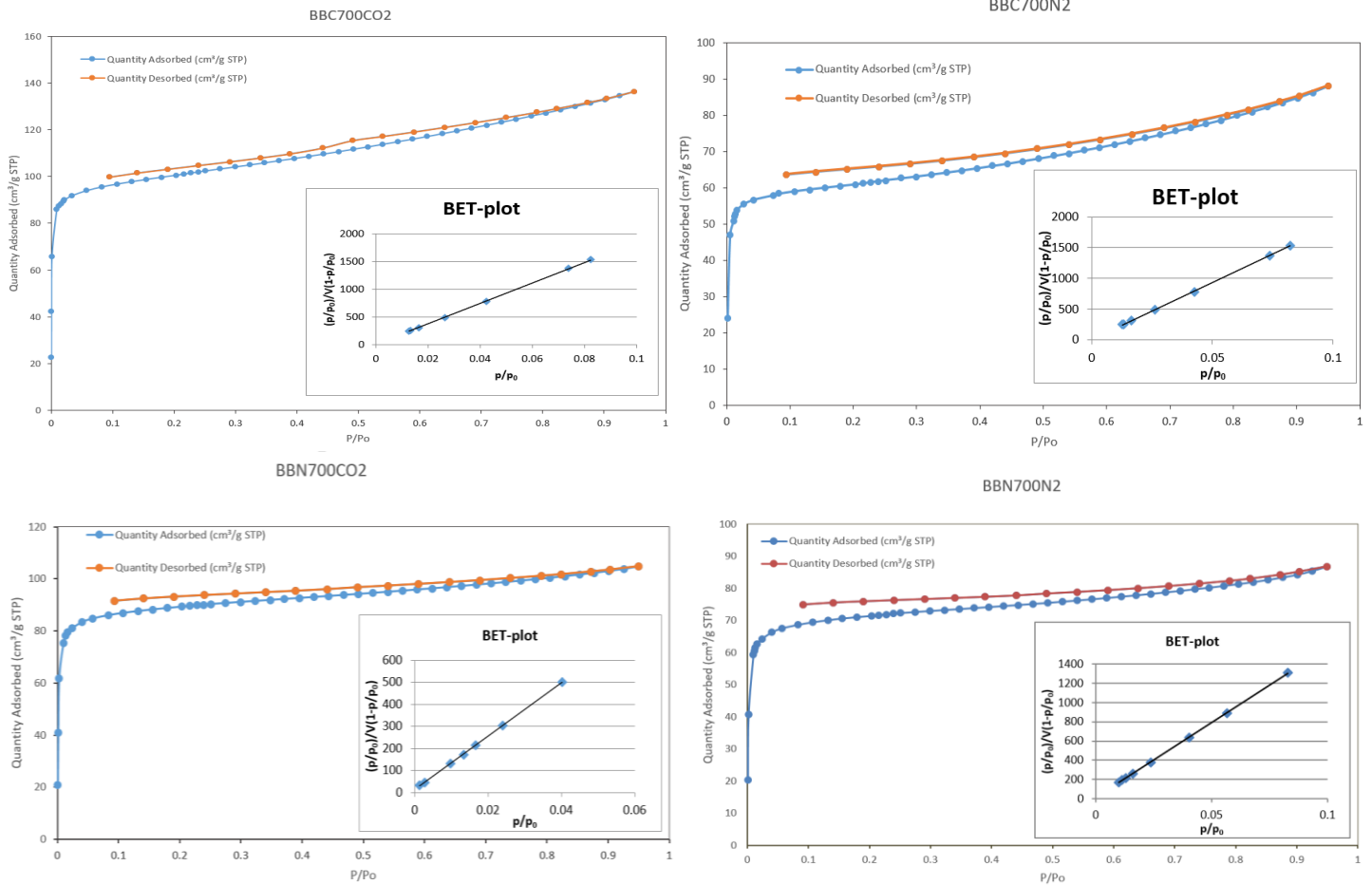
Figure 10 BET adsorption and desorption curve. The curve show hysteresis possibly caused by irreversible change of the adsorbent under sorption.

The adsorbtion/desorption procedure was completed around 24 hours of measurement except for BBN700N2 which undergone 36 hours of measurements. However, the surface area, pore size data does not reflect the reason of long measurement time. It could be said that the instrument might took longer to reach equilibrium and continue measurement when the nitrogen amount was stable inside the system. BET plot was also made. The adsorption drastically increases at low pressure indicating micro porous structure for biochar sample which have chips like morphology. It can be said that the nitrogen molecules are strongly connected to the adsorbent by chemisorption as indicated by the hysteresis formed. The open hysteresis indicated that there is a possibility of adsorbent to get changed during sorption when it comes to lower pressure and the nitrogen molecules are firmly entrapped in biochar structure. Thommes et. al. indicated the reason of such hysteresis to be pore blocking that occur when larger and smaller pores lies in

close affinity and makes the escape of gas molecules difficult een by larger pores. (32) Thommes et. al. further explains different hysteresis types and the experimental data of biochar resembles the hysteresis observed for micro-mesoporous carbon. Pore volume is plotted against cumulative pore volume which shows higher pore size distribution of larger pores > 3nm for both the samples which shows smaller average pore diameters.
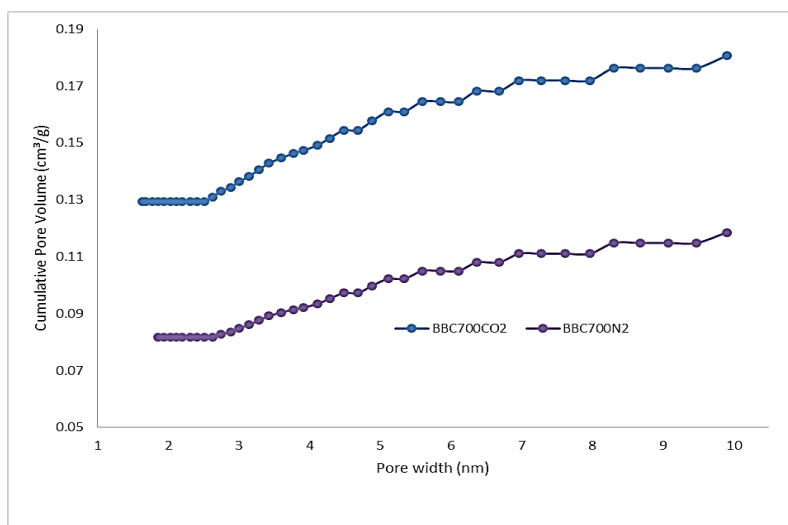

Figure 11 Cumulative pore volume vs pore width for samples with average pore size <2nm

6.4. UV vis spectrum

Full spectrum scan was carried out for 6 different TC concentration solutions. The spectrum shows relatively smooth curves for lower concentrations i.e. 10-40mg/L. The chosen wavelength was calculated by averaging the wavelengths from the highest peaks observed in the full spectra measurements. Two absorption peaks were observed at wavelengths of 276 and 357 nm as described by Wang et al in their studies (14). However 357 nm was identified as the maximum absorption wavelength for the determination of tetracycline concentration (33). The similar peak lies at 357nm and identifies the presence of TC in the solution. Calibration curve was calculated by linear approximation using the six concentration range from 10-60mg/L. The linear approximation gives a good fit with correlation constant of 0.953. The equation was later used to determine the concentration of the solutions after adsorption experiments.
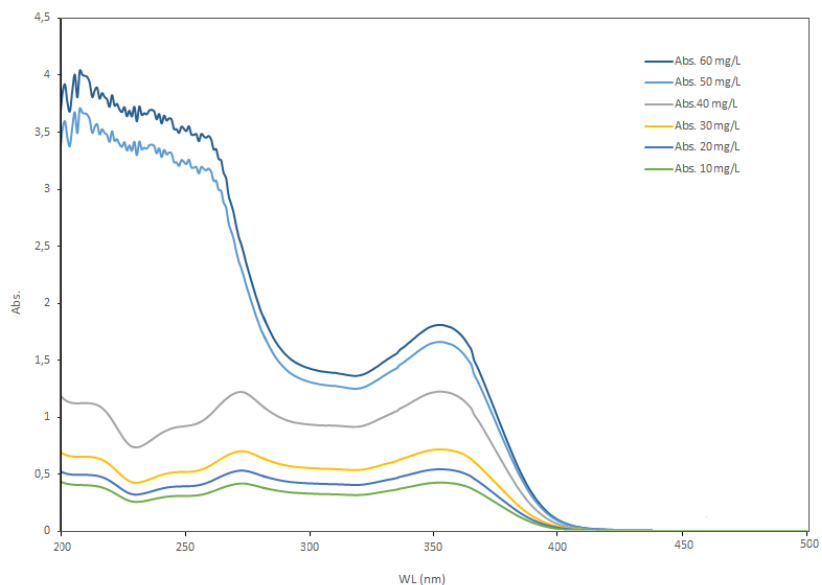
Figure 12 Full-specter UV-spectrophotometry of TC in concentration range (10 – 60 mg/L).
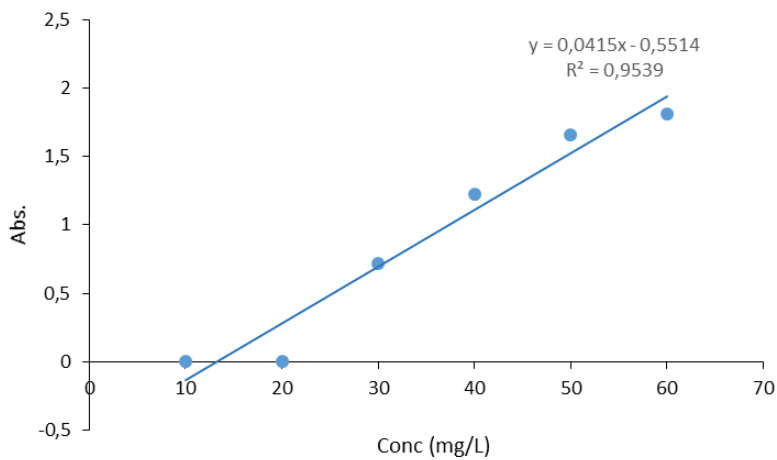

Figure 13 The calibration curve made by linear approximations of the absorbance at different concentration for wavelength 357nm

The calibration curve was made by linear approximations of the absorbance at different concentration against determining wavelength 357nm. The curve is made using Beer Lambert Law to relate the concentrations and absorbance. Y is the absorbance and x is the equilibrium concentration.

6.5. Change of pH effect on adsorption capacity

The pH has been studied as a determining parameter for adsorption capacities because of altered oxygen species that will be available to react after pH change. The TC solutions were made with varying pH and constant concentration. It was observed that increase in oxidative ability makes the TC molecule more adsorbed than that of less in OH^- ions. [20]There is an observation of peak changes that might happened due to possible reaction between the species or there might be decomposition of TC that have taken place. The standard pH of TC is pH4 which shows least uptake of TC on biochar figure 15.
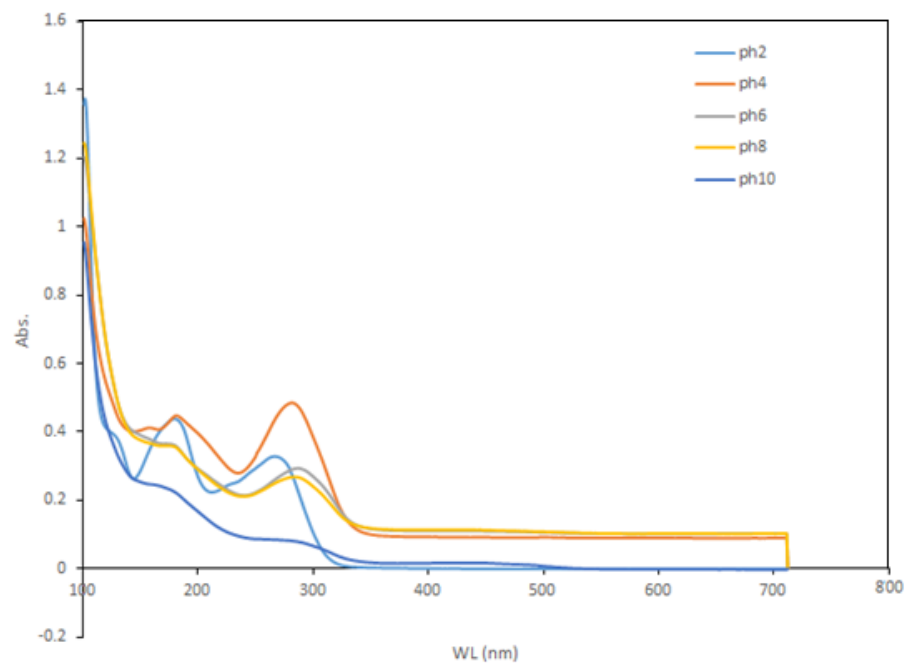

Figure 14 Full-specter UV-spectrophotometry of TC at concentration of 20mg/L and pH ragnge of 2-10
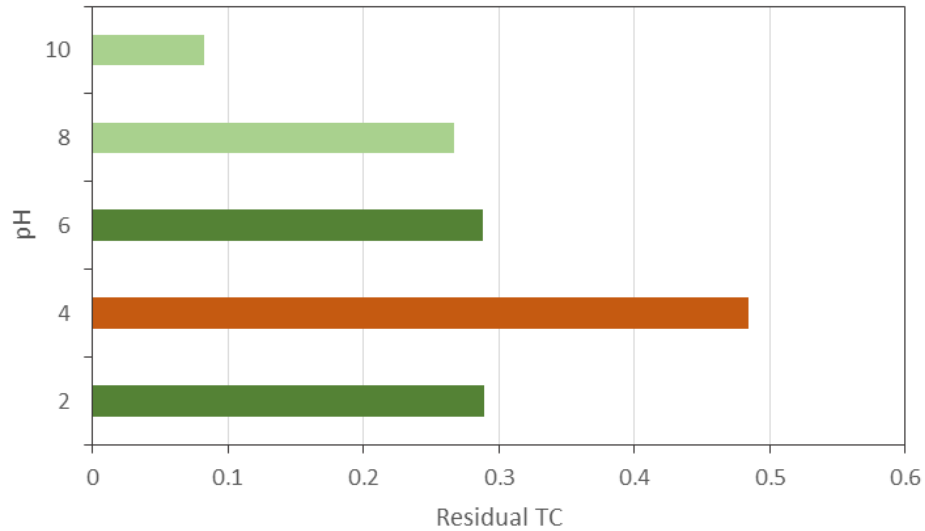
Figure 15 Bar chart indicating the residual TC in the solution after biochar adsorption experiment

The adsorption experiments were done with alkaline solutions of TC to evaluate maximum uptake on biochar. The concentration from 5-50mg/L were observed to be well adsorbed. The UV vis spectrum shows almost disappeared TC peaks besides some of the quantity left in case of 50mg/L solution. It can be asssumed to have biochar sample quantity exposed in the solution has reached equilibrium. The adsorbtion isotherm, figure 17 indicates the adsorbtion is achieved even at lower concentrations of TC. The pH10 adsorption isotherm shows that biochar is not fully saturated and could retain more TC if the residence time will be increased. On the other hand, the isotherm for pH4 solution does not seem to have attained, but will stabilise at higher equilibrium concentration. The adsorbtion capacities of biochar studied for TC by Yingjie et. al. states that the biochar prepared by pyrolysis at higher temperatures tend to have higher adsorbtion capacites. Their studied sample prepared at 700°C shown uptake of 11.90 mg/g of TC, however the data does not state about the pH of adsorbant (34). The maximum uptake of TC by BBN700CO2 was calculated to be 28.3 mg/g at pH10 and 19.5mg/g when the pH of solution was kept unchanged.
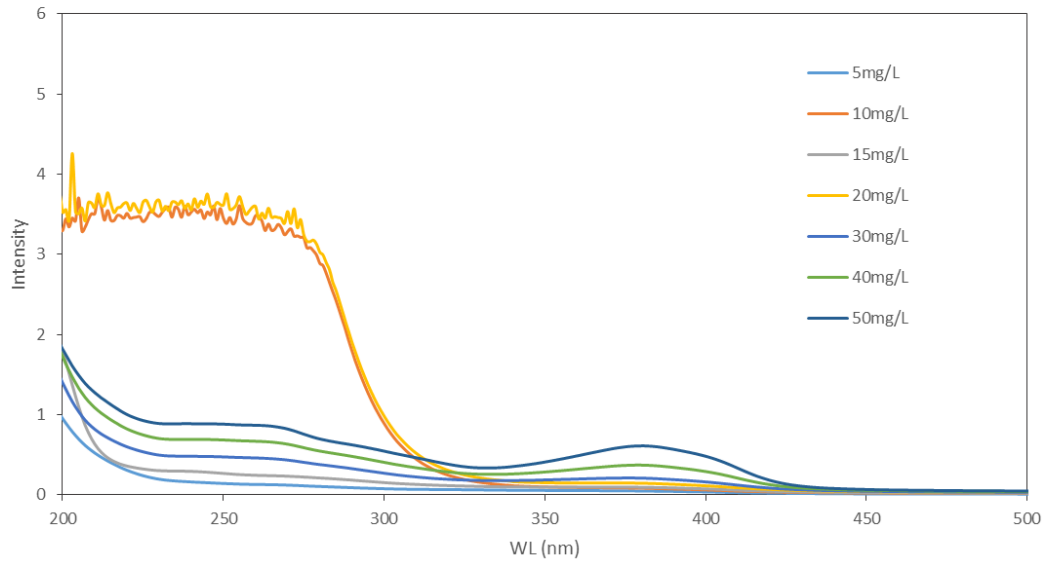
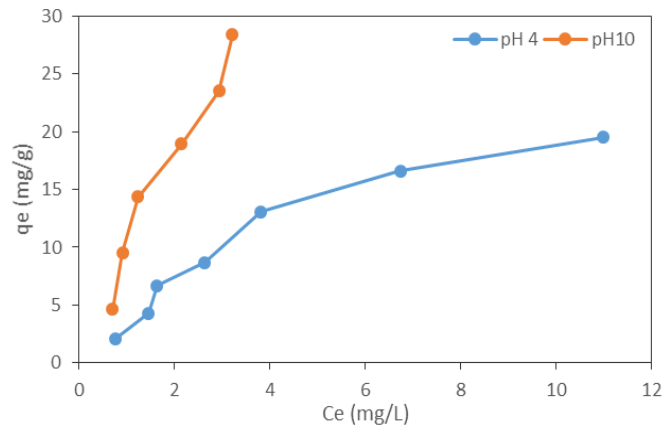*Figure 16 Full UV spectrum of solution in range of 5mg/L to 50mg/L at pH10 after biochar adsorption*

Figure 17 Adsorption isotherm from adsorption experiments for solution pH10 and standard pH

7. Conclusion and future work

The study intended to examine the characteristics of biochar and explore its applicability in removal of toxic pharmaceutical is attained positively. This study will help researchers to develop cost-effective treatment technologies for the removal of tetracycline and provides a rational support framework for the removal of other pharmaceutical pollutants in the future. The biochar samples were characterized by various methods to bring light to its physical attributes. An amorphous structure is highlighted in XRD study along with some degree of crystallinity due to traces of inorganic content. Biochar samples that were prepared by pyrolysis in the presence of Nitrogen shows no signs of crystalinity in XRD analysis. Raman or H-NMR techniques should also be used to gather information about functional groups for biochar. The TGA highlights very low content of ash for biochar samples. All of the four types followed similar loss of weight and content despite their difference in preparation methods. The ash content could have been lower for biochar prepared in the presence of N2 as no inorganic content was discovered. It can however be similar due to presence of silica region in each of the samples. BET analysis displayed micro and mesoporous structure of the biochar samples. The hysteresis observed suggest pore blocking and trapping of the nitrogen molecules in the larger pores which was seen much prominent for both morphologies i.e. chips and needle type where N2 was used during pyrolysis. Adsorption analysis shows conformational data and the change in pH of TC solution changes the surface charges of tetracycline and biochar and affected the adsorption processes. Adsorption isotherms were intended to fit the Langmuir and Freundlich models and it can be done as further steps in future to help predict the monolayer or multilayer adsorption on biochar surface. The biochar initially used for adsorption analysis is BBC700CO2 due to larger surface area. It was anticipated to observe similar adsorption behavior for other three samples due to least variation of characteristics observed from analysis. It should however be performed to validate the supposition. The alteration of pH to high OH^- species tend to adsorb more TC on biochar surface. The adsorption equilibrium took longer than other relevant studies i.e. 120 hours. The concentration checks were done at 24h, 72h, 96h and 120h interval to indicate highest drop of concentration in residual solutions. Such long residence time should be addressed in future. The

adsorption capacity of biochar was significantly improved by adjusting pH and this can be further studied in addition of other parameters i.e. temperature or biochar loading. This will help reduce the batch adsorption time without losing the efficiency.

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