**Biochar II: Synthesis, Characterization and Application**

**SYNTHESIS OF BIOCHARS**

1. **Pyrolysis or Thermochemical Method:**

The first method of synthesis or production of biochar/s employed is/are the Pyrolysis. Pyrolysis involves the chemical transformation (decomposition) of a sample on heating to a high temperature (400–1000 °C) [1, 2]. Pyrolysis is also known as a thermochemical treatment method, which can be applied to any organic (carbon-based) product. In this treatment, the material is exposed to high temperatures without oxygen, and separation is achieved via chemical and physical means. Historically, charcoal from wood via pyrolysis was essential for the extraction of iron from iron ore in the preindustrial era. Also, the invention of kerosene, the first transportable liquid fuel, brought about a revolution in lighting that touched and is still the case in even the remotest parts of the world using the pyrolysis method of kerosene production. Today the modern petrochemical industry owes a great deal to the invention of kerosene production using pyrolysis.

The pyrolysis is broadly classified into three types, viz.

* 1. Conventional or Slow Pyrolysis
	2. Fast Pyrolysis and
	3. Ultra-fast pyrolysis.
	4. **Conventional or Slow Pyrolysis Method:** In this method, the biomass is heated at low to moderate temperatures of around 300°C and a heating rate (<10°C/minute). The biomass feedstock particle size used in slow pyrolysis is in the range of (26.5–925 µm). Usually, the reaction time is long, and sometimes it may take many days to convert biomass to biochars. It has been used for thousands of years to convert wood into high yields of charcoal (bio-carbon). The main disadvantage of the slow pyrolysis process is that it generates lower yields of biochar, bio-oil, and gaseous products.
	5. **Fast Pyrolysis Method:** Fast pyrolysis is a process in which biomass and/or organic materials are rapidly heated between the temperature range of 450 - 600°C with a heating rate of 10-200 °C/s in the absence of air. Under these conditions, organic vapors, pyrolysis gases, and charcoal are produced. The biomass feedstock particle size must be < 1 mm. During the fast pyrolysis, the products obtained during the fast pyrolysis are of high grade or quality because of this vantage over the slow pyrolysis. It has gained worldwide interest, both in research and practical use.

Although fast pyrolysis was first investigated as early as 1875, various reactors were analyzed with the goal of heating biomass to temperatures exceeding 400 °C in a few seconds. Suitable reactors include bubbling fluidized beds, circulating fluidized beds, rotating cone reactors, auger reactors, entrained flow reactors, and ablative reactors. [3] Key features of these different classes of fast pyrolysis reactors are summarized in Table 1.1. [4]

Table 1.1 An overview of different fast pyrolysis reactor technologies (reproduced from ref. 17 with permission from Dr. Anthony V. Bridgwater)

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **Reactor type** | **Development****Status** | **Max. yield****wt%** | **Complexity** | **Feed size****specification** | **Inert gas****requirements** | **Specific****reactor size** |
| Bubblingfluidized bed | Commercial | 75  | Medium  | High  | High  | Medium |
| Circulatingfluidized bed | Commercial | 70  | High  | High | High | Medium |
| Rotating cone  | Commercial  | 70 | High  | High | Low | Low |
| Auger  |  Pilot | 60  | Medium  | Medium  | Low  | Low |
| Entrained flow  | Laboratory | 60  | Medium  | High  | High | Medium  |
| Ablative | Laboratory | 75  | High  | Low  | Low | Low |

It is enlightened from the above table that between the various kinds of reactors, fluidized beds have received the most attention for fast pyrolysis due to excellent heat and mass transfer characteristics, simplicity of operation, and relative ease of scale-up.

**1.3 Ultra-fast or Flash Pyrolysis:** Flash pyrolysis or ultra-fast pyrolysis, characterized by rapid heating rates (>1000 °C/s) and high reaction temperatures (900–1300 °C), has been shown to afford high yields of bio-oil with low, resulting in water content and conversion efficiencies of up to 70%. The residence times used are even shorter than those of fast pyrolysis, typically less than 0.5 s. To obtain such high heating and heat transfer rates, the biomass feedstock particle size must be as small as is practically possible, usually around 105–250 μm (60–140 mesh size) [5]. Compared to all pyrolysis methods discussed above, it is concluded that when the temperature is increased, the aromaticity, hydrophobicity, and surface area of biochar also increase, which makes it a suitable adsorbent for hydrophobic organic compounds.

1. **Torrefaction:** Torrefaction is a french word that means “roasting.” The art of torrefaction has been used in a host of industries for tea and coffee making, but only recently has it caught the attention of power industries to produce a coal substitute from biomass. Torrefaction is often called a pretreatment process as it prepares biomass for further use instead of direct use in its raw form. Torrefaction is defined as “ a thermochemical process in an inert or limited oxygen environment where biomass is slowly heated to within a temperature range of 200–300°C and retained there for a stipulated time such that it results in near-complete degradation of its hemicellulose content while maximizing mass and energy yield of solid product.” [6]. The distinctive features like low-temperature range, slow heating rate, and the low amount of oxygen, unlike in pyrolysis where zero or absence of oxygen is needed. These reasons have gained importance in the torrefaction process for synthesizing the biochars from biomass. The typical temperature range and heating rate for torrefaction are 200–300°C and < 50°C/min, respectively.
2. **Hydrothermal carbonization (HTC):** Hydrothermal carbonization is a thermal pretreatment coalification process used to convert the biomass into a coal-like product called hydrochar. The hydrochar produced by employing HTC processes has high carbon content and has high releasing heat energy, i.e., calorific value. Hydrothermal carbonization is also known as Wet Torrefaction as it uses hot compressed subcritical water. The HTC process is performed in high-pressure vas by applying relatively high temperature generally in the range 180–250°C and pressure of 1-5 MPa to biomass in liquid water for a few hours (0.5–8 h) in the absence of air. The heating rate is usually between 10-20 °C/s. The biomass experiences the following reactions, namely dehydration, decarboxylation, and decarbonylation, during the hydrothermal carbonization process. Hydrochar produced via HTC is hydrophobic and has brilliant binding capacities. Due to this, HTC hydrochar finds ample applications in fuel, as soil nutrient, as an adsorbent in material chemistry, as hydrogen storage, in lithium-ion batteries, or as supercapacitors and recently attracted considerable interest in the research field.
3. **Gasification:** The conversion of solid/liquid biomass or carbon-based fossil fuel materials into a gas or vapor and solid phase is known as Gasification. The gas-phase generally includes gases like [nitrogen](https://en.wikipedia.org/wiki/Nitrogen) (N2), [carbon monoxide](https://en.wikipedia.org/wiki/Carbon_monoxide) (CO), [hydrogen](https://en.wikipedia.org/wiki/Hydrogen) (H2), [carbon dioxide](https://en.wikipedia.org/wiki/Carbon_dioxide) (CO2), low molecular weight hydrocarbon gases like methane(CH4), ethane, and propane, as well as high molecular hydrocarbon such as tar. The gaseous phase is usually called “syngas,” The solid phase obtained during the conversion process is called “char or biochar.” The gaseous phase has a high heating power and can be used for power generation or biofuel production. The solid phase “char or biochar” includes the inert material having high adsorption capacity and unconverted organic compounds used in various applications such as wastewater treatment. Due to these reasons, biomass gasification is considered a way to increase the use of biomass for energy production, allowing widespread biomass utilization. The biomass gasification is carried out at very high temperatures, usually in the range of 800–1300°C with heating of 100 °C/s as compared to other processes employed for the synthesis of biochar from biomass. The gasifying agent or gasifying mediums used in the gasification process are; Oxygen, Air, and Steam. The heating value range in biomass gasification based on the gasifying medium used. Generally for oxygen 12-28, air 4-7, and steam 10-18 MJ/Nm3. The following are the main four steps involved in biomass gasification; oxidation (exothermic stage), drying, pyrolysis, and reduction (endothermic stages). [7]

**Typical operating parameters and products for Some Thermal Decomposition Processes**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Process**  | **Solid Residence Time (s)**  | **Heating Rate (°C /s)** | **Particle Size (mm)**  | **Final Temperature****(°C)** | **Product Yield (%)**  |
|  |  |  |  |  | Oil  | Char  | Gas  |
| Slow | 450–550  | 0.1–1  | 5–50  | <300  | 30  | 35  | 35 |
| Fast | 0.5–10  | 10–200  | <1  | <600  | 50  | 20  | 30 |
| Flash | <0.5  | >1000 | <0.2 | >1000 | 75  | 12  | 13 |
| Torrefaction | 10–60 min | <0.8 | <1 | 250 | <20 | 50-60 | <10 |
| Hydrothermal carbonization (HTC) | Days | <20 | <1 | >400 | 5-10 | 70-80 | <10 |
| Gasification | <1 hour | <100 | <1 | >800  | <10 | 10-12 | 70-80 |

**Why Do You Need to Characterize Biochar?**

Various applications of biochars depend on the biochar quality, which is determined by the biochar porosity, a functional group attached to the surface of the biochar, and material used to synthesize biochar. Preparation conditions like the type of reactor, synthesis temperature, reaction time will affect the properties of biochar. Whereas, when we consider the activation process of biochar to increase its properties towards application, it will change its morphology. The Morphology in surface area, pH, the molar ratio of elements, surface change, mineral contents, elemental composition, and active binding sites.

Physically and chemically active biochar also results in the different characteristics of the product. E.g., It was observed that physically activated biochar shows the microporous structure and increases surface area up to 880m2/g, while chemically activated biochar using phosphoric acid indicates the mesoporous structure and surface area up to 600m2/g.

BET surface area instruments indicate that physically activated pistachio shell biochar gives a surface area of 2596m2/g with about 90% burn at temperature 850 °C for 20 min of activation time prepared in spouted bed reactor. The minor heat and mass transfer resistances took place inside the spouted bed reactor. However, steam-activated biochars prepared through vacuum pyrolysis reactors have a lower concentration of functional groups, and surface area has increased from 50 to 1025 m2/g.

Therefore characterization of Biochar is necessary to find out chemical nature, surface area, functional group, active sites present on biochar. There are several analytical techniques used for the same, such as nitrogen adsorption isotherm, Fourier transform infrared spectrometry (FTIR), X-ray diffraction (XRD), Raman spectroscopy, NMR, scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) technique, BET isotherm models and X-ray spectroscopy (EDS), to name a few, all of which were briefly summarized.

**Fourier transforms infrared spectrometry (FTIR)**

FTIR is an analytical technique based on the absorption of infrared radiation by the sample material versus wavelength between 4000 and 400 cm−1. It is used to identify organic as well as inorganic materials. Mainly FTIR applies to detect functional groups present in materials like solid, liquid, and gases. When samples interact with light through absorption, emission and photoconductivity will result in FTIR spectra.

# Basic Principle:

The elements and bonds present in molecules are responsible for molecular bond vibration at various frequencies. According to quantum mechanics theory, a particular bond vibrates at several specific frequencies, corresponding to the ground state (lowest frequency) and several excited states (higher frequencies). The light energy for the transition from the ground state to the first excited state is equal to its energy difference. e.g., when Chinese author Yang Liu et al. prepared biochar in 2020 using Ca-bentonite, kaolin, and CaO at different temperatures like 450, 550, 650, 750, and 850 °C. The prepared biochar when characterized by an FTIR instrument. The broad absorption band observed around 3385 cm-1 because of O-H stretching, while the weak absorption band observed around 2921 cm-1 was due to O-H stretching and C-H stretching vibrations. The peak at 1707 cm-1 was for C=O stretching, associating with organics such as ketones, carboxylic acids, aldehydes, and esters in BC.[8] The weak peak around 1607 cm-1 might result from C=C stretching and N-H bending, showing alkenes and amines in BC. The peak around 1509 cm-1, 1109 cm-1, and 1057 cm-1 could be assigned to the N-O, C-N, C-O, and S=O stretching, indicating the existence of nitrogen-containing and sulfoxide compounds in BC. The absorption band of about 599 cm-1 was because of the C-Br, C-Cl, and C-I stretching vibrations, showing the presence of halogen compounds in BC. The peak observed at around 3385 cm-1, 2921 cm-1, and 1707 cm-1 found much weaker, indicating the decomposition of some organic compounds, such as alcohols, amines, alkanes, esters, ketones, and aldehydes, with temperature increasing from 450 °C to 850 °C. But the peak observed around 1100 cm-1 (C-O stretching) became stronger with temperature increasing from 450 oC to 750 °C, which indicated that enhanced the formation of alcohols, phenols, and carboxylic acids at a higher temperature. [9]

 **X-ray diffraction (XRD)**

XRD technique is mainly used to measure the intensity and angle of diffracted beams present in samples. As we know that Biochar is prepared by a pyrolysis method which mainly contains carbon or inorganic matters. Most commonly observed carbon crystallites in biochar are classified into two types: the first one is graphitized, and the second is non-graphitized carbon. The graphitized carbon is recognized by getting a sharp and narrow reflection pattern, while a broad reflection pattern indicates non-graphitized carbon [10]. e.g., In 2014, Yao et al. (2014) synthesized biochar using bamboo, bagasse, and hickory chips by incorporating montmorillonite. The presence of montmorillonite in the biochar matrix was identified by XRD for analysis. The peaks of montmorillonite observed at 6.4˚ (d = 13.840 A ˚), 6.9˚ (d = 12.803 A ˚), 19.9˚ (d = 4.449 A ˚), and 35.1˚ (d = 2.555A ˚) [11]

**Raman spectroscopy**

**Raman spectroscopy is studied to find out the structural characteristics of biochar. Researchers applied Raman spectroscopy to evaluate** functional groups present, graphite structures, and the amorphous nature of biochar. In Raman Spectroscopy, we observed Stokes **lines**occur at lower energy or longer wavelength than the Rayleigh line spectra, and the **anti-Stokes line** has higher energy. The higher and lower energy is correlated to the vibrational energy levels in the ground electronic state of the molecule.

e.g., Jorio et al. (2012) studied the C nanostructures of biochar with Raman spectroscopic analysis to evaluate crystalline C structures. The in-plane crystallite size distribution (La) was estimated using the ratio of D and G band intensities (ID/IG) of C nanostructures in biochar. Their findings revealed that the distribution of La in charcoal form biochar was 8–12 nm. The D and G bands of the Raman spectrum represent the breathing mode sp3 C in disordered graphite rings and sp2 C in ring structures and C D C bonds, respectively. [12]

**Scanning electron microscopy (SEM) and transmission electron microscopy (TEM)**

Scanning electron microscopy and Transmission electron microscopy are mainly concern with surface characterization techniques. SEM is having a focused and fine beam with lower resolution as compare to TEM analysis. It is taken topographical image, or we can consider a surface image with magnification capacity up to 2,000,000 times. The required sample can be thick or thin for SEM analysis, and without penetrating the sample, it will give you a 3D image analysis. When we compare SEM with TEM analysis, it will require less effort to prepare the sample, faster, easy to use, and economically favorable.

As compare to SEM with TEM analysis having a broad beam with higher resolution. It is capable of analyzing the internal structure of the sample with a magnification capacity up to 50,000,000 times. TEM required a more specific ultrathin sample with penetration it will give you a 2D image. When we observe, TEM analysis will require more effort to prepare the sample, slower, more complicated with trained analysts, and more expensive.

SEM and TEM are valuable microscopic tools in scientific research, such as biological, physical, and chemical. By comparing the differences between these two electron microscopes and sample information requirements, scientists can choose a more appropriate type of microscope to analyze the sample.

At the time of biochar characterization by using SEM instrument, generally studied with combined EDX techniques. For example, A. Ahmad et al. published an article in 2020 to remove methylene blue dye using biochar. For the synthesis of biochar, they choose materials like rice husk biochar (RHB)​, cow dung biochar (CDB), and domestic sludge biochar (SB) by pyrolyzing at 500 °C. On characterizing respective biochar using SEM-EDS analysis, they observed that the surface of RHB, CDB, and SB biochar was thick and porous. The pretreated elemental composition of Biochar in RHB, CDB, and SB was C, O, Al, Mg, Si, Ca, P, K, Cl, while in addition to these elements, Na was also found in CDB and Fe was present in SB. However, an increase in C, Cl, and S percentage was found in RHB, CDB, and SB post-MB treatment. [13]

When we discuss TEM analysis for biochar samples, it gives information about the particle size of the material. In 2014 G. Quanet. al. prepared nanoscale zero-valent iron supported on biochar (B-nZVI). The TEM images of B-nZVI are shown two comprise phases nZVI with a diameter around 20–60 nm and biochar. In additional information related to composite observed, a good dispersion of individual nZVI adhering to biochar's surface without notable aggregation.[14]

BET isotherm models

BET isotherm model used to calculate the surface area of the solid material by physically adsorbing inert gas most commonly utilize nitrogen on the solid surface. As gas is used to calculate the surface area of material, the most crucial factor affecting gas is temperature; therefore, the whole experiment is performed at a constant temperature. BET results also give information about pore size and pore volume. When we study surface area changes using the BET technique for solvent effect indicates that using solvents, methanol will provide a higher surface than sodium hydroxide and phosphoric acid.

e.g., The BET isotherm analysis results showed an increase in the oxygen-containing functional groups on the hydrochar surfaces. In contrast, no enhancement in the surface area was observed, as Tan et al. [15] reported. The Wang H. et al. (2015) study shows, the modification of hickory-wood-derived biochar by potassium permanganate enhanced its surface area from 101 m2/g to 205 m2/g and then improved its adsorption capacity toward Pb, Cu, and Cd [16]

**Removal of estrogen from wastewater by using Biochar**

Female sex hormones are also known as estrogen. Estrogens are the category of sex hormones responsible for developing and regulating the female reproductive system and secondary sex characteristics. Three major endogenous estrogens have estrogenic hormonal activity [17].

They include estrone (E1), estradiol (E2), estriol (E3), and estetrol (E4), which is produced only in pregnancy from which estradiol is most potent and important. In the abbreviated form, E stands for estrogens, and number stands for the presence of hydroxide groups in their respective positions in the structures. The ethynylestradiol (EE2) is a synthetic hormone secondary to the natural hormone estradiol (E2). The structures of four major naturally occurring estrogen in women are estrone (E1), estradiol (E2), estriol (E3), estetrol (E4), and ethynylestradiol (EE2) are shown here [17-20].





The actions of estrogen are mediated by the estrogen receptor, which is a dimeric nuclear protein that binds to DNA and control gene expression. Estrogen is present in both men and women; they are usually present at significantly higher levels in women of reproductive age. They promote female secondary sexual characteristics, such as breasts, thickening of the endometrium, and regulating the menstrual cycle. In the male, it holds the reproductive system to the maturation of sperm, necessary for a healthy libido [17-20].

The name estrone is derived from the chemical terms estrin and ketones. Estrone is the first steroid hormone to be discovered. It is a steroid, a weak estrogen, and a minor female hormone. Estrone with other estrogen is synthesized from cholesterol and secreted mainly from glands, though they can also form from adrenal androgens from adipose tissue. Compared to E2, the E1 and E3 estrogen have weaker activity When E1 is converted into E2, which acts as a precursor or metabolic intermediate of E2 [17-20].

Estradiol E2 is an estrogen and the major female sex hormone. It is involved in the regulations of the estrous and menstrual female reproductive cycles. It is responsible for the development of female secondary sexual characteristics. Though estradiol level in males is significantly less as compared to females it has an important role. Apart from the human and other mammals, estradiol is also found in most vertebrates and crustaceans, insects, fish, and other animal species. Estradiol is an estrarne steroid and the most potent of the three major estrogens.

Estriol is a weak estrogen and minor female sex hormone. It is produced in high quantity in the placenta during pregnancy. It is used in hormone therapy in menopausal symptoms, premenopausal and menopausal periods, skin atrophy, and the sign of genital degeneration [17-20].

Ethynylestradiol EE2 is an orally bio-dynamic estrogen and is perhaps the most ordinarily utilized meds for people, just as domesticated animals and hydroponics action. EE2 has become an inescapable issue in the climate because of its high protection from the interaction of debasement. Various investigations have announced the capacity of EE2 to modify sex assurance, defer sexual development, and lessen the optional sexual qualities of uncovered life forms even at a low fixation by copying its characteristic simple, 17β-estradiol [17-20].

**Sources and occurrence and effect of estrogen-**

The small amount of estrogen hormones present in the environment is contaminated, and various factors have produced critical issues many researchers have studied. The earth's surface occupied by water is contaminated by hormone estrogen incoming from the livestock feed and wastewater treatments. The primary source of the mixing of estrogen in the environment is dairy work causes excess use of different types of steroids for cattle growth, enhancing feedstuff material and production of lean mass. However, most of the estrogen is obtained from the material like feces, fluid manure, solid sewages obtained from cattle waste, the receiver of sewage waste area, and the agricultural material used in the field [21]. The large production of estrogen hormones in the environment is animal manure produced from cow, horse manure, and source of poultry [22]. In the USA, estrogen from farm animals is about 49 tons in 2002[23].

 It has been reported that the female excretion on an average about 200–800, and 300–600 μg/day of hormone E1 and E2, respectively, and near about 6000-1000 ug/day E3. These are much higher than estrogen produced from menopausal females and young females, male and pregnant females [24].

 If a minimal amount of estrogen is present in the marine system, it creates enormous vitellogenin formation changes [25,26]. Likewise, estrogenic endocrine disruptors (EDC) are responsible for causing fatness, testicular cancer-causing disease, and infertility in human beings [27-29]. The estrogen hormones present in the human body show adverse effects like irregular menstruation cycle, bleeding during menstruation, infertility, night sweat, mood change, cancer-causing diseases, fatigue, sex problem, etc. To sort out this problem, there is needed to separate estrogen from wastewater to save the marine system and reduce diseases caused by estrogen.

**Methods used for removal of estrogen**

Matteo T et al. studied the effective separation of hormone steroids from waste water effectively using a polymer membrane with activated carbon [30]. The effective separation of estrogen activates sludge in wastewater in the biological process [31]. For the separation of estrogen from wastewater by flocculation, precipitation, adsorption, etc. this kind of regular method is used, but several limitations are there. Specifically, estrogen separation methods are studied, including the traditional procedures of estrogen separation, photocatalysis, biodegradation of estrogen, and the latest research results of estrogen separation from waste water [32, 33].

 The estrogen separation is effectively carried out by the use of adsorptive and non-adsorptive methods [34]. In the non-adsorptive methods, oxidative cycle and some of the natural strategies are carried out, but it shows side effects for that purpose; one of the easy methods used for separation of estrogen is the adsorption method in which use of the nanomaterial for separation of estrogen [35, 36].

In the adsorption methods, biochar (BC)material effectively separates estrogen present in wastewater. Biochar is a porous, carbonaceous adsorbent obtained from the carbonization of lignocellulose-rich biomass. It is generally used to remediate drugs, pesticides, natural impurities, and modern colors from liquid water [37, 38].

The adsorptive property of inorganic mixtures like heavy metals, halides, and oxyanions are different utilizations of BC [39, 40]. Natural waste is frequently utilized as feedstock to make biochar as it is abundantly accessible and helps to reduce waste sustenance. The production of biochar from raw material shows good adsorption properties. The physicochemical properties of BC are impacted by the feedstock type and pyrolysis conditions [41].

During the preparation of biochar, the composite material has been incorporated to enhancing adsorption properties. A few such composites contain graphene-based composites, carbon nanotube-based composites, CuO–ZnO composite nanofibers for developing biochar composite [42, 43].

Ongoing work on the remediation of steroidal estrogens utilizing BC and BC-composites shows assurance, and various investigations on the adsorptive removal of estrogens using BC created from different feedstocks under various pyrolysis and adsorption conditions have been accounted for. Remediation of estrogens from wastewater has been studied in reviews covering a collective assessment of minute toxins [44].

Adsorption isotherms assign the balance dispersion of an analyte between the adsorbent surface and the watery medium. Isotherms for adsorption in unsolidified media discover essential data regarding the adsorption components occurring at a strong liquid interface. Estrogen expulsion utilizing BC has been demonstrated utilizing the Langmuir, Freundlich, Langmuir-Freundlich, Dubinin-Radushkevich, and Temkin, Redlich Peterson, and Polanyi Manes models. Among these, the Freundlich model and Langmuir models were the most ordinarily detailed. The Freundlich model showed best fits for E1, E2, E3, and EE2; recommending heterogeneous adsorption on BC surfaces [45-49].

The functioned biochar effectively removes endocrine-disrupting chemicals (EDC) through the adsorption mechanism at the pH level 3-3.5 due to H Bond and pi interaction. Langmuir's model of adsorption isotherm is suitable for EDC [50-53].

Contrastingly, Ning and Tong et al. seen that the adsorption of E2 is all around portrayed by both the Langmuir and Freundlich models, meaning that there were various components included. A Farming residue like cow manure and wheat straw was used to form montmorillonite biochar, which was useful for the effective separation of estradiol from wastewater. The effective separation of estradiol from wastewater is about 42 mg/g by using cow manure and 62 mg/g by using wheat straw [54]. The physicochemical properties of binary oxide hydrochar are prepared by depositing Fe-Mn nanomaterial and applying estradiol adsorption from waste material [55].

The lotus seed pot biochar prepared by reacted with KOH increases the rate of adsorption of estrogen E2. It can be easily separated directly from an aqueous solution due to enhancing polar characters. This method shows better efficiency and the simplest method [56].

Wu Lin et al. and its coworker stated that vermicomposting biochar is efficient and less expensive, which is more effectively used to separate E2 estrogen from the aqueous solution. The vermicomposting biochar shows a better result at increasing temperature due to increased surface area and porous nature capacity of biochar. The experimental results show a pseudo-second-order reaction and suitable for Langmuir and Freundlich model isotherm [57].

Liu Shaobo et al. reported that the separation of E2 from the wastewater solution is done by synthesizing composite biochar containing graphene oxide with activated magnetite nanoparticles. The separation of E2 takes place on a single-step mechanism on the surface of biochar by carbonization, activation, and magnetization of biochar. Compared to different reported E2 separations, this method gives good results and is more cheap, suitable, and recyclable adsorbent. Graphene oxide activated magnetite biochar shows a pseudo-second-order reaction and follows the Freundlich isotherm mechanism [58].

Loffredo et al. reported that the removal of pesticides and estrogen E2 from wastewater in the agricultural field. The experimental work showed that biochar production for the separation of pesticides and E2 was made by using plant residue like coffee grounds, tea plants leaves, and compost humic acid material. This method is strongly related to the linear, Langmuir, and Freundlich isotherm mechanism and shows a better kinetic effect for the rapid adsorption rate of biochar. This method was low-cost and green to separate estrogen from wastewater in the agricultural field [59].

Jiang L et al. and coworkers studied that the graphene-based biochar has shown better estrogen from natural organic material than biochar form by using carbon single-walled and multiwall nanotube, powdered granular activated carbon. Graphene-based biochar adsorbs estrogen from wastewater to reduced environmental hazards [60].

In biochar exposed to various pyrolysis conditions and worth expansions, the non-linearity noticed was attributed to the fragrant spaces, expanded porosity, and surface area of the biochar. The properties of biochars shift drastically with heat treatment temperature (HTTs) and feedstock sources, and in this way, fundamentally influence their adsorption limit with regards to hydrophobic organic compounds (HOCs) [61-63].

The swine biochar (SWBs), the biochars with the most prominent substance, showed a higher adsorption limit than the plant residue-derived biochar (PLABs) of the two sorts of PLABs; it observed that maize biochar having grater adsorbivity than wood dust biochar. When HTTs were low, the greater carbon dioxide surface area and organic component composite (CO2-SA/OC) remains a substance [61-63].

Zhou, Liu, and coworkers studied graphene-based magnetic biochar by using potassium ferrate solution to increase sawdust biochar and improvising surface area and porosity of biochar at 9000C. The experimental results show a pseudo-first-order reaction and suitable for the Langmuir model isotherm [64].

The separation and E2 and heavy metal copper by single-step adsorption mechanism use of activated magnetic biochar. The activated magnetic biochar showed different pyrolysis temperatures. At the temperature of 700 ◦C, the activated magnetic biochar also increased surface area and pore size. The experimental results showed that the activated magnetic biochar more effectively adsorbed E2 and Copper on the surface of biochar from the single or binary mixture in a single-step mechanism [65].

Tong, Y et al. and coworkers observed that the wastewater containing micropollutant associated with E2 and EE2 could be removed from wastewater by the thermodynamic process. This process carried out the temperature in between 4-500c. In this investigated study they observed the initially, the neutral impurities associated with wastewater is adsorbed but at room temperature than polar impurities but if the temperature rises it gives opposite results because of polar compound enhancing their hydrophobic characters and physical character enthalpy, entropy and free energy of pollutant associated with wastewater changes [66, 67].

Rice straw biochar influences the characteristic of E2 separated from wastewater at the pyrolysis temperature. The pyrolysis temperature affects the concentration of estradiol, pH, and ionic strength. The experimental results showed that ionic strength had a minor impact on the adsorption of E2 at the pyrolysis temperature 5000-6000c. This adsorption mechanism is followed by pseudo-second-order and Freundlich isotherm [68].

The functionalized biochar effectively removes endocrine-disrupting chemicals estrone, estriol, estradiol, and ethynylestradiol from wastewater. The adsorption isotherm is based on the Langmuir model and separation of estrogens depending on pH values [69].

Shin Y et al. observed that the wastewater containing estrogen was removed by biochar containing swine manure with algal bacteria by hydrothermal process. The advantages of this method were observed in the experimental approach. It also helps to remove heavy metals with estrogen from wastewater [70].

The granular material is used to filtrate contaminated water to separate pollutants and estrogens present in it. The experimental work showed that the laboratory and pilot-scale sand and granular activated carbon filter were used to remove estrogens from contaminated water [71].

Activated carbon and ozone treatment techniques are employed to remove estrogen from single or multiple solutions. Estrogen separations dependency and efficiency based on chemical oxygen demand and pH of solution [72].

The activated charcoal is used as an adsorbent for the removal of estriol. The use of the agitated batch process enhanced the estriol removal efficiency. The experimental work evaluated that estriol is more efficiently separated at neutral pH, and the rate of adsorbivity increases by increasing temperature [73, 74].

References

1. Moldoveanu, S. C. Analytical Pyrolysis of Natural Organic Polymers. Elsevier: Amsterdam, 1998
2. [H.L.Lord, E.A.Pfannkoch](https://www.sciencedirect.com/science/article/pii/B9780123813732000612#!), Sample Preparation Automation for GC Injection, [Comprehensive Sampling, and Sample Preparation](https://www.sciencedirect.com/science/referenceworks/9780123813749), Analytical Techniques for Scientists, [Volume 2](https://www.sciencedirect.com/science/referenceworks/9780124095472), 2012, Pages 597-612 [Cross Reference]
3. A. V. Bridgewater Chem. Eng. J., 2003, 91, 87
4. Kaige Wang and Robert C. Brown, CHAPTER 1:Prospects for Fast Pyrolysis of Biomass, in Fast Pyrolysis of Biomass: Advances in Science and Technology, 2017, pp. 1-11. [Cross Reference]
5. H.F. Gercel, Production and characterization of pyrolysis liquids from sunflower-pressed bagasse, Bioresour. Technol. 85 (2) (2002) 113–117.
6. PrabirBasu, [Biomass Gasification, Pyrolysis and Torrefaction (Third Edition)](https://www.sciencedirect.com/science/book/9780128129920), Practical Design and Theory, 2018, Pages 93-154.
7. Antonio Molino, SimeoneChianese and Dino Musmarra, Biomass gasification technology: The state of the art overview, Journal of Energy Chemistry 25(2016)s 10–25.
8. Arazo RO, Genuino DAD, de Luna MDG, Capareda SC. Bio-oil production from dry sewage sludge by fast pyrolysis in an electrically-heated fluidized bed reactor. Sustain Environ Res 2017;27:7–14. <https://doi.org/10.1016/j.serj.2016.11.010>
9. Yang Liu, Yongmeng Song, Chunmei Ran, Asif Ali Siyal, PolinaChtaeva, Jianjun Dai, Zhihui Jiang, Zeyu Deng, Tianhao Zhang, WenyaAo, Jie Fu, Pyrolysis of furfural residue in a bubbling fluidized bed reactor: Biochar characterization and analysis. Energy (2020), 211, 118966.
10. Yoo S, Kelley S, Tilotta D et al (2018) Structural characterization of loblolly pine derived biochar by x-ray diffraction and electron energy loss spectroscopy. ACS Sustain ChemEng 6:2621–2629.
11. Yao, Y., Gao, B., Fang, J., Zhang, M., Chen, H., Zhou, Y., Creamer, A. E., Sun, Y., and Yang, L. (2014). Characterization and environmental applications of clay–biochar composites. Chem. Eng. J., 242, 136–143. doi:10.1016/j.cej.2013.12.062
12. Jorio, A., Ribeiro-Soares, J., Can¸cado, L. G., Falc~ao, N. P. S., Dos Santos, H. F., Baptista, D. L., Martins Ferreira, E. H., Archanjo, B. S., and Achete, C. A. (2012). Microscopy and spectroscopy analysis of carbon nanostructures in highly fertile Amazonian anthrosoils. Soil TillageRes., 122, 61–66. doi:10.1016/j.still.2012.02.009.
13. **Anees Ahmad,** Nawaz Khan, ShekherBalenduGiri, PankajChowdhary, PreetiChaturvedi, Removal of methylene blue dye using rice husk, cow dung, and sludge biochar: Characterization, application, and kinetic studies. **Bioresource** **Technology** (**2020**), 306, 123202
14. GuixiangQuan, Wenji Sun, Jinlong Yan, YeqingLan, Nanoscale Zero-Valent Iron Supported on Biochar: Characterization and Reactivity for Degradation of Acid Orange 7 from Aqueous Solution. Water Air Soil Pollut (2014) 225:2195.
15. Tan, X.; Liu, S.; Liu, Y.; Gu, Y.; Zeng, G.; Hu, X.; Wang, X.; Liu, S.; Jiang, L. Biochar as potential sustainable precursors for activated carbon production: Multiple applications in environmental protection and energy storage. Bioresour. Technol. **2017**, 227, 359–372.
16. Wang, H.; Gao, B.; Wang, S.; Fang, J.; Xue, Y.; Yang, K. Removal of Pb(II), Cu(II), and Cd(II) from aqueous solutions by biochar derived from KMnO4 treated hickory wood. Bioresour. Technol. **2015**, 19, 356–362
17. Santen RJ, Simpson E, History of Estrogen: Its Purification, Structure, Synthesis, Biologic Actions, and Clinical Implications, Endocrinology, March 2019, 160, 605–25.
18. Vardanyan R, Hruby V, Synthesis of Best-Seller Drugs, Chapter 27 - Steroid Hormones, Academic Press, 2016, 459-93.
19. Ryan KJ, Biochemistry of aromatase: significance to female reproductive physiology, Cancer Res. 1982, 42, 3342s-44s.
20. JieC, Yong S, Rena Li Estrogen synthesis and signaling pathways during aging: from the periphery to brain [Trends Mol Med. 2013, 19(3): 197–09.](https://www.ncbi.nlm.nih.gov/entrez/eutils/elink.fcgi?dbfrom=pubmed&retmode=ref&cmd=prlinks&id=23348042)
21. Biswas, S, Shapiro C, Kranz, W, Mader, T, Shelton D, Zhang T, Current knowledge on the environmental fate, potential impact, and management of growth-promoting steroids used in the US beef cattle industry J. Soil Water Con. 2013, 68, 325-36
22. Andaluri G, Suri RP, Kumar K, Occurrence of estrogen hormones in biosolids, animal manure, and mushroom compost. Environ. Monit. Assess. 2012 184, 1197–05.
23. Ray P, Zhao Z, Knowlton K, emerging contaminants in livestock manure: hormones, antibiotics, and antibiotic resistance genes. In: Kebreab, E. (Ed.), Sustainable Animal Agriculture. CabiInternaional, Boston MA, U.S.A. 2013, pp. 268–83.
24. Gunatilake, S R, Jeong K, Todd M, A novel approach to determine estrogenic hormones in swine lagoon wastewater using the QuEChERS method combined with solid-phase extraction and LC/MS/MS analysis. Anal. Methods2014, 6, 9267–75
25. Jobling, S, Casey D, Tyler C, Pawloski S, Comparative responses of mollusks and fish to environmental estrogens and an estrogenic effluent.Aquat. Toxicol 200365, 205–20.
26. Strech G., Chemical and biological analysis are of estrogenic, progestogenic, and androgenic steroids in the environment. Trends Anal Chem. 2009,28, 635-652.
27. Newbold RR, Padilla-Banks E, Jefferson WN, Environmental estrogens and obesity. Mol Cell Endocrinol. 2009, 304:84–9.
28. Bouskine A,  Marielle N, Baharia M. Estrogens promote human testicular germ cell cancer through a membrane-mediated activation of the extracellular regulated kinase and protein kinase A. Endocrinology. 2008, 149(2):565-73.
29. Diamanti E., Bourguignon J.P, Giudice L.C, Hauser R., chemicals: an Endocrine Society scientific statement. Endocr Rev 2009, 30, 293–42.
30. Matteo T, Peter G, Christian N, Julia P, Dennis R, Bertram B, Andrea I S, Polymer-based spherical activated carbon – ultrafiltration (UF-PBSAC) for the adsorption of steroid hormones from water: Material characteristics and process configuration. Water Research, 2020; 185: 116249.
31. Koh Y, Chiu T, Boobis A, Cartmell E, Scrimshaw M, Lester J, Treatment and removal strategies for estrogens from wastewater, Environmental Technology, 2008, 29:3, 245-67.
32. Aliakbar R, MashallahR, Hormones removal from municipal wastewater using ultrasound [AMB Express.](https://www.ncbi.nlm.nih.gov/pmc/articles/PMC5984614/) 2018; 8: 91.
33. Ming C, Shuangk,rangwoi X, Environment-Friendly Removal Methods for Endocrine Disrupting Chemicals, Sustainability 2020, 12, 7615.
34. Racz, L, Goel R, Fate and removal of estrogens in municipal wastewater. J. Environ. Monit 2010, 12, 58–70.
35. Jiang L. Duan N, Hao L, Adsorption of estrogen contaminants by graphene nanomaterials under natural organic matter preloading: comparison to the carbon nanotube, biochar, and activated carbon. Environ. Sci. Technol. 2017, 51, 6352–59.
36. Jaroslava, B, Filip k, Tucek J, Simek Z, Can zero-valent iron nanoparticles remove waterborne estrogens? J. Environ. Manag. 2015, 150, 387–92.
37. Ahmad, M, Rajpaksha A, Jung L, Ming Z, Biochar as a sorbent for contaminant management in soil and water: a review. Chemosphere 2014, 99, 19–33.
38. Inthapanya X, Shaohua W, Zhenfeng H, Guangming Z, MengjieW, Chunping Y, Adsorptive removal of anionic dye using calcined oyster shells: isotherms, kinetics, and thermodynamics. Environ. Sci. Pollut. Control Ser. 2019, 26, 5944–54
39. Jayawardhana Y, Gunatilake S, Mahatantila K, Ginige M, Sorptive removal of toluene and m-xylene by municipal solid waste biochar: simultaneous municipal solid waste management and remediation of volatile organic compounds. J. Environ. Manag. 2019, 238, 323–30.
40. Navarathna, C, Alchouron j, Herath A, Wathudu P, Recent Developments in Aqueous Arsenic (III) Remediation Using Biomass-Based Adsorbents. Contaminants in Our Water: Identification and Remediation Methods. ACS Publications, pp. 2020, 197–51.
41. Guntilake S, Peiris C, The influence of three acid modifications on the physicochemical characteristics of tea-waste biochar pyrolyzed at different temperatures: a comparative study. RSC Adv. 2020, 9, 17612–22.
42. Kim S, Park C, Jang M, Son A, Aqueous removal of inorganic and organic contaminants by graphene-based nano adsorbents: a review. Chemosphere 2018, 212, 1104–24.
43. Malwal, D, Gopinath, P, Efficient adsorption and antibacterial properties of electrospunCuO-ZnO composite nanofibers for water remediation. J. Hazard Mater. 2017, 321, 611–21.
44. Tong, Y, Mayer b, Mcnamara P, Adsorption of organic micropollutants to bio solids-derived biochar: estimation of thermodynamic parameters. Environmental Science: Water Research & Technology 2019, 5, 1132–44.
45. Jung C, Park J, Lim K, Park S, Heo J, Adsorption of selected endocrine disrupting compounds and pharmaceuticals on activated biochars. J. Hazard Mater. 2013, 263, 702–10.
46. Son A, Kim E, Han J, Her N, Park C, Sorptive removal of selected emerging contaminants using biochar in aqueous solution. J. Ind. Eng. Chem. 2016, 36, 364–371.
47. Shaobo L, Yunguo L, Luhua J, Guangming Z, Ya L, Zhiwei Z, Xiaohua W, Qimeng N, Removal of 17ß-Estradiol from water by adsorption onto montmorillonite-carbon hybrids derived from pyrolysis carbonization of carboxymethyl cellulose. J. Environ. Manag. 2019 b, 236, 25–33.
48. Liu N, Liu Y, Zeng G, Gong J, Tan X, Wen J, Liu S, Jiang L, Li m, Yin Z, Adsorption of 17ß-estradiol from aqueous solution by raw and direct/pre/post-KOH treated lotus seedpod biochar. J. Environ. Sci. 2020, 87, 10–23.
49. Peterson SC, Michel A, Akwasi A, Michel J, Comparing Corn Stover and Switchgrass Biochar: Characterization and Sorption Properties Journal of Agricultural Science; 2013, Vol. 5.
50. Ahmed M B, Zhou J, Ngo H, Johir M, Sorptive removal of phenolic endocrine disruptors by functionalized biochar: competitive interaction mechanism, removal efficacy, and application in wastewater. Chem. Eng. J. 2018, 335, 801–811.
51. Dong X, He L, Hu H, Song G, Removal of 17β-estradiol by using highly adsorptive magnetic biochar nanoparticles from aqueous solution. Chem. Eng. 2018, J. 352, 371–379.
52. Liu N, Liu Y, Zeng G, Gong J, Tan X, Wen J, Liu S, Jiang L, Li m, Yin Z, Synthesis of graphene-like magnetic biochar by potassium ferrate for 17β-estradiol removal: effects of Al2O3 nanoparticles and microplastics. Science of The Total Environment, 2020a, p. 136723.
53. Yu J, Zhu Z, Zhang H, ken T, Qiu Y, Efficient removal of several estrogens in water by Fe-hydrochar composite and related interactive effect mechanism of H2O2 and iron with persistent free radicals from hydrochar of pinewood. Sci. Total Environ. 2019, 658, 1013–1022.
54. Ning Q, Liu Y, Jiang L, Zeng G, Zeng Z, Fabrication of hydrochar functionalized Fe–Mn binary oxide nanocomposites: characterization and 17β-estradiol removal. RSC Adv. 2017, 7, 37122–37129.
55. Tong X, Jiang L, Li Y, Chen X, Zhao Y, Function of agricultural waste montmorillonite-biochars for sorptive removal of 17β-estradiol. Bioresour. Technol. 2020, 296, 122368.
56. Liu N, Yunguo L Y, Zeng G, Jilai G J, Tan X, Adsorption of 17β-estradiol from aqueous solution by raw and direct/pre/post-KOH treated lotus seedpod biochar, journal of environmental sciences 2020, 87 10-23.
57. Wu L, Ying L, Yan L, Fei S, Gang Y, Wu J Removal of 17-estradiol from aqueous solutions by vermicompost-derived biochars adsorption HuanjingKexueYanjiu 2016, 29(10), 1537-45.
58. Liu S, Meifang L, Yunguo L, Liu N, Tan Xi; Jiang L, Removal of 17-estradiol from aqueous solution by graphene oxide supported activated magnetic biochar: Adsorption behavior and mechanism Journal of the Taiwan Institute of Chemical Engineers 2019, 102, 330-39.
59. Loffredo E, Castellana G, Taskin E, A Two-Step Approach to Eliminate Pesticides and Estrogens from a Wastewater and Reduce Its Phytotoxicity: Adsorption onto Plant-Derived Materials and Fungal Degradation Water, Air, & Soil Pollution 2016, 227(6), 1-12.
60. Jiang L, Yunguo L, Shaobo L, Zeng G, Hu X, Tan, X, Lele W, Adsorption of Estrogen Contaminants by GrapheneNanomaterials under Natural Organic Matter Preloading: Comparison to Carbon Nanotube, Biochar, and Activated Carbon Environmental Science & Technology 2017, 51(11), 6352-59.
61. Sun k, Ro k, Guo M, Novak J, Xing B, Sorption of bisphenol A, 17α-ethinylestradiol and phenanthrene on thermally and hydrothermally produced biochars. Bioresour. Technol. 2011, 102, 5757–5763.
62. Tao H, Ge H, Shi J, Liu X, The characteristics of oestrone mobility in water and soil by the addition of Ca-biochar and Fe–Mn-biochar derived from Litchi Chinensis Sonn. Environ. Geochem. Health 2019, 1–15.
63. Wang Z, Han L, Sun k, Jin J, Sorption of four hydrophobic organic contaminants by biochars derived from maize straw, wood dust, and swine manure at different pyrolytic temperatures. Chemosphere 2016, 144, 285–91.
64. Zhou Y, Shaobo L, Yunguo L, Tan, Liu X, Efficient removal 17-estradiol by graphene-like magnetic sawdust biochar: preparation condition and adsorption mechanism International Journal of Environmental Research and Public Health 2020, 17, 8377.
65. Liu S; Meifang L, Yunguo L, Liu N, Tan Xi; Jiang L, Activated magnetic biochar by one-step synthesis: Enhanced adsorption and coadsorption for 17-estradiol and copper Science of the Total Environment 2018, 639, 1530-42.
66. Tong Y, Mayer B K. McNamara J, Adsorption of organic micropollutants to biosolids-derived biochar: estimation of thermodynamic parameters Environmental Science: Water Research & Technology 2019, 5(6), 1132-44.
67. Tong Y, Mayer B K, McNamara J, Biosolids-derived biochar for adsorption of organic micropollutants: The impact of temperature and pore size Abstracts of Papers, 255th ACS National Meeting & Exposition, New Orleans, LA, United States, 2018, 18-22.
68. Wang X, Liu N, Yunguo L, Jiang L, Zeng G, Tan X, Jiang L, Adsorption removal of 17-estradiol from water by rice straw-derived biochar with special attention to pyrolysis temperature and background chemistry International Journal of Environmental Research and Public Health 2017, 14, 1213/1-17.
69. Ahmed M, Zhou J, Hao H, Hasan A, Sorptive removal of phenolic endocrine disruptors by functionalized biochar: Competitive interaction mechanism, removal efficacy, and application in wastewater Chemical Engineering Journal 2018, 335, 801-11.
70. Shin Y, Peng Z, Yuanhui Z, Shin H, Fate and transport of estrogenic compounds in an integrated swine manure treatment systems combining algal-bacterial bioreactor and hydrothermal processes for improved water quality. Environmental science and pollution research international 2019, 26(16), 16800-13.
71. Lionel H, Charlotte G, Daniel H, Dixon B, Assessing granular media filtration for the removal of chemical contaminants from wastewater Water research 2011, 45(11), 3461-72.
72. Fumihiko O, Hisato T, Hitoshi Y, Removal of estrogens from water using activated carbon and ozone, Journal of oleo science 2011, 60(12), 609-11.
73. Kiran K, Venkata M, Sarma P, Sorptive removal of endocrine-disruptive compound (estriol, E3) from the aqueous phase by batch and column studies: kinetic and mechanistic evaluation, Journal of hazardous materials 2009, 164(2-3), 820-8.
74. Carter P Preparation of ligand-free human serum for radioimmunoassay by adsorption on activated charcoal, Clinical chemistry 1978, 24(2), 362-4.