

BIOCHAR II: SYNTHESIS, CHARACTERIZATION AND APPLICATION

Abstract

This chapter, which falls under the category of sustainable development, discusses how biomaterials are converted into biochar and used in a variety of applications. This cuts down on biowaste while emphasising biochar applications. The authors discuss various biochar synthesis methods, the effect of each method on biochar yield, and the synthesis time. During the synthesis, talk about the side product form as well. Biochar characterization using various methods and specific information obtained through instrumental analyses are included. The chapter also addresses a number of environmental applications, such as the use of biochar to remove "estrogens," a type of sex hormone, from wastewater samples.

Keywords: Biochar, torrefaction, Raman spectroscopy, estrogen, Isotherms.

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I. SYNTHESIS OF BIOCHARS

1. Pyrolysis or the thermochemical method: The first method of synthesis or production of biochar employed is pyrolysis. Pyrolysis involves the chemical transformation (decomposition) of a substance by the action of heat up 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 process, the material is heated at high temperatures in the absence of oxygen, and chemical and physical separation techniques are used to accomplish the separation. Iron was historically obtained from iron ore via pyrolysis to make charcoal from wood in pre - industrial times. A revolution in lighting was also sparked by the discovery of kerosene, the first transportable liquid fuel, and it continues to be so today thanks to the pyrolysis technique of kerosene manufacturing. The development of kerosene production through pyrolysis is largely responsible for the modern petrochemical sector that exists today.

Three different forms of pyrolysis are generally recognised:

- Conventional or Slow Pyrolysis
 - Fast Pyrolysis and
 - Ultra-fast pyrolysis.
- **Conventional or Slow Pyrolysis Method:** With this technique, the biomass is heated at a pace of approximately 10°C per minute at low to moderate temperatures of roughly 300°C. 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 biochar. It has been used for thousands of years to convert wood into high yields of charcoal (bio-carbon). The lower yields of biochar, bio-oil, and gaseous products are the main drawbacks of the slow pyrolysis process.
 - **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. These variables lead to the production of organic vapors, pyrolysis gases, and charcoal. The biomass feedstock particle size must be < 1 mm. Because of this advantage over slow pyrolysis, the products obtained during the fast pyrolysis are of high grade or quality. It has gained worldwide interest, both in research and practical use.

Diverse reactors were studied with the aim of heating biomass to temperatures reaching 400 °C in a matter of seconds, even though fast pyrolysis was originally researched in 1875.

There are several types of reactors that can be used, including ablative reactors, rotating cone reactors, auger reactors, bubbling fluidized beds, and circulating fluidized beds. [3]

Table 1.1 lists the salient characteristics of the various kinds of fast pyrolysis reactors. [4]

**Table 1.1 Summary of various fast pyrolysis reactor technologies
 (reproduced from reference 17 with permission from Dr. Anthony V. Bridgwater)**

| Reactor type | Development Status | Maximum Yield % weight | Complexity | Feed Size Specification | Inert gas requires | Specific Reactor size |
|---------------------------|--------------------|------------------------|------------|-------------------------|--------------------|-----------------------|
| Bubbling fluidized bed | Commercial | 75 | Medium | High | High | Medium |
| Circulating fluidized 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 clear from the above table that, among the several types of reactors, fluidized beds have attracted the most interest for fast pyrolysis because of their superior heat and mass transport properties, ease of operation, and relative scale-up simplicity.

- **Ultra-fast or Flash Pyrolysis:** Flash pyrolysis, also known as ultra-fast pyrolysis, has been proven to produce significant yields of bio-oil with low water content and conversion efficiencies of up to 70%. It is characterised by rapid heating rates (>1000 °C/s) and high reaction temperature range of 900–1300 °C. All of these have residence times that are often less than 0.5 seconds, which is even lower than those of fast pyrolysis. The particle size of biomass feedstock must be as fine as is technically practicable, typically between 105 and 250 m, to achieve such high heating and heat transfer rates (60–140 mesh size) [5]. It is observed that the rise in temperature enhances the aromaticity, hydrophobicity, and surface area of biochar, making it a suitable adsorbent for hydrophobic organic molecules in comparison to all the pyrolysis techniques outlined above.
- 2. Torrefaction:** Torrefaction is a French word that means “roasting.” Torrefaction is a process utilized in many businesses, including those that produce tea and coffee, but the power sector has only recently been interested in using biomass as a coal substitute. Since it prepares biomass for subsequent use rather than using it directly in its raw state, torrefaction is frequently referred to as a pretreatment process. Torrefaction is described 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 optimising the mass and energy yield of a solid product." [6]. The low-temperature range, slow heating rate, and the low amount of oxygen are distinctive

features compared to pyrolysis, where zero or absence of oxygen is needed. These features have gained importance in the torrefaction process for synthesizing biochar using biomass. The typical temperature range and heating rate for torrefaction are 200–300°C and < 50°C/min, respectively.

- 3. Hydrothermal carbonization (HTC):** A thermal pretreatment coalification method called hydrothermal carbonization (HTC) is used to transform biomass into hydrochar, a substance that resembles coal. The hydrochar generated by HTC techniques has a high carbon content in addition to a high calorific value. Wet torrefaction is another name for hydrothermal carbonization, which utilizes hot compressed subcritical water. The HTC process is carried out in high-pressure tubes by applying relatively high temperatures to biomass in liquid water for a short period of time (0.5-8 h) in the absence of air at a typical heating rate of 10–20 °C/s, at pressures ranging from 1–5 MPa. The biomass experiences the following reactions, namely dehydration, decarboxylation, and decarbonylation. Hydrochar produced via HTC is hydrophobic and has brilliant binding capacities. As a result, HTC hydrochar has recently drawn a lot of interest in the research community and is once again gaining popularity in the fields of fuel, soil nutrition, adsorbent material chemistry, hydrogen storage, lithium-ion batteries, and supercapacitors.

- 4. Gasification:** Gasification is the process of turning solid or liquid biomass or materials used to make carbon-based fossil fuels into a gas, vapor, or solid phase. Nitrogen, carbon monoxide, hydrogen, carbon dioxide, low-molecular-weight hydrocarbons like ethane, propane, and methane, as well as high-molecular-weight hydrocarbons like tar, are among the common gases found in the gas-phase. 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 capacity and can be used to produce energy for biofuel production. The "char" or "biochar" in the solid phase includes inert substances with high adsorption capacities and unconverted organic compounds employed in a variety of applications, including wastewater treatment. For the aforementioned reasons, biomass gasification is seen as a means of expanding the use of biomass for energy production and enabling wider biomass utilization. The biomass gasification is carried out at very high temperatures, usually in the range of 800–1300 °C with a heating rate of 100 °C/s as compared to other processes employed for the synthesis of biochar. The gasifying agents or gasifying mediums used in the gasification process are oxygen, air, and steam. The heating value ranges 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 are listed.

| 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 biochar rely on the biochar quality. The porosity of the biochar, a functional group connected to its surface, and the substance utilized to make the biochar all impact the quality of the material. The preparation conditions, like the type of reactor, synthesis temperature, and reaction time, will affect the properties of biochar. When we consider the activation process of biochar to increase its properties towards application, it will change its surface morphology, which depends on the surface area, pH, the molar ratio of elements, surface change, mineral contents, elemental composition, and the active binding sites.

Physically and chemically active, biochar results in different characteristics of the product. E.g. Physically activated biochar has been found to have a mesoporous structure with a surface area of up to 600 m²/g, whereas chemically activated biochar (biochar treated with phosphoric acid) exhibits a microporous structure with a surface area of up to 880 m²/g.

BET surface area instruments indicate that physically activated pistachio shell biochar gives a surface area of 2596 m²/g with about 90% burns at a temperature of 850 °C for about 20 minutes of activation time required for a spouted bed reactor. In the reactor's spouted bed, there were only negligible heat and mass transport resistances. Steam-activated biochar from vacuum pyrolysis reactors, however, increased the surface area from 50 to 1025 m²/g while reducing the concentration of functional groups.

Therefore, biochar characterization is needed to determine the chemical nature, the surface area, the functional group, and the active sites present on the biochar.

Numerous analytical methods are employed to characterize biochar, including the 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).

- 5. Fourier Transform Infrared Spectrometry (FTIR):** A method of analysis known as Fourier transform infrared spectroscopy (FTIR) is based on how well a sample material absorbs infrared light with wavelengths between 4000 and 400 cm^{-1} . It is used to identify organic as well as inorganic materials. FTIR is primarily used to identify functional groups in solid, liquid, and gaseous materials. When samples interact with light through absorption, emission, and photoconductivity, FTIR spectra will result.
- 6. Basic Principle:** An element and bonds present in molecules are responsible for the molecular bond vibration at various frequencies. A certain bond vibrates at specific frequencies according to quantum mechanics theory, which correspond to the ground state (lowest frequency) and other excited states (higher frequencies). The energy difference between the ground state and the first excited state determines the amount of light energy needed to make the transition.

Yang Liu et al. prepared the biochar using Ca-bentonite, kaolin, and CaO at different temperatures like 450, 550, 650, 750, and 850 °C, and the prepared biochar was characterized by an FTIR instrument. O-H stretching caused the broad absorption band to be noticed at 3385 cm^{-1} , while O-H stretching and C-H stretching vibrations were responsible for the weak absorption band at 2921 cm^{-1} . In BC, C=O stretching peaked at 1707 cm^{-1} and was associated with organic compounds such as ketones, carboxylic acids, aldehydes, and esters. [8] The weak signal at 1607 cm^{-1} may be the result of C=C stretching and N-H bending, revealing alkenes and amines in BC. The N-O, C-N, C-O, and S=O stretching could be responsible for the peaks at 1509 cm^{-1} , 1109 cm^{-1} , and 1057 cm^{-1} , respectively, confirming the presence of nitrogen- and sulfoxide-containing compounds in BC. The stretching vibrations of C-Br, C-Cl, and C-I caused an absorption band of about 599 cm^{-1} , which indicated the presence of halogen compounds in BC. The peaks measured at approximately 3385 cm^{-1} , 2921 cm^{-1} , and 1707 cm^{-1} was much weaker than expected, showing that several organic molecules, including alcohols, amines, alkanes, esters, ketones, and aldehydes, were decomposing as the temperature rose from 450 °C to 850 °C. However, as the temperature rose from 450 °C to 750 °C, the peak at 1100 cm^{-1} (C-O stretching) grew more pronounced. This showed that higher temperatures were more favourable for the synthesis of alcohols, phenols, and carboxylic acids. [9]

- 7. X-ray diffraction (XRD):** The XRD technique is mainly used to measure the intensity and angle of the diffracted beams present in samples. Biochar, prepared by pyrolysis, mainly contains carbon or inorganic substances. The most commonly observed carbon crystallites in biochar are classified into two types: graphitized and 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]. In 2014, Yao et al. 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° ($d = 13.840 \text{ \AA}$), 6.9° ($d = 12.803 \text{ \AA}$), 19.9° ($d = 4.449 \text{ \AA}$), and 35.1° ($d = 2.555 \text{ \AA}$) [11]

- 8. Raman spectroscopy:** The structural properties of biochar are investigated using Raman spectroscopy. To assess functional groups present, graphite structures, and the amorphous character of biochar, researchers used Raman spectroscopy. In Raman spectroscopy, we observed Stokes lines occurring at lower energy or longer wavelengths 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.

To assess crystalline carbon structures, Jorio et al. (2012) used Raman spectroscopy analysis to examine the carbon nanostructures of biochar. Using the ratio of D and G band intensities (ID/IG) of carbon nanostructures in biochar, the in-plane crystallite size distribution (L_a) was calculated. According to their research, the distribution of L_a in biochar was 8–12 nm in size. The breathing mode of sp^3 hybridised carbon in disordered graphite rings and sp^2 hybridised carbon in ring structures.[12]

- 9. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM):** Scanning electron microscopy and transmission electron microscopy are mainly concerned with surface characterization techniques. SEM has a focused and fine beam with lower resolution as compared to TEM analysis. It is taken as a topographical image, or we can consider it a surface image with a magnification capacity of up to 20,00000 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. SEM analysis is faster, easier to use, and more cost-effective than TEM analysis when compared. It also requires less work to prepare the sample.

As compared to SEM, TEM analysis has a broad beam with higher resolution. It is capable of analysing the internal structure of the sample with a magnification capacity of up to 50,000,000. TEM requires a more specific ultrathin sample with penetration. It will give you a 2D image.

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 the sample information requirements, scientists can choose a more appropriate type of microscope to analyse the sample.

The characterization of biochar using SEM instrument is generally studied by combining EDX techniques. A. Ahmad et al. published an article in 2020 to remove methylene blue dye using biochar. They use materials including domestic sludge biochar (SB), cow dung biochar (CDB), and rice husk biochar (RHB) for the pyrolysis of biochar at 500°C . On characterization of the respective biochar using SEM-EDX analysis, they observed the thick and porous surface for RHB, CDB, and SB biochar. Biochar in RHB, CDB, and SB had the following pretreatment elemental compositions: C, O, Al, Mg, Si, Ca, P, K, and Cl. In addition to these elements, Na and Fe were also present in CDB and SB, respectively. However, RHB, CDB, and SB post-MB therapy, showed an increase in C, Cl, and S %. [13]

TEM analysis for biochar samples gives information about the particle size of the material. Zero-valent iron supported on biochar was created at the nanoscale by G. Quenet et al. in 2014. (B-nZVI). Two phases of nZVI with a diameter of roughly 20–60 nm and biochar are visible in the TEM pictures of B-nZVI. According to composite information, the surface of the biochar was found to have a decent dispersion of individual nZVI clinging to it without any discernible aggregation. [14]

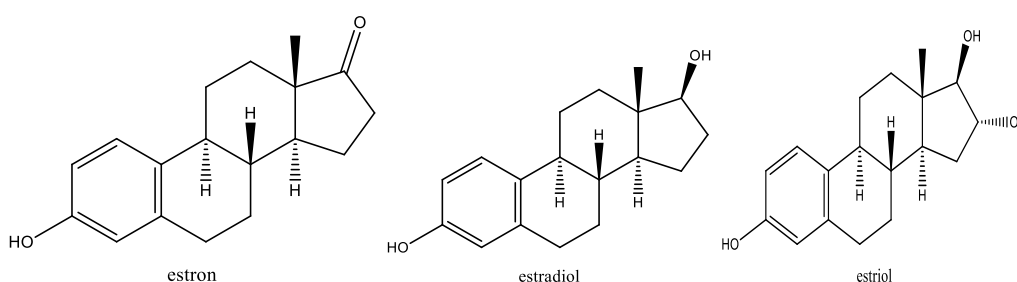
10. BET isotherm models: A BET isotherm model is used to calculate the surface area of the solid material by physically adsorbing inert gas, most commonly utilizing nitrogen on the solid surface. As the gas is used to calculate the surface area of material, the most crucial factor affecting the gas is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

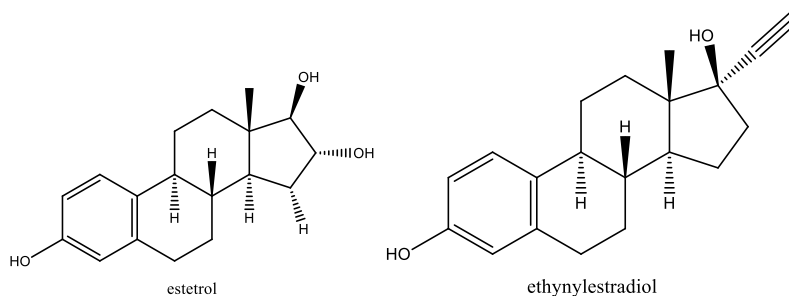
The results of a BET isotherm study revealed an increase in oxygen-containing functional groups on the surfaces of the hydrochar. Tan et al. [15] reported that there was no improvement in the surface area. According to a study by Wang H. et al. (2015), The modification of hickory-wood-derived biochar using potassium permanganate raised its surface area from 101 m²/g to 205 m²/g and improved its adsorption ability toward Pb, Cu, and Cd [16].

II. APPLICATIONS OF BIOCHAR

1. Removal of estrogen from wastewater by using biochar: The term "estrogen" also refers to female sex hormones. Estrogens are a class of sex hormones that are in charge of regulating and developing the female reproductive system and secondary sex traits. Three main endogenous estrogens are active in the hormone estrogen [17].

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





The estrogen receptor, a nuclear protein that is composed of dimers and binds to DNA to regulate gene expression, regulates the effects of estrogen. Both men and women have estrogen, although women of reproductive age often have it in much higher amounts. They encourage the development of secondary female sexual traits like breasts, endometrial thickness, and menstrual cycle regulation. It supports the development of sperm in the male reproductive system, which is essential for a strong libido [17–20].

The name estrone is derived from the chemical terms estrin and ketones. The first steroid hormone to be identified is estrone. It is an unimportant female hormone, a weak estrogen, and a steroid. Although they can also originate from adrenal androgens from adipose tissue, estrogen and other estrogens are primarily produced by glands and made from cholesterol. Compared to E2, the E1 and E3 estrogens have weaker activity when E1 is converted into E2, which acts as a precursor or metabolic intermediate of E2 [17-20].

The main female sex hormone is estradiol E2, which is an estrogen. It plays a role in controlling the female reproductive cycles of estrus and menstruation. It is in charge of the growth of secondary female sexual traits. Though estradiol levels in males are significantly lower as compared to females, they have an important role. In addition to humans and other mammals, estradiol is present in the majority of vertebrate species, including crustaceans, insects, fish, and other animals. The strongest of the three main estrogens is an estrane steroid called estradiol.

A weak estrogen and insignificant female sex hormone is estriol. During pregnancy, the placenta produces a large amount of it. It is used in hormone therapy for menopausal symptoms, the pre- and menopausal states, skin atrophy, and genital degeneration signs. [17-20].

Ethynylestradiol EE2 is an orally bio-dynamic estrogen and is perhaps the most ordinarily utilized med for people, just like domesticated animals and hydroponics. 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, 17 β -estradiol [17-20].

- 2. Sources, occurrence and effects 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 the hormone estrogen incoming from livestock feed and wastewater treatments. Dairy work is the main cause of the environment's estrogen mingling, which

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 materials like feces, fluid manure, solid sewage obtained from cattle waste, the receiver of sewage waste area, and the agricultural material used in the field [21]. Animal manure made from cow, horse, and chicken manure is a major source of estrogen hormones in the environment [22]. About 49 tons of estrogen from farm animals were produced in the USA in 2002[23].

It has been reported that the female excretion on an average is 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 menstrual cycle, bleeding during menstruation, infertility, night sweat, mood change, cancer-causing diseases, fatigue, sex problems, etc. To sort out this problem, there is a need to separate estrogen from wastewater to save the marine system and reduce diseases caused by estrogen.

3. Methods used for the removal of estrogen: Matteo T et al. studied the effective separation of hormone steroids from wastewater using a polymer membrane with activated carbon [30]. The effective separation of estrogen activates sludge in wastewater in the biological process [31]. This kind of regular method is used for the separation of estrogen from wastewater by flocculation, precipitation, adsorption, etc., but several limitations are present. Specifically, estrogen separation methods are studied, including the traditional procedures of estrogen separation, photocatalysis, biodegradation of estrogen, and the latest research results on estrogen separation from wastewater [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. A porous, carbonaceous adsorbent called biochar is created when biomass high in lignocellulose is carbonized. Drugs, pesticides, organic contaminants, and contemporary colored liquids are typically cleaned up using this method [37, 38].

Different applications of BC include the adsorptive qualities of inorganic mixtures, including those containing heavy metals, halides, and oxyanions [39, 40]. Natural waste is frequently utilized as feedstock to make biochar as it is abundantly accessible and helps to reduce waste sustenance. Biochar made from raw materials exhibits strong adsorption abilities. The feedstock type and pyrolysis conditions have an impact on the physicochemical characteristics of BC [41].

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

Assertive progress is being made in the remediation of steroidal estrogens using BC and BC-composites, and numerous studies into the adsorptive removal of estrogens using BC made from diverse feedstocks under various pyrolysis and adsorption conditions have been taken into account. In reviews examining a broad range of minute contaminants, the remediation of estrogens from wastewater has been studied.[44]

Adsorption isotherms explain how an analyte disperses between the adsorbent surface and the aqueous medium. Using isotherms for adsorption in unsolidified media, researchers can learn crucial information about the factors involved in adsorption at a potent liquid interface. The Langmuir, Freundlich, Langmuir-Freundlich, Dubinin-Radushkevich, Temkin, Redlich, Peterson, and Polanyi Manes models have all been used to illustrate the removal of estrogen using BC. The Freundlich model and the Langmuir model were the most comprehensive of them. The Freundlich model demonstrated the best fits for E1, E2, E3, and EE2, and suggested 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].

Ning and Tong et al., in contrast, observe that the adsorption of E2 is broadly described by both the Langmuir and Freundlich models, indicating that diverse components were present. Montmorillonite biochar, which proved useful for the efficient removal of estradiol from wastewater, was created using agricultural wastes like cow manure and wheat straw. 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 reacting with KOH increases the rate of adsorption of estrogen E2. It can be easily separated directly from an aqueous solution due to its enhanced polarity. This method shows better efficiency and is the simplest method [56].

Wu Lin et al. and their coworkers stated that vermicomposting biochar is efficient and less expensive, which is more effectively used to separate E2 estrogen from the aqueous solution. Because biochar has a larger surface area and is porous, it performs better in vermicomposting at rising temperatures. The experimental results show a pseudo-second-order reaction suitable for the Langmuir and Freundlich model isotherms [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 in 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 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 plant leaves, and compost humic acid material. This method is strongly related to the linear, Langmuir, and Freundlich isotherm mechanisms 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 the biochar form by using carbon single-walled and multiwalled nanotubes and powdered granular activated carbon. Graphene-based biochar adsorbs estrogen from wastewater to reduce environmental hazards [60].

The non-linearity observed was related to the biochar's fragrant gaps, enlarged porosity, and surface area in biochar exposed to diverse pyrolysis settings and value expansions. The properties of biochar 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 was observed that maize biochar has greater adsorbivity than wood dust biochar. When HTTs were low, the greater carbon dioxide surface area and organic component composite (CO₂-SA/OC) remained a substance [61-63].

Zhou, Liu, and coworkers studied graphene-based magnetic biochar by using potassium ferrate solution to increase sawdust biochar and improvise the surface area and porosity of biochar at 900⁰C. The experimental results show a pseudo-first-order reaction 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. The activated magnetic biochar expanded in surface area and pore size at a temperature of 700 ⁰C. 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 micropollutants 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 absorbed 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 characteristics of E2 separated from wastewater at the pyrolysis temperature. The pH, ionic strength, and estradiol concentration are all impacted by the pyrolysis temperature. According to the experimental findings, at pyrolysis temperatures between 500 and 600 °C, ionic strength had a negligible effect on the adsorption of E2. The pseudo-second-order and Freundlich isotherm are the adsorption mechanisms that come after these [68].

The functioned biochar effectively removes endocrine-disrupting chemicals such as estrone, estriol, estradiol, and ethinyl estradiol from wastewater. The adsorption isotherm is based on the Langmuir model and the 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 algal bacteria by a hydrothermal process. The advantages of this method were observed in the experimental approach. It also helps to remove heavy metals like estrogen from wastewater [70].

The granular material is used to filtrate contaminated water to separate pollutants and estrogens present in it. The experimental work demonstrated that estrogens may be removed from contaminated water at laboratory and pilot scales using sand and granular activated carbon filters [71].

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

The activated charcoal acts 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].

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