

Review

Biochar as an Eco-Friendly and Economical Adsorbent for the Removal of Colorants (Dyes) from Aqueous Environment: A Review

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Abstract: Dyes (colorants) are used in many industrial applications, and effluents of several industries contain toxic dyes. Dyes exhibit toxicity to humans, aquatic organisms, and the environment. Therefore, dyes containing wastewater must be properly treated before discharging to the surrounding water bodies. Among several water treatment technologies, adsorption is the most preferred technique to sequester dyes from water bodies. Many studies have reported the removal of dyes from wastewater using biochar produced from different biomass, e.g., algae and plant biomass, forest, and domestic residues, animal waste, sewage sludge, etc. The aim of this review is to provide an overview of the application of biochar as an eco-friendly and economical adsorbent to remove toxic colorants (dyes) from the aqueous environment. This review highlights the routes of biochar production, such as hydrothermal carbonization, pyrolysis, and hydrothermal liquefaction. Biochar as an adsorbent possesses numerous advantages, such as being eco-friendly, low-cost, and easy to use; various precursors are available in abundance to be converted into biochar, it also has recyclability potential and higher adsorption capacity than other conventional adsorbents. From the literature review, it is clear that biochar is a vital candidate for removal of dyes from wastewater with adsorption capacity of above 80%.

Keywords: adsorption; biochar; dyes removal; wastewater treatment

1. Introduction

Water pollution has become a major environmental problem globally. Different types of contaminants, mainly discharged from the industrial and agricultural activities, significantly contribute to water pollution. One of the major contributors to water pollution is the release of untreated dye effluents. These dyes are not only harmful to the plants and aquatic life, but also to human beings. Cancer, allergies, skin diseases are some of the health complications that may arise due to the ingestion and absorption of dye-contaminated water by humans [1]. Biochar has been identified as a potential candidate for wastewater treatment. The use of biochar for wastewater treatment has an added advantage due to the availability of abundance of surface functional groups on biochar surface and having a large surface area. Biochar is produced by the decomposition of biomass by thermochemical methods in the absence or low amount of oxygen. Different biomass feedstocks could

be utilized to synthesize biochar, which include algae, crop residues, forests biomass, and animal manures. Torrefaction, hydrothermal carbonization, microwave heating, and gasification are some of the methods available for thermal decomposition of biomass [2,3]. Before biochar can be used, it has to be subjected to pretreatment processes (e.g., sieving, washing, crushing, etc.), followed by pyrolysis.

Biochar is a heterogeneous, carbonaceous char obtained from thermally treating a large amount of organic waste/mixture that has been heated and decomposed completely. Biochar exhibit properties, such as catalytic activity, adsorption efficiency, high porosity, and high surface area, and has been found to enhance various processes, such as anaerobic digestion, soil retention, and adsorption [4]. As other methods of controlling pollution of water/air/soil, such as membrane separation, ion exchange filtration, etc., have exhibited significant economic demerits and low efficiencies, biochar has become an important material to remove the aquatic pollutants [5].

Environmentally friendly, economically feasible, and easily designable adsorbents for the treatment of water have gained popularity in the past few decades. In this regard, use of biochar, obtained from natural sources, such as forest and agricultural biomass, organic waste, and animal waste has become important [6,7]. This review focuses exclusively on how biochar works as an adsorbent for the removal of dyes, present in water as pollutants. The inherent properties of biochar make it an ideal candidate for the adsorptive removal of dyes from water. Biochar has already been established as a viable non-toxic and environmentally-friendly adsorbent capable of adsorbing a large spectrum of compounds from wastewater [8,9]. The potential of biochar is influenced by a variety of factors starting from the source of biomass from which biochar is prepared along with the method of preparation, reaction conditions, nature of pollutants, and the mechanism of action, all of which have been examined extensively in this review. The use of biochar as being eco-friendly for the removal of dye from wastewater has been examined in the past by several researchers [10–13]. This review aims to summarize and provide a holistic view on the research on biochar as an adsorbent for the removal of dyes from wastewater.

2. Colorants in Water and Toxicity

2.1. Natural and Synthetic Dyes

Dyes can be defined as color-imparting organic compounds that are water or oil soluble; they are distinguished from pigments that are insoluble. Natural dyes are those that are derived or extracted from natural sources, such as animals, flowers, roots, mollusks, minerals, etc. Natural dyes are broadly classified into two types: adjective and substantive [14]. Adjective dyes give permanent color only when used along with a mordant to bind them to the fabric; meanwhile substantive dyes contain a natural mordant, called tannin, and can give fast color without the use of additional mordants [15]. Mordants are compounds that act as a bridge between the fabric molecules and the dye, holding it in place to promote fastness [16]. Weak acids, such as tannic acid and acetic acid, are some natural mordants [17,18], while metal salts, such as copper sulfate and ferrous sulfate, can also be utilized. The use of natural dyes is advantageous as these are relatively non-toxic and renewable in nature, but their use is not cost-effective in the industrial context, and they fail to give an even consistent hue when compared to the synthetic dyes. Natural dyes may still be used in domestic and small-scale operations.

Synthetic dyes are usually unsaturated organic molecules. The first synthetic dye prepared was Mauve, a reddish-purple dye, which quickly degraded under water or direct sunlight to form a pale purple color. The first synthetic dye was derived from coal tar, the product resulting from the carbonization of coal. In the current context, synthetic dyes are more economical and exhibit better color fastness in comparison to natural dyes; thus, they dominate the market. Though they are more economical, synthetic dyes are also decidedly more toxic and polluting than natural dyes, causing environmental pollution and adverse health effects on living organisms [15].

2.2. Classification of Dyes

2.2.1. Chromophores and Color Index (C.I.)

Atoms or groups of atoms are said to be chromogenic if they are able to impart colour to the dye, and different arrangements and numbers of these chromogenic groups in a molecule impart different colors to the dyes. The other atoms or groups of atoms in the molecule, which are bound to the chromophore, and influence or bring a change in the color of the dye, are called auxochromes [19]. Thus, different textile dyes have specific structures that contribute to their characteristic colors. Some examples of chromophores are carbonyl groups, nitro groups, azo groups, or a conjugated pi electron system. Groups such as hydroxyl, aniline, and sulfonic acid act as auxochromes [20]. Dyes are classified by their applications and are given a unique identifying name called the Color Index (CI). As dye structures can be very complex, referring to it by its chemical name can be impractical, and common names can change between regions; thus, the name of the dye is standardized by using its CI. Every dye is issued a generic name and a CI number; the generic name consists of the method of application of the dye (e.g., direct, reactive etc.), the hue, and an identification number. The dye is also given a CI number based on the functional group and configuration of the molecule. For example, the dye commonly known as Remazol Red B is referred to as CI Reactive Red 22 (CI number: 14,824) under CI classification rules [21].

2.2.2. Disperse Dyes

Disperse dyes are mostly non-ionic in nature and are insoluble or very sparingly soluble in water; they are named so because their application involves dispersing the dye into a very fine suspension in solvent [22]. The chromogenic groups in disperse dyes are azo, anthraquinone, or nitro groups. The non-ionic nature of disperse dyes make them an ideal choice for dyeing synthetic and hydrophobic fibers, such as acetate, polyester, and sometimes nylon and acrylic fibers [23]. This is because these fibers are negatively charged and so reactive or basic dyes cannot be used. Only the non-ionic disperse dyes, which are not affected by surface charge, are able to reliably dye these fabrics. Traditionally, a carrier is added to the dye to improve the dispersion action and to aid dyeing. Disperse dyes can be classified from class A to class D based on their sublimation temperature, with class A having the lowest and class D the highest [24]. Since sublimation temperature depends on the size of the molecule, class A dyes have lower relative molecular size compared to class D dyes. Due to its sparing solubility, non-ionic nature, and non-biodegradability, disperse dyes are particularly harmful when left untreated in wastewater [25].

2.2.3. Direct Dyes

Direct dyes are water-soluble, anionic dyes that, unlike reactive or vat dyes, can be applied directly onto substrates using a neutral or alkaline bath (using sodium chloride or sodium sulfate) [26]. These dyes have an affinity to cellulosic materials, such as paper, cardboard, cotton, etc., but can also be applied on fabrics, such as, rayon and silk, with the use of mordants. The chromogenic functional groups in direct dyes include stilbene, phthalocyanine, oxazine, thiazole, but mainly azo groups [27]. Direct dyes are advantageous compared to other dyes because they have superior lightfastness compared to most reactive dyed hues, even though they cost less and are, thus, more economical. They also require less water use and the salt concentrations of the effluent are much less, compared to most reactive dyes. Some direct dyes, such as, Congo red, are carcinogenic, and have been banned from use [28].

2.2.4. Reactive Dyes

Reactive dyes have become one of the most widely used synthetic dyes in the industrial context due to their excellent wash fastness and bright and varied types of hues [29]. The chromophores in reactive dyes are largely azo groups; blue and green colors are given due to the presence of

anthraquinone and phthalocyanine structures [30]. Direct dyes are largely used to dye cellulosic substrates and fibers, although other substrates can be used too. Unlike direct dyes, however, reactive dyes form new covalent bonds with the nucleophilic sites in fabric molecules, thus leading to its remarkable wash fastness [21]. Some of the most commonly utilized groups in reactive dyes are trichloropyrimidine, sulphatoethylsulphone, dichloroquinoxaline, and dichlorotriazin [13]. The major disadvantage regarding reactive dyes is their environmental threat. Effluent from dyeing cotton, using reactive dyes, are extremely polluted, having very high chemical oxygen demand (COD), salt load, and visible color in water [31]. Both, the unfixed dye and its hydrolyzed form, are soluble in water, and thus their removal is particularly challenging [32]. Some reactive dyes are also associated with heavy metals, such as chromium, copper, or nickel, and these can later be released into aquatic ecosystems on degradation of the dye molecule.

2.3. Toxicity of Dyes

The global textile industry is estimated to be worth around \$1 trillion USD and its contribution towards total world exports is around 7%, employing 35 million people worldwide [33]. Thus, this industry has a high impact on the environment and human health in general, due to the pollution it causes. The most prominent and destructive form of pollution, caused by the textile industry, is the water pollution due to manufacturing of dyes. Textile effluents are both aesthetically polluted, and have high salinity, chemical oxygen demand, and ecotoxicity [34], and due to their increasing ubiquity in surface water, can lead to adverse effects to human and wildlife health and to aquatic ecosystems in general. Most synthetic dyes are highly toxic to humans and aquatic beings, and have acute and chronic effects. For example, reactive dyes are notorious, causing health issues such as, dermatitis, occupational asthma, rhinitis, and other allergic reactions for the workers involved in these dyes manufacturing [32]. Dyes are also mutagenic and carcinogenic in nature [35,36], which leads to chronic effects, such as kidney, urinary bladder, and liver cancer in dye workers. A xanthene dye called erythrosine is carcinogenic, neurotoxic and DNA-damaging for humans and animals alike [30]. Metal complexed dyes, which are widely used for their resistance, have heavy metals, such as copper, nickel, and chromium. When discharged to aquatic environments, these metals can be taken up by fish gills and can be transferred to humans through the food chain [36]. Current treatment methods are inadequate to treat dye effluents effectively, because of their recalcitrant nature in aerobic environments [37], and thus, these substances can linger in soil and lead to bioaccumulation, leading to complications in organisms higher up the food chain [38]. Thus, current effluent treatment techniques are inadequate for the dyeing industry and to prevent the further insemination of surface water with such mutagenic and carcinogenic molecules, we must adopt novel and more effective treatment techniques, such as bioremediation or biochar adsorption.

3. Treatment Technologies for Dyes Removal from Water

3.1. Coagulation

Coagulation is one of the most popular wastewater treatment techniques used since the early 20th century. Coagulation is the process of adding chemical compounds to bind particles together until they acquire a large mass to ultimately settle down. These chemicals are known as coagulants and carry a positive charge, which are mixed rapidly in the wastewater for uniform distribution. Most of the dissolved/suspended particles encountered in wastewater carry a negative charge, which are neutralized by these coagulants, thus making these capable of sticking together. Coagulation process is usually employed as a preliminary step in wastewater treatment process. The most frequently used coagulants are iron or aluminum salts. However, wastewater (containing dyes) is rich in color, and have high COD levels. Hence, conventional methods, such as coagulation, prove inefficient and moreover cause the problem of sludge disposal [39]. A combination of the conventional coagulation technique with other treatment methods must be innovated to improve its efficiency. For example,

combination of coagulation and adsorption techniques was a feasible way for the removal of reactive dyes from water [40]. The adsorbent used was activated carbon, derived from coconut shells, and the coagulation process was carried out using aluminum chloride as the coagulant. It was found that the removal efficiencies for Orange 16 and Black 5 reactive dyes were 84% and 90%, respectively [40].

3.2. Advanced Oxidation Processes (AOPs)

AOPs are chemical treatment methods used to remove the organic/inorganic contaminants present in wastewater by the oxidizing action caused due to the in-situ production of hydroxyl radicals ($\bullet\text{OH}$) [41]. These radicals are produced by oxidizing agents (H_2O_2 , O_3 , KMnO_4), catalysts, or UV light. Some of the AOPs include photocatalysis, ozonation etc. [42]. The following sections briefly explain some of the AOPs used in dye removal from wastewater.

3.2.1. Ozonation

Most of the dyes, encountered in wastewater, have polycyclic aromatic structures containing elements, such as nitrogen, metals, and sulfur, which makes it difficult to treat the wastewater by physical, chemical, and biological methods. Conjugated chains present in the dye structures, responsible for imparting color, are actively destroyed by ozonation, which is an AOP method that involves the chemical treatment of wastewater by dissolving ozone in water [43]. Employing ozonation as a treatment technique is advantageous as zero sludge is generated. Degradation of the dye is achieved in a single step and furthermore, ozone decomposes into stable oxygen [44]. However, ozonation as a treatment process very rarely results in complete oxidation, so by-products are usually formed in the effluent stream [45].

3.2.2. Fenton's Reagent and Fenton-Like Processes

Fenton's reagent is a solution of ferrous iron along with hydrogen peroxide, which finds its use as a catalyst in oxidizing various contaminants present in wastewater. A composite of La-Fe-O [46] was used as a photo-Fenton catalyst in the presence of light irradiation and hydrogen peroxide, and it was found that rhodamine B dye was oxidized to 98% within 25 min.

3.3. Membrane Processes

Membranes have been in use for wastewater treatment as early as the 1960s. Since membrane processes were too expensive at that time, this process was only chosen for specialized applications. Since the 2000s, membranes have been made cost-effective and are being used with other conventional water treatment processes. A membrane is a thin, semi-permeable material that is attached to a porous support, and is used for the removal of dissolved substances, based on properties, such as, size or charge, when a driving force is applied on it. Membrane processes are used in reverse osmosis (RO), forward osmosis, nanofiltration, and ultrafiltration.

3.3.1. Nanofiltration

The membranes used for nanofiltration have pore size within the range of 0.1–10 nm. Nanofiltration membranes have the advantages of separating dyes with a high molecular weight and also have >90% rejection efficiency for dye removal, making it a promising approach towards dye removal [47]. For example, positively charged polyethylenimine-modified nanofiltration membrane showed semi-xylene orange, Tropaeolin O, Victoria blue B dyes removal efficiency of 99%, 98.3%, and 99.2%, respectively [48].

3.3.2. Forward Osmosis (FO)

FO is a water treatment process that utilizes the osmotic pressure gradient to separate water from its dissolved solutes. Since FO process is completely devoid for the requirement of a driving force, it is

more energy efficient compared to reverse osmosis and other membrane separation processes [49]. A thin-film composite membrane was used under forward osmosis by [50], and it was found that it had a dye rejection rate of $\geq 96\%$ for commonly used dyes in the textile industries.

3.4. Biological Process

Biological process involves the usage of bacteria, microbes, and other microorganisms to treat wastewater. These biological processes are environmentally friendly, energy saving, generate low sludge, and require zero to minimal amount of chemicals to be used. The efficiency of biological processes could further be increased by varying the environmental conditions to favor the growth of the microorganisms. Algae is widely used by researchers as a potential option for the purpose of biosorption, as algae contains proteins, lipids and functional groups such as amino, carboxylate, sulfate, etc., in its structure [51]. Since algae possesses a wide surface area and excellent binding affinity in its cell structure, it results in high biosorption capabilities [52]. As algae is easily accessible (highly abundant in saltwater oceans and freshwater lakes), the use of algae could subsequently be extended for the dye removal from textile wastewater. For example, chemically (sulfuric acid) modified defatted *Laminaria japonica* biomass (renewable brown algae) showed methylene blue adsorption capacity of 549.45 mg/g, and quasi-equilibrium was achieved within 60 min under optimal conditions with a biosorbent dose of 0.6 g/L, pH 6 and temperature of 308 K [53].

Bioreactors are also becoming increasingly popular for dyes removal. Usually, a combination of both aerobic and anaerobic processes is used for the treatment of azo dyes. For example, the removal of Alizarin Yellow R dye was studied by the combined process of up-flow bio-electrocatalyzed electrolysis reactor and aerobic bio-contact oxidation reactor in just 6 h of hydraulic retention time [54]. Moreover, the COD removal efficiency and decolorization efficiency was found to be $93.0 \pm 0.5\%$ and $93.8 \pm 0.7\%$, respectively, in the process.

3.5. Adsorption Process

As far as dye removal from water is concerned, adsorption has been found as one of the best treatment processes among other conventional water treatment methods due to its low-cost, affordability, greater efficiency, and the fact that it requires minimum maintenance [55]. Adsorption also has the added advantage of producing no detrimental residues and having the capacity to treat a large volumes of water [56]. An adsorbent could also be recycled multiple times for its usage in subsequent treatment processes [57]. Common materials, such as activated carbon, zeolites, activated alumina, silica gel and polymeric adsorbents have been widely used for water treatment. The use of biomaterials for adsorption processes instead of conventional materials is now being the subject of interest by many researchers as the commercial value of biomaterials is low, and also they are available in abundance [58]. Naturally-derived biopolymers, which are hyperreactive, chemically stable, possess good physicochemical properties have garnered significant attention that is worth looking into for employing these biopolymers for the role of green adsorbents [59]. Table 1 highlights the major advantages and disadvantages of treatment techniques, available for dye removal from water.

Table 1. The advantages and disadvantages of various treatment technologies for dyes removal from water.

Treatment Technology for Dyes Removal	Advantages	Disadvantages
Coagulation	<ul style="list-style-type: none"> Reduced time for settling of suspended solids Easy removal of fine particles Effective in removing bacteria, protozoa, and virus 	<ul style="list-style-type: none"> High cost to spend for frequent monitoring and accurate dosing Huge volume of sludge generation
Advanced Oxidation Processes (AOP)	<ul style="list-style-type: none"> •OH radicals can treat a wide range of organic material Zero sludge production 	<ul style="list-style-type: none"> Fenton's reagent AOP results in iron sludge generation High capital and maintenance costs are expected

Table 1. Cont.

Treatment Technology for Dyes Removal	Advantages	Disadvantages
Membrane Processes	<ul style="list-style-type: none"> • Minor, valuable products can be recovered from the feed stream • Process can be easily “scaled-up” • No-phase changes involve between the feed and product stream • Eco-friendly as simple and non-toxic materials are used 	<ul style="list-style-type: none"> • High flow rate has the potential to damage the membrane • This process results in membrane fouling effects. Regeneration and extensive cleaning are required. • High equipment cost
Biological Processes	<ul style="list-style-type: none"> • Almost all biodegradable organic matter is effectively removed • Efficient attenuation of color • Eco-friendly and a common wastewater treatment mechanism 	<ul style="list-style-type: none"> • Slow process • An optimal favorable environment is crucial • Biological sludge generation • Remediation of dye molecules is tough
Adsorption Processes	<ul style="list-style-type: none"> • Highly efficient process • Applicable for a wide variety of target contaminants • Treatment technology is easy to employ 	<ul style="list-style-type: none"> • Deterioration of adsorbent performance when subjected to multiple operational cycles • Spent adsorbent is likely to be a hazardous waste • Regeneration of adsorbent material is expensive

4. Biochar

4.1. Biochar Synthesis by Various Methods

Biochar is essentially a by-product formed when a large amount of organic matter (biomass) is heated at high temperatures in the absence or low amount of oxygen. Therefore, depending on the source and nature of the raw material, the process to prepare biochar also varies. In the industries however, there are mainly three processes, which dominate when it comes to the preparation of biochar. These are pyrolysis, hydrothermal liquefaction, and hydrothermal carbonization [60,61]. The three processes mentioned are used, depending on the raw material, hence the nature of biochar prepared by these three processes vary from one another.

4.1.1. Hydrothermal Carbonization

Hydrothermal carbonization in simple words is a method used to produce “structured” carbon such as charcoal, biochar, etc., from organic matter [62,63]. The main concept behind hydrothermal carbonization is to replicate natural carbon formation (when bioorganic compounds are exposed to extreme pressures and temperatures over thousands of years), but accomplish the same result in a shorter duration. In essence, hydrothermal carbonization is done by taking a mixture of biomass (animal wastes, plants etc.) and water in a pressure vessel, which is then heated to high temperatures (180–250) °C and extremely high pressures of 10 bars or more [62–66]. At such high temperatures and pressure, the pH of the solution decreases due to the increase in production of oxonium ion. At these specific conditions, more and more organic matter releases into the water due to the low pH conditions, which causes the formation of a sludge-like compound that is predominantly made of carbon. The sludge obtain can be separated and dried. Various compounds such as bio-oil, hydrochar, biochar, carboxylic acids, ketones, aromatics, etc., can then be used for various purposes [64,67]. Depending on the required product, the reaction can be stopped at multiple stages to obtain a variety of products. The biochar produced from regular pyrolysis varies in many aspects from the biochar produced by hydrothermal carbonization; hence, the product obtained from hydrothermal carbonization is called as hydrochar rather than biochar. Hydrochar and biochar vary in properties and conditions in which they are prepared [68], but they are essentially composed of the same chemical constituents and are prepared from the same raw material [64,65].

Hydrochar produced as a result of hydrothermal carbonization has shown to have large amount of polyfuran and N-heterocyclic aromatics, which have a tendency to reduce the mobility of nitrogen thereby, preventing its quick release into the soil [69]. Unlike many types of biochars, it has been seen that hydrochar produced as a result of hydrothermal carbonization has low organic content and reduced mobility of heavy metals, which makes it ideal for soil amendment. Addition of hydrochar to soil has shown to improve water retention capacity, microbial community, nutrient holding capacity, and much more [69,70]. Since the use of hydrochar has grown considerably only during the last decade, research on different aspects of hydrochar is still yet to be studied thoroughly. The extreme conditions of hydrothermal carbonization not only lead to the decomposition and dissolution of organic matter, but also makes heavy metals “bio-available”. Therefore, detailed research is needed in order to ascertain the total capacity and effect of hydrochar, especially its use as a soil amendment, and how different hydrochar produced from different raw materials behave.

4.1.2. Hydrothermal Liquefaction

Hydrothermal liquefaction is essentially a decomposition process in which wet biomass is converted into a variety of products including bio-oil (liquid), biochar (solid) by means of thermal depolymerization. Wet biomass is exposed to extreme temperatures (250–550 °C) and pressures of (5–25) MPa. During hydrothermal liquefaction, a variety of chemical processes take place on biomass including hydrolysis, fragmentation, dehydration, aromatization and repolymerization, which results in the formation of biochar along with other compounds [71–74]. As stated before, the nature of the biochar obtained depends on different factors, such as, temperature, pressure, nature of raw material, residence time, etc. [75]. Extensive research into composition of biomass, and hence the properties of biochar, suggests that the main constituents of biomass (lignin, cellulose, and hemicellulose) play a key role in influencing the formation, as well as properties of biochar, especially lignin [76–79]. When biomass is heated at 220 °C, lignin gets dissolved very easily into water by hydrolysis leading to the formation of many phenolic compounds. Similarly, cellulose and hemicellulose, which are present in the biomass, also undergo various reaction leading to the formation of char [71]. Rice husks/pinewood was used as feedstock into a 100 mL autoclave along with deionized water. The autoclave was operated for 20 min at 573 K and the products that were formed (bio-oil and biochar) were removed using acetone, and the biochar was subsequently dried in a hot-air oven [71]. At very high temperatures, all of the biomolecules present in biomass, such as lignin, completely degraded and, therefore, the conversion needed to form biochar ceased to occur [71]. Very fast heating and sudden rises in temperatures inhibit biochar formation and slower and steadier processes are preferred [71]. Many studies show that physical properties, such as surface area and volume of biochar, is much lower while producing biochar from hydrothermal liquefaction (HTL) than from pyrolysis, however, recent studies suggest that biochar produced using HTL seems to be effective in adsorbing heavy metals and acting as biological catalysts [80].

Even though water is an abundant resource and is easy to use, it has been seen that use of different types of alcohols (butanol, methanol, etc.) improves the properties of biochar, as well as the amount of biochar that will be produced by HTL [81]. However, it was observed that water does not support polymerization reactions and, hence, production of bio-oil is more preferential as compared to biochar when water is used as a solvent [71]. Chemically prepared biochar as a result of hydrothermal liquefaction, has been found to have very high oxygen content in the form of hydroxyl, carboxyl, cyclic oxygenates, such as phenyls, glycerol, etc., and particularly phenol and lactone hydroxyls in biochar formation from rice husks/pinewood [71,75,81]. The functional groups in each biochar vary significantly and temperature plays a key role in determining the functional group. For example, if biochar is prepared at 280 °C and 360 °C, the functional groups were significantly less in the biochar prepared at higher temperatures [71].

Alcohol as solvent has significant advantages over the use of water, some of which include better reaction conditions, ability to release hydrogen for stabilization, higher reactivity with acid-components

to form esters compared to water [81]. Apart from increase in biochar production, bio-oil production is also significantly increased, when alcohol is used as a solvent. Usage of glycerol as co-solvent acts as a high lipid additive and helps in converting low-lipid algae into bio-oil and biochar, which would usually be difficult and would require extreme conditions, which are not economical [81]. In conclusion, hydrothermal liquefaction is a process, which is still improving, and certain characteristics can be helpful under certain specific conditions when necessary.

4.1.3. Pyrolysis

Pyrolysis is mainly used to produce many forms of carbons from biomasses under high temperature and inert conditions. However, as engineering advances, the use of pyrolysis for converting biomass to syngas and biochar has grown significantly. As the other processes described earlier, the products that are formed as a result of pyrolysis significantly depend on the biomass, reaction conditions, and feedstocks used. Bio-oil, which is formed as a pyrolysis result, can easily be upgraded into higher grade fuel and can be used for various applications [82]. Biochar is a valuable product formed from pyrolysis and has seen growth in applications such as improving soil retention, soil amendment, catalyst, carbon sequestration [82] and, hence, learning and gaining knowledge of production of biochar is of great interest. Use of biochar as soil amendment has shown promising results in the agricultural field and, hence, different types of biochars and different type of preparation techniques are studied in order to obtain the most effective biochar, which is capable of increasing soil nutrient availability, porosity, fertility, etc. [82]. Biomass with higher calcium oxide (lime) content when heated at temperature above 450 °C results in biochar with low amounts of oxygen functional groups and increased stability [82]. Further use of additives, such as phosphorus, zinc, iron, etc., during pyrolysis also modify biochar and, hence, expands its applications in various fields [83–85].

In the past few years, there has been extensive research on different methods of pyrolysis, which can affect the conversion of biomass to biochar. Optimization of pyrolysis methods makes it economic and advantageous over other processes. Figure 1 highlights the most preferred techniques for biochar production from various biomasses. The nature of biochar produced, as a result of pyrolysis, depends on many factors, some of which are biomass pre-treatment, reactor type, and dimensions, pressure, residence time in the reactor [86]. Compared to other processes, such as hydrothermal carbonization or hydrothermal liquefaction, pyrolysis has an advantage because of the fact that it can be used for a wide range of biomass and waste materials [87].

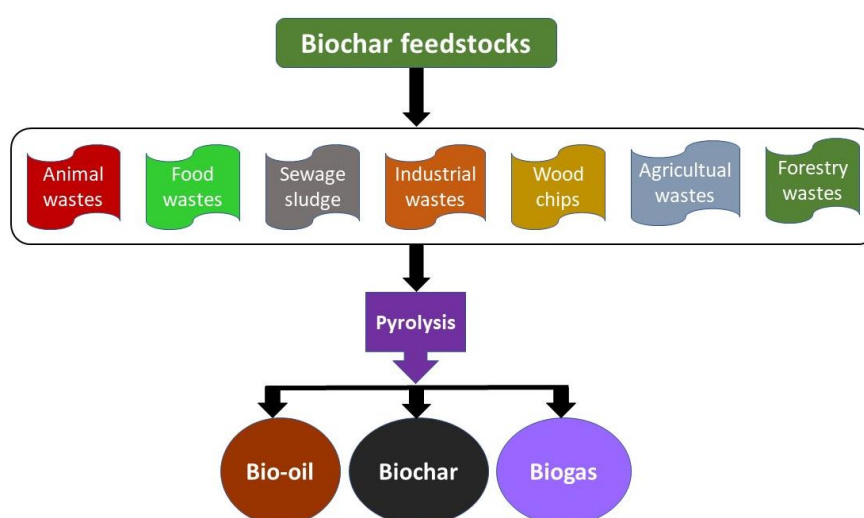


Figure 1. Schematic diagram showing biochar formation routes from different feedstocks.

Reactor designs and reactor types also have an important role to play and information regarding their influence on the type of pyrolysis has been studied [87]. In general, reactors such as auger

reactors, rotary and drum Kilns are commonly used for pyrolysis. When the operating temperatures in these reactors are extremely high in the range of 800 °C to 1300 °C, the pyrolysis is referred to as fast pyrolysis [87]. The concept behind fast pyrolysis is that when the temperature is very high and residence time is low, char formation is prevented and the biomass undergoes thermal cracking. Slow pyrolysis, such as the name suggests, involves very slow rise in temperatures and very high residence time, thereby getting maximum exposure of biomass to heat [88]. Contrary to fast pyrolysis, in slow pyrolysis, liquified products are kept to a minimum and solid carbonaceous char is preferentially produced. Finally, pyrolysis is flexible in the sense that it can operate at varying reaction conditions and with different types of feedstocks, hence, resulting in a large variety of products. The biochar obtained as result of pyrolysis of sludge (wastewater sludge) has seen to have many properties, such as nutrient recyclability, heavy metal immobilization, good pore structure, and alkaline nature [89].

Due to its versatility and flexibility and its ability to operate on a wide range of raw feedstock, it is the ideal process to choose. Further, biochar formed because of pyrolysis is extremely valuable, and can be modified in a multitude of ways for various purposes. In recent times, pyrolytic biochar has been used in soil remediation, wastewater treatment, catalytic enhancer, and much more. Since research on this particular subject is still ongoing and different strides are being done on a consistent basis, one can only assume that this process is going to be more efficient and more economical in the future. Supplementary Table S1 depicts different methods of biochar synthesis, based on their sources, methods of preparation, and preparation conditions.

5. Biochar as an Adsorbent

Biochar, being environmentally friendly and extremely versatile, has been seen as a novel material for treating wastewater. Due to biochar adsorption properties, it has been a viable method to adsorb colorants that are potentially toxic and harmful to the environment.

5.1. Effect of Operational Parameters on the Adsorption of Dyes by Biochar

Biochar as an adsorbent works under extremely specific conditions. Concentration of dye/biochar, temperature and solution pH play important roles in determining the efficiency of biochar [90–95]. Nickel modified biochar was capable of adsorbing methylene blue with an adsorption capacity of 479.49 mg/g at 20 °C from wastewater [96]. Initially when the concentration of methylene blue was low, the adsorption by biochar was high due to the large number of active sites still available on the biochar for adsorption. Competitive adsorption was found to hinder the efficiency of adsorption of methylene blue by the biochar [96]. Research on the adsorption and degradation of acid red dye revealed that increase in temperature of the solution increased the rate of decolorization [97]. In this particular study, the temperature was maintained between 30 to 50 degree Celsius and it was observed that increase in temperature increased the rate of molecular collisions and, hence, the rate of the reaction resulting in the rapid increase of adsorption and decolorization of the solution.

One major factor that has constantly been seen to affect the way biochar behaves as an adsorbent is pH. In most studies, we see that the variation in pH causes major effects on the adsorption process using biochar. In study [91], on the investigation of the adsorption of methylene blue from wastewater, authors noted that the pH had a great influence on the degradation process of the dye. They observed that the efficiency of removal of the dye increased from a pH of 2 to 7 and then decreased from a pH of 7 to 11, which was due to the fact that the active sites on the surface of the biochar combined with the abundantly present hydroxyl groups, which caused a decrease in efficiency. A similar study was conducted by other researchers [92] on the adsorption of Congo red dye using biochar, made from organic peel waste, and the effect of different operational parameters on its adsorption was examined. It was observed that when the pH was kept between the range of 2–3, acidic conditions prevailed and the presence of H⁺ ions aided the adsorption of Congo red dye onto the active sites present on the biochar. At the same time, however, for a pH of higher than 7, alkali conditions prevailed and the presence of OH⁻ ions hindered the adsorption of dye onto the biochar by competing for the active sites

on the biochar. The results obtained in this study [92] were similar to that of other study [91], as both studies concluded that higher levels of pH are not ideal for the adsorption of dye using biochar due to undesirable electro-static conditions that were developed. The adsorption of organic dyes using food waste biochar was conducted and the effect of different parameters were examined [93]. As far as the effect of pH is concerned [93], authors observed that the removal efficiency of dye decreased by around 5% only, when the pH was altered from 3 to 11. However, when looked at more deeply, it was seen that the decrease in removal efficiency was not uniform overall, but was uniform between pH of 3–9 and a drastic decrease was observed, when pH approached to 11. Authors attributed this effect to the fact that when pH increased, decomposition of hydrogen peroxide decreased along with the conversion of carbonate and bicarbonates to their corresponding acid, which caused low reaction with OH^- radicals, which finally led to the decrease in solubility of iron that was present in the biochar. Therefore, in this particular case observed by [93], we see that the decrease in removal efficiency, due to changes in pH, is not as pronounced as in the other cases. In the experiment pertaining to adsorption of methyl violet dye using biochar conducted by [98], for pH values > 6 , it was found that the adsorption of dye was favored, and the trend observed was due to the fact that at very low pH, the concentration of H^+ ions is significant and, hence, they compete along with the cationic dye (methyl violet) for the active adsorption sites on the biochar, thereby decreasing the percentage of removal of the dye. When an anionic dye, such as Congo red, is to be removed, the trend relating to the effect of pH may vary compared to other commonly seen dyes. In another study [99] focusing on the removal of dye using biochar, it was observed that when pH increased from 2 to 11, a significant decrease in removal percentage of dye was observed. Authors of this study [99] inferred from the observations that the decrease in removal efficiency between pH of 2 and 6 was due to the fact that at low pH < 2 , the number of H^+ ions were significantly more and, hence, the adsorbent molecules acquired a positive charge and became cationic, increasing the adsorption of an anionic dye, such as Congo red, significantly. We see from the above-mentioned studies that the nature of dyes has played a significant role in determining the optimum pH for adsorption. When a dye is anionic, it has been observed that acidic pH (< 2) is favored since the adsorbent surface (biochar) being positively charged due to the increase in presence of H^+ ions and it electrostatically favors attraction of anionic dyes and when a dye is cationic, increase in pH (> 2) is favored as higher pH increases the presence of OH^- ions, which in turn makes the surface of biochar negative, which promotes the electrostatic attraction between the positively charged cationic dye and the negatively charged biochar surface [100,101]. From the studies we discussed above, it can be said that the interdependence between pH and adsorption is a key concept needed to understand the process of adsorption and that a large number of factors are responsible for different trends that may be observed. Figure 2 provides the schematic route of adsorption of dye from wastewater by biochar.

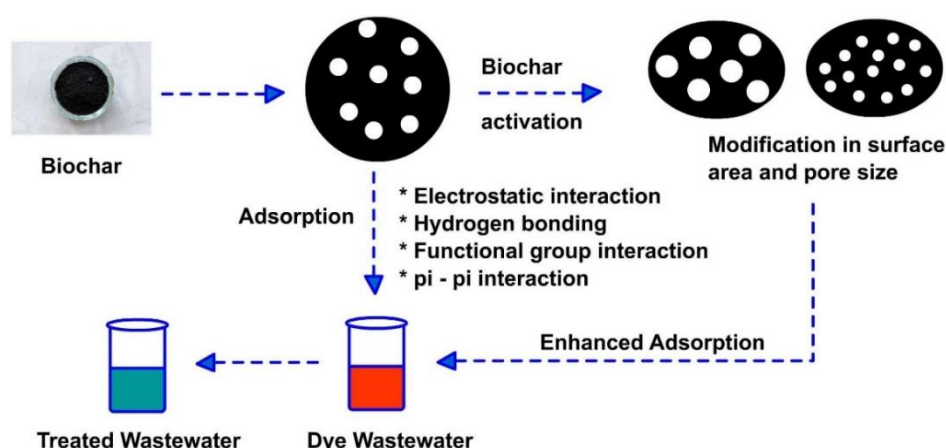


Figure 2. Schematic diagram of dye adsorption mechanism using biochar.

The dosage of adsorbent as well as adsorbate influence the extent of adsorption of dye and are important parameters to be considered. In a study of adsorption of dye using biochar [102], the removal percentage and capacity of adsorption were influenced heavily by the dosage of adsorbent. Even for a small increase in dosage of adsorbent caused the removal percentage to increase significantly (almost an 80 percent increase) and remained constant after a certain maximum dosage was reached. This phenomenon, according to authors [102], was due to the fact that at higher dosages of adsorbent, the number of active sites, as well as surface area of adsorption, will increase drastically, which in turn will increase the removal percentages of the dye present in water. A similar increase in percentage of dye removal with increase in adsorbent dosage was also observed in other studies [99,103,104]. The removal percentage of dye increased significantly for a very small increase in adsorbent (<1 g/100 mL) in all of the above-mentioned studies. This was similar to another study [102], which concluded that the increase in percentage of dye removal was because of the increase in dosage of adsorbent, which in turn increased the active sites for adsorption as well the surface area of adsorbent. However, the percentage of dye removal remained constant after a certain dosage of biochar due to the decrease in amount of dye molecules adsorbed per unit mass of adsorbent and the decrease in specific uptake [99]. Therefore, there will be no change in overall removal efficiency of dye by biochar after an equilibrium point has been reached. A similar conclusion was also achieved by [105], where switchgrass biochar was used as an adsorbent. It was observed that an increase in the dosage of biochar increased the removal percentage of dye and it reached an equilibrium percentage at around 50 mg of adsorbent dosage. Authors of this study [105] related this behavior to the increase in active binding sites and surface area due to the increase in dosage, which is similar to what has been concluded previously by other researchers [97,106]. When we assume the contrary, i.e., if the amount of dye is increased with the constant dosage of the adsorbent, the kinetics will depend on the equilibrium point, where the rate of adsorption of dye is equal to the desorption of already existing dye molecules [99]. The percentage removal will initially increase, and a small decrease may be seen, owing to the fact that the active sites present on the adsorbent (biochar) are completely occupied and the surface area that is free for adsorption decreases, while the number of dye molecules/reactive species adsorbed increases [99,106,107]. However, there are cases where the increase in concentration of dye indirectly increases the adsorption capacity of biochar until an equilibrium point after which no more adsorption is observed as all active sites on the biochar surfaces have been completely occupied by dye molecules, leaving no room for further adsorption [101]. The trends we discussed above, more or less, are similar in many aspects when it comes to the reason behind the increase/decrease in efficiency of dye removal. The operational parameters under which biochar works are of vital importance in order to understand and interpret the process of adsorption or other similar processes that might occur.

5.2. Adsorption Kinetic Studies

In order to understand the adsorption process and the rate of adsorption, kinetic studies are conducted. Kinetic studies have been extensively used by many researchers in order to study the mechanism by which adsorption takes place. Most adsorption kinetic studies apply pre-existing models, which act as guide to illustrate the adsorption mechanism. Pseudo first order, pseudo second order, and particle diffusion models are among the widely used models to describe the adsorption process. A wide range of standard models are available that describe adsorption at different conditions and the most suitable can be chosen for the given experimental conditions [108]. Adsorption of dyes using rice husks biochar was investigated, and from various kinetic models that were tested, pseudo second order model was the most suitable one to describe the experimental observations of the adsorption of malachite green dye using biochar [104], and the Elovich model was used in order to conclude that the mechanism of adsorption was chemisorption. In comparison, a similar study conducted on adsorption of Congo red by manganese composite biochar, it was observed that pseudo first order model was able to explain the kinetics of adsorption for a fixed amount of adsorbent and

adsorbate [103]. These kinetic models not only can be used to describe the experimental observations of adsorption capacity, but they also indirectly indicate a way to describe the mechanism of adsorption.

In a study [109], the adsorption of methylene blue was examined using sugarcane bagasse biochar, and it was observed that pseudo second order kinetic model fitted well to the experimental results. It was also inferred that the mechanism of adsorption was chemisorption. Hence, the use of kinetic models is not restricted to only a mathematical result, but can also provide information regarding the mechanism of action. Factors, such as nature of biochar and the nature of the dye to be removed, also play key roles in determining the adsorption kinetics. The adsorption kinetics varied depending on the biochar used and the rate of adsorption varied progressively (fast to slow) [110]. Authors inferred that it was because of inherent properties, such as pore volume and size, that caused the discrepancy in the rate of adsorption and choice of kinetic model, which was in conjunction to similar observations made by other researchers [111–113]. In examination of adsorption of reactive red dye using ball-milled biochar, the adsorption rate was initially fast and then gradually became slower [111]. From calculating the values of coefficient of determination (R^2), it was able to conclude that intra particular diffusion model had the most appropriate fit and hence, the mechanism of adsorption was primarily diffusion, and the removal of dye was influenced mainly by the external surface area [111].

Adsorption of acid chrome blue K onto Cetyl trimethyl ammonium bromide modified magnetic biochar was reported in [112]. The first 600 min showed a rapid increase in adsorption of the dye by biochar until it slowed down and reached an equilibrium stage after 60 min. In most cases, we see that the increase in dosage increases the rate of the adsorption (Section 5.1), i.e., removal efficiency of dye and, hence, the kinetics vary correspondingly. Another study involved the adsorption and degradation of acid red 88 dye from solution using Fe-Mn composite biochar [114]. In this study, authors observed that the change of dosage of biochar increased the removal efficiency and increased the rate of adsorption, which agreed with the pseudo first order kinetic model theoretically. Similar to the method used by [111,115], which inferred using a pseudo second order kinetic model that, in the adsorption of methylene blue using biochar (municipal waste derived biochar), the rate limiting step was the chemisorption step, and that the pseudo second order kinetic model was much more efficient than the other models in describing the particulate and liquid film diffusion and surface adsorption processes.

Thus, we see that the use of kinetic models is not entirely restricted to just correlating the experimental and theoretical values of adsorption efficiency, rate of adsorption and equilibrium adsorption, but can also be used to infer various possible mechanisms of adsorption based on the numerical values that are obtained. Contrary to previous observations by a large number of researchers, it is not always possible to obtain the mechanism of adsorption by using a suitable kinetic model [116]. The reason for this discrepancy stated by [116] was that the mechanisms of dye adsorption by hydrogen bonding (as dyes are present in the solution phase) may have been misrepresented diagrammatically in the previously established standards, which researchers often refer to. Therefore, if we look at what has been observed and concluded by the various researchers of this specific topic (adsorption of dyes using biochar), we see that, even though adsorption kinetic studies have their merits, they may be inherently flawed, if they are not studied extensively and deeply.

Table 2 elaborates the description of different kinetic models that are used in adsorption studies for dyes removal. To summarize, we see that the knowledge regarding kinetics of adsorption is an extremely helpful and intuitive way of understanding how adsorption takes place. Primarily a mathematical concept, one can infer various aspects regarding adsorption from kinetic studies. Considering all the influencing factors and different experimental conditions, one can apply kinetic studies to study the adsorption of dyes or any such pollutant using biochar and gain a much deeper and greater understanding of the concept [108].

Table 2. Adsorption kinetic studies of different dyes onto biochar.

Adsorbent	Adsorbate	Applicable Kinetic Models	Reference
Steam activated spent mushroom substrate (SMS)	Congo red and crystal violet	Pseudo first order Pseudo second order	[100]
Nickel aluminum layered double oxides modified magnetic biochar	Acridine orange	Pseudo first order and Pseudo second order	[101]
Chemically modified lychee seed biochar	Methylene blue	Pseudo second order	[117]
Triethylenetetramine biochar	Sunset yellow dye	Pseudo second order	[94]
Orange peel waste microwave activated biochar	Congo red dye	Pseudo second order	[92]
Fe ₂ O ₃ /TiO ₂ functionalized biochar	Methylene blue, Methyl orange, Rhodamine B	Pseudo first order	[91]
Switchgrass biochar	Methylene Blue, Orange G, Congo red	Pseudo first and second order model, Intra particular diffusion model	[90]
Biochar derived from <i>Opuntia ficus-indica</i> (OFI) cactus	Malachite green	Pseudo second order model, Elovich model	[118]
N-doped biochar	Acid red 18	Intra particular diffusion model	[113]
Ag-TiO ₂ biochar	Methyl orange	Pseudo first order kinetic model	[119]
Biochar derived from mixed municipal discarded material	Methylene blue	Pseudo first and second order model Intra particular diffusion model	[115]
Mesoporous nano-zerovalent manganese (nZVMn) and <i>Phoenix dactylifera</i> leaves biochar (PBC) composite.	Congo red	Pseudo first and second order model	[103]
Cetyl trimethyl ammonium bromide modified magnetic biochar derived from pine nutshells	Acid chrome blue K	Pseudo first order model Pseudo second order model	[112]
Pristine and ball milled biochar	Reactive red 120	Pseudo-second order kinetic model Intra-particle diffusion model	[111]
Wood based biochar	Acid orange 7	Langmuir-Hinshelwood (L-H) kinetic mode	[107]
Pyrolyzed rice husk biochar	Malachite green	Intraparticle Diffusion Model Elovich models Pseudo second order model Pseudo-first order model	[104]
Animal waste biochar	Basic red 9	Pseudo first order model Pseudo second order model Pseudo Nth order model	[110]

5.3. Adsorption Isotherm Studies

An adsorption isotherm is an empirical equation, which relates the equilibrium concentration of solute, and is adsorbed on the surface of an adsorbent to the concentration of solute present in the liquid solution with which it is in contact with, as a function of pressure under constant temperature. For choosing the optimal isotherm model for the adsorption process, the following criteria must be fulfilled: (1) the isotherm model and the calculated equilibrium data must have a good fit; (2) the function of isotherm must be thermodynamically realistic; and the (3) analytical calculation of concentration from capacity and vice versa must be possible even in ideal scenarios [120].

A biochar prepared from pyrolyzed rice husk showed that the maximum removal of Malachite green dye by the biochar was 99.98% with an adsorbent dosage of 0.2 mg/L, dye concentration of 20 mg/L at pH of 6.2 over a period of 2 h [104]. Freundlich, Dubinin–Radushkevich, Langmuir, and Temkin isotherms were studied in order to determine the best fitting of the models. Langmuir isotherm model was found to have the best fit. This led to the inference that Malachite green dye had uniform binding energy with the active sites on the biochar, which was distributed homogeneously across the adsorbent via the mechanism of physisorption. An eco-friendly biochar was synthesized by the pyrolysis of Ashe Juniper and, thereafter, functionalized by sulfuric acid for the removal of methylene blue, a hazardous dye [121]. The Langmuir model had a higher correlation coefficient (R^2) value of 0.96 compared to the Freundlich model, which only had an R^2 value of 0.94. Since the Langmuir model was determined as the better fit, it implied that the biochar was monolayered, had identical binding sites distributed equally across its surface for dye adsorptive removal.

The fallen leaves from *Magnolia Grandiflora* L. were converted into biochar by subjecting it to slow pyrolysis for the removal of methylene blue dye [122]. Maximum dye adsorption was observed as 101.27 mg/g at an ionic strength (NaCl) of 0.1 M, pH level of 12 and at 303 K. Langmuir, Freundlich, Temkin, and Harkins–Jura models were tested. The experiments were performed at three temperatures (293 K, 298 K, and 303 K). Langmuir isotherm model was the best-fitted one and the adsorption process of methylene blue onto the biochar was found to be endothermic process. Furthermore, the dimensionless separation factor (R_L) had values of 0.139, 0.273, and 0.139, respectively, which clearly ranged between 0 and 1 for all three temperatures, suggesting favorability for the adsorption process. Freundlich isotherm model also proved favorable as the Freundlich adsorption intensity ($1/n$) values were 0.12, 0.09, 0.14, respectively, which were also between 0 and 1 for all three different temperatures. Temkin model had shown binding energies of 33.98, 51.36, and 46.78 kJ/mol, respectively, at the above different temperatures, implying that the adsorption process not only consists of an ion-exchange mechanism, as the binding energy should be within the range of 8–16 kJ/mol for the model to be accepted. For the Harkins–Jura model, the correlation coefficient (R^2) values were the lowest compared to other models, implying that multi-layer adsorption process had low correlation. The Langmuir model was concluded to be the best fitted among other models due to a high R^2 value of >0.99 . This demonstrated that the biochar surface was homogenous and methylene blue was adsorbed as monolayer, distributed equally throughout its surface.

Empty-fruit bunch fibers were activated by chemo-physical processes to prepare the biochar for the removal of Cibacron Blue 3G-A dye from aqueous solution [123]. The maximum dye removal was 99.05% by the biochar at optimal conditions of an adsorption dosage of 0.10 g/100 mL, dye concentration of 100 mg/L at a pH value of 10, temperature at 343 K over a period of 45 min of contact time. The adsorption isotherm models considered in this study were only Langmuir and Freundlich models. The correlation coefficient (R^2) for both models was greater than 0.9. The dimensionless separation factor (R_L) for Langmuir isotherm was found to be between 0 and 1, suggesting that the adsorption process was feasible. For the Freundlich isotherm, the Freundlich adsorption intensity ($1/n$) was also between 0 and 1, which was a good indication of favorability of the adsorption process. It was finally concluded that Freundlich isotherm was a better fit compared to Langmuir, due to its high R^2 value compared to the latter. This also led to the inference that the surface of the biochar was heterogeneous, multilayer and the mechanism of adsorption was physisorption. Table 3 summarizes the most common

isotherms studies in dye removal studies. Table 4 elaborates the detailed literature on the adsorption capacity of biochar adsorbents on dye removal.

Table 3. Adsorption isotherm studies of different dyes onto biochar.

Adsorbent	Adsorbate	Applicable Isotherm Models	Reference
Mg-Al-layered hydroxide intercalated date-palm biochar composites	Methylene blue	Langmuir, Freundlich	[124]
Rice husk biochar	Congo red	Langmuir, Freundlich	[125]
Cow dung biochar	Congo red	Langmuir, Freundlich	[125]
Magnetic chicken bone biochar	Rhodamine B	Freundlich	[126]
Chitin derived biochar	Methyl violet	Freundlich, Langmuir, Liu	[98]
Switchgrass biochar	Methylene blue	Langmuir, Freundlich	[90]
Switchgrass biochar	Orange G	Langmuir, Freundlich	[90]
Switchgrass biochar	Congo red	Langmuir, Freundlich	[90]
Banana peel extract and FeSO ₄	Methylene blue	Langmuir, Freundlich, Dubinin-Radushkevich	[127]
Chemically modified lychee seed biochar	Methylene blue	Langmuir, Freundlich, Temkin, Dubinin-Radushkevich	[117]
Bamboo shoot shell biochar	Rhodamine B	Langmuir, Freundlich	[128]
Cetyl trimethyl ammonium bromide modified magnetic biochar from pine nut shells	Acid chrome blue K	Langmuir, Freundlich	[112]
Bovine bone biochar	Basic Red 9	Langmuir, Freundlich	[110]
Fish scale biochar	Basic Red 9	Langmuir, Freundlich	[110]

Table 4. Adsorption capacities of various biochar adsorbents for the removal of different dyes from water.

Adsorbent	Adsorbate	Adsorbent Dose	Contact Time (min)	Adsorption Capacity (mg/g)	Temperature (°C)	pH	References
Chitosan Based Material	Basic Blue 7	0.3 g/L	60	1174 mg/g	25	6	[57]
Wet-torrefied microalgal biochar	Methylene blue	1 g/L	7200	113.00 mg/g	25	6	[129]
Wet-torrefied microalgal biochar	Congo red	2 g/L	240	164.35 mg/g	25	6–8	[129]
Surfactant Modified Chitosan Beads	Crystal violet	0.36 g/L	120	97.09 mg/g	50	6	[130]
Surfactant Modified Chitosan Beads	Tartrazine	0.72 g/L	120	30.03 mg/g	50	3	[130]
Calcium rich biochar from Crab Shell	Malachite green	0.5 g/L	150	12,501.98 mg/g	25	7	[131]
Calcium rich biochar from Crab Shell	Congo red	0.5 g/L	2	20,317 mg/g	25	4	[131]
Ziziphus Lotus stones	Basic Yellow 28	0.5 g/L	180	424 mg/g	20	8	[132]
Ziziphus Lotus stones	Basic Red 46	0.5 g/L	180	307 mg/g	20	8	[132]
Date palm petiole derived biochar	Crystal violet	NA	15	209 mg/g	30	7	[133]
Activated wakame biochar material	Methylene blue	0.06 g/50 mL	NA	841.64 mg/g	20	2–12	[96]
Activated wakame biochar material	Rhodamine B	0.06 g/50 mL	NA	533.77 mg/g	20	2–12	[96]
Activated wakame biochar material	Malachite green	0.06 g/50 mL	NA	4066.96 mg/g	20	2–7	[96]
Activated biochar derived from <i>Opuntia ficus-indica</i>	Malachite green	60 mg/100 mL	120	1341.38 mg/g	30	6	[118]
Biochar derived from <i>Caulerpa scalpelliformis</i>	Remazol brilliant blue R	2 g/L	300	129.00 mg/g	30	2	[134]
Biochar derived from <i>Caulerpa scalpelliformis</i>	Remazol brilliant orange 3R	2 g/L	300	130.11 mg/g	30	2	[134]
Biochar derived from <i>Caulerpa scalpelliformis</i>	Remazol brilliant violet 5R	2 g/L	300	139.76 mg/g	30	2	[134]
Biochar derived from <i>Caulerpa scalpelliformis</i>	Remazol black B	2 g/L	300	159.08 mg/g	30	2	[134]

5.4. Mechanisms of Dyes Adsorption onto Biochar

The mechanism of removal of dyes from wastewater using biochar involves many complex interactions (both chemisorption and physisorption) between the adsorbate (dye) and adsorbent (biochar). Current literature leads us to a conclusion that the adsorption involves multiple mechanisms working together, some dominating, others based on prevailing conditions of the system. Depending on the dyes, biochar and solvent, mechanisms, such as pore-filling effect, van der Waals interaction, electrostatic interaction, chemical action, ion exchange, surface complexation, π - π interactions, cation- π interactions could play important roles in the adsorption process [135].

Adsorption of positively charged methylene blue dye (MBD) using municipal sewage sludge and tea waste derived biochar was investigated [11]. The impact of pH on adsorption showed that adsorption was influenced by the pH; for pH lower than 2, the removal efficiency of MBD was only 80%, while it was nearly 100% at a pH of 11 [11]. This strongly suggests that the adsorption mechanism involved electrostatic interaction. At low pH, the abundant H^+ ions occupied the limited bonding sites on biochar and repelled the positively charged MBD molecules, but as pH was increased, the bonded sites were deprotonated and were free for the MBD molecules to interact, thus, greatly increasing the adsorption capacity. The alternate mechanism could involve ion exchange; as the concentration of released metal cations (Ca^{2+} , Na^+ , K^+ , Mg^{2+}) by the biochar in the equilibrium solution was recorded and it was found that concentration of these ions was greatly increased after MBD adsorption, especially Na^+ and K^+ ions, indicating that these ions were involved in the ion exchange process.

A study of malachite green dye (MGD) on activated biochar, derived from *Opuntia ficus-indica*, possessing a meso-porous structure showed increased physical adsorption capabilities; which indicated that the pore filling effect was the main mechanism [118]. Hydrogen bonding between the MGD functional groups and the biochar could have supplemented the adsorption process. The activated biochar also possessed amine and hydroxyl groups (according to XRD and FTIR analyses), which are electron rich in nature, while the MGD possessed electron-deficient functional groups as part of the aromatic ring. Thus, depending on the pH of the solution, π - π electron donor-acceptor (EDA) interactions and cation- π interactions would have also been possible.

A study of surface and structural parameters of biochar and their impacts on Q_m (maximum adsorption capacity) of MBD was conducted using biochar, derived from cashew nut shells [136]. It was found that Q_m varied linearly with the volume of pores having a diameter between 1.6 and 2 nm, and adsorption capacity was mainly dependent on these pores. This was because this pore size diameter closely corresponds with the size of the MBD molecule; thus, biochar adsorption can be very selective in the wastewater treatment by closely controlling the volumes and diameter of surface pores. The study also found high correlation between Q_m and presence of weakly acidic phenolic groups on the surface of the biochar. These groups attract MBD molecules by dipole-dipole interactions or hydrogen bonding, both facilitated by the aforementioned phenolic groups.

Removal of MGD, MBD, and Rhodamine B dye (RBD) using biochar was examined and it was found that the intramolecular diffusion process, involved in adsorption, is rate-limiting [96]. The first step is fast, getting progressively slower due to the reduced adsorption intensity and decrease of unoccupied active sorption sites on biochar surface. Fourier Transform Infrared Spectroscopy (FTIR) analysis also showed the presence of hydroxyl and carbonyl groups leading to adsorption by hydrogen bonding and π - π stacking. Biochar derived from crab shells, which were rich in calcium, was studied to adsorb MGD and Congo red Dye (CRD) [131]. Zeta potential analysis showed normal electrostatic interaction activity for both dyes but FTIR and XPS analysis of biochar showed a marked difference before and after adsorption, with typical calcite bands (1440 , 873 and 710 cm^{-1}) in biochar missing after CR adsorption, corroborated with the results of XPS spectra (decreased intensity of peaks at 348 and 438 eV) [131]. This suggested that calcite and CaO were involved in CR adsorption by biochar; this theory was further proven by the fact that crab shell biochar was more efficient without acid washing, indicating that the calcium ion interactions in adsorption had a positive effect in dye adsorption.

From the current literature review, it is apparent that there is a lack of studies to assess biochar performance in systems with more than one dye. Studies thus far have only utilized single dyes, adsorbed using batch processes. While studies such as [137,138] used textile effluents, which contained more than one particular dye, they failed to enumerate them and thus, the influence of the interactions of multiple dyes and biochar is unknown. It is essential, in an industrial wastewater treatment setting to determine the performance of biochar while simultaneously adsorbing multiple dyes. As [139] suggests, depending on the type of effluent, multiple treatment technologies could be combined to treat wastewater.

5.5. Potential Drawbacks of Using Biochar as an Adsorbent

In the above-mentioned sections, we extensively reviewed the potential of biochar as an adsorbent for the removal of dyes; however, the use of biochar possesses certain drawbacks. In most of the research that has been cited, we see that biochar is used under extremely specific conditions of dosage, temperature, etc., which determine how the process takes place. Hence, subsequent steps need to be performed to remove the biochar from the wastewater before reusing it for other applications, which can increase the cost of treatment. Few studies [116,126] which investigated the use of biochar as an adsorbent for dyes removal, concluded that in both cases, the efficiency of biochar decreased after prolonged usage. Therefore, we see that biochar as an adsorbent may require additional processes of desorption and that this could cause potentially economic drawbacks. Most commonly used biochars contain a significant amount of heavy metals, thereby increasing the risk of pollution due to excess desorption of these heavy metals [140–142]. Moreover, ref. [142] studied the environmental risk associated with different types of biochar containing heavy metals (derived from sludge of swine wastewater) and examined how they may affect the environment during the application of the biochar. Authors observed that the temperature, at which the biochar was prepared, played a crucial role in immobilization of heavy metal ions and it was found that 600 degrees Celsius was the ideal temperature for immobilization and heavy metals seemed to contaminate the environment at other undesirable temperatures. Moreover, ref. [140] extensively studied the effects of environmentally persistent free radicals on wastewater and soil. The free radicals (produced under certain carbonization and pyrolysis conditions), which may mobilize, may pose a significant threat to the environment if they are not monitored and managed. Furthermore, [140] research led to the conclusion that even though biochar finds a plethora of applications in various fields, it still possesses a significant threat as a pollutant to the environment if not used properly. A similar study was conducted by [141], in which the effect of temperature and raw material on biochar toxicity was studied. Their study suggested that at certain temperatures, heavy metals tend to diffuse and, hence, pollute the surrounding environment (wastewater in this case). It was observed that at exceedingly high temperatures, the heavy metals tend to volatilize and temperatures of around 400 degrees proved to increase the volatility of cadmium in comparison to the other heavy metals, hence enabling pollution of the surroundings through heavy metal contamination. Therefore, we see heavy metals diffusion into the surroundings, while biochar is used as an adsorbent, is of crucial environmental concern, and despite its wide application, it does possess certain drawbacks, which need to be taken into account before its usage.

6. Conclusions and Future Perspective

Biochar was found to be an outstanding candidate for the remediation of dyes from wastewater, as evident by the literature reviewed herein. Advanced oxidation processes (AOPs), such as ozonation and Fenton oxidation processes, provide a good removal of dyes and colorants, ranging from 85% to 95% within a time span of 30 min to 1 h. However, these processes have disadvantages, such as being expensive and skill intense. Whereas, the membrane-based processes, such as nanofiltration and forward osmosis, are highly effective, and result in more than 99% removal rates within a few minutes. These membranes are highly vulnerable and need replacement very often. Biochar produced in hydrothermal processing of biomass, upon surface modification, would act as an effective adsorbent

that could remove dyes from synthetic and real industrial wastewater. Pyrolysis and hydrothermal carbonization have been the most preferred techniques to processing various types of feedstocks (agricultural waste, algae biomass, sludge, plant residue, etc.) for biochar production. Most of the biochar-based adsorption processes exhibit chemisorption mechanism. Kinetic studies were exclusively carried out to these systems. Pseudo first or second order kinetic models fit well with experimental data. Furthermore, adsorption isotherm studies were also carried out by many researchers. Of all the isotherm models studied, Langmuir or Freundlich isotherm models fit most of the systems with R^2 values higher than 0.95, showing it as a good fit. The adsorption capacities of biochar-based adsorbents sometimes resulted in as low as 30.03 mg/g to as high as 20,317 mg/g. pH values play an important role in deciding the adsorption capacity of the biochar. Many studies were carried out to study the threshold pH values and results showed that in most of the cases, biochar could tolerate lower pH values up to 2 and higher pH values up to 11. Still, the removal efficiencies reached more than 80%.

The future scope in using biochar as adsorbent is huge. Engineered biochar and selective modifications will improve the efficiency of the biochar. Embedding metal frameworks derive catalyst quality biochar, which can be used for many advanced oxidation processes as a cheap catalyst. Moreover, regeneration and reuse of spent biochar adsorbent is a prominent niche in the research of biochar adsorbents. Very few studies have emerged in using spent biochar as soil amendment and additive in various biological degradation processes. Biochar can also be used as biocarriers after using as adsorbents. Studies on biochar–dye interaction will be important, as the problem of dye contamination in water is growing in most of countries worldwide.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4441/12/12/3561/s1>, Table S1: Summary of most preferred synthesis routes for biochar production from different feedstocks.

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