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REVIEW

Review on biochar as an adsorbent material for removal of dyes from waterbodies

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Abstract
Biochar has emerged as a potential candidate with a multi-faceted application in recent times. Abundant availability, high surface area coupled with porosity, and low cost have transformed biochar into a sustainable candidate for versatile applications such as wastewater treatment, soil nutrient enrichment, and many more. A growing number of researches have been exercised to produce biochar and composites derived thereof. This review article presents an in-depth discussion of biochar including its synthesis via hydrothermal and pyrolysis methods, elemental composition, role of O/C ratio, structural characteristics, physicochemical properties, and applications in dye removal from simulated and contaminated water. Role of diversified feedstock on the efficiency of biochar is presented. Physiochemical properties of biochar such as pH, water holding capacity, specific surface area, and stability have been illustrated in detail. The effect of operational parameters such as pH, temperature, dose, and nature of dyes on the adsorption has been thoroughly discussed. A comparative study on adsorption kinetics reveals that the pseudo-first-order and pseudo-second-order are the most followed ones. Adsorption capacities of differently prepared biochar suggest a wide range of effectiveness, starting from 30.03 mg/g up to as high value of 12,501.98 mg/g. Mechanistic interpretation of dye binding with biochar has been proposed to be a combination of electrostatic interaction, hydrogen bonding, π-π interaction, etc. Economic viability of biochar in soil quality improvement and water detoxification has been outlined. Waste management covering the safe disposal and utilization as building blocks is proposed.

Keywords Biochar · Feedstock · Pyrolysis · Dye · Adsorption · Kinetics · Mechanism

Introduction

Rapid industrialization coupled with increased water demand seriously creates problems for the environment and humans. Increased use of dyes and heavy metals make water bodies and soil contaminated thereby decreasing their potability. While heavy metals are not biodegradable, dyes impart serious deterioration in water quality leading to a threat to aquatic biota. Thus, an urgent need arises to search for cost-effective techniques to decontaminate water. Recent years witnessed a surge in the preparation and utilization of biochar as an alternative adsorbent for water treatment. Biochar is a highly porous and high-carbon form of charcoal. It is prepared by pyrolysis or by heating organic material and biomass in the absence or limited supply of air. Hydrothermal carbonization and hydrothermal liquefaction have been exercised in detail. Various pyrolysis techniques are commercially available that yield different proportions of biochar and bioenergy products such as bio-oil and syngas. The gaseous bioenergy products are typically wont to generate electricity; the bio-oil could even be used directly for low-grade heating applications and potentially as a diesel substitute after suitable treatment.

Biochar has recently grabbed the focus of researchers for environmental remediation and removal of industrial waste from water (Thines et al. 2017). The characteristic of biochar depends on the nature of biochar feedstock, the condition in which it has been prepared, and the method of synthesis or the technique which has been followed for the preparation. These factors affect various elemental properties namely the surface functional group, charge on the surface, pH, porous nature, and specific surface area. All these factors are largely responsible for the adsorption efficiency. By the virtue of

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these factors, biochar is regarded as a cost-efficient treatment and an effective technique for the removal of water contaminants. (Praveen et al. 2022).

The key objective of this review paper is to provide a clear understanding of different feedstock, operational parameters, physicochemical properties, and a detailed investigation of kinetic and isotherm study followed by adsorption efficiency. The mechanism involved in the adsorption of dye and regeneration of biochar is discussed. Environmental and economic advantages are also studied regarding the implementation of biochar on a broad scale. The manuscript also implied the future prospective, especially regarding its application on the industrial scale.

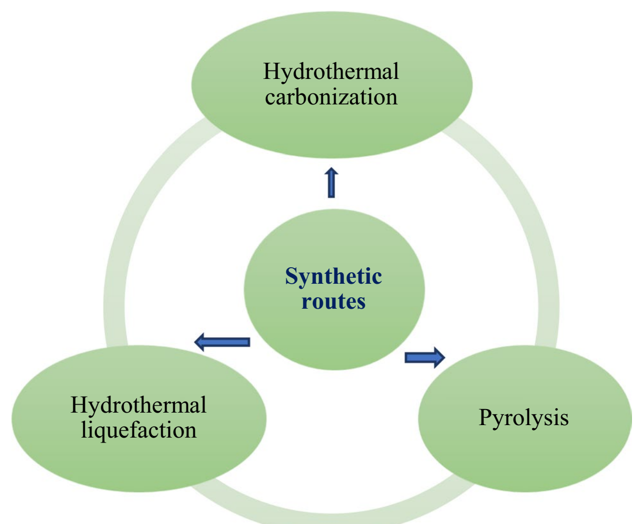
Date and location of the research

Date: May–July 2021, location: as provided in the author affiliation.

Biochar preparation methods

In earlier days, it was not known chemically what does biochar means, and hence Jones back in 1997 came across this problem in all biochar-related literature and proposed the guideline. (Hedges et al. 2000)A close inspection of the O/C molar ratio reveals that in the graphite, O/C molar ratio is 0, showing that no oxygen is there in their structure. In soot, the ratio ranges between 0–0.2, in charcoal, it is 0.2–0.5, whereas in char it is > 0.5. So, char is the name given to the material ranges between 0.4 to about 0.6. Biochar usually has a O/C ratio of more than 0.6. Summing up, the biochar spans multiple divisions in the black C continuum. However, it is noteworthy that biochar has no separate division though the property may vary with the oxygen and carbon ratio. Scheme 1 represents the variation of oxygen to carbon molar ratio in various carbon forms. This was used to differentiate between different black carbons and biochar.

Several synthetic routes that are available for biochar preparation are hydrothermal carbonization (Niinipuu et al. 2020), hydrothermal liquefaction (Li et.al. 2020), and pyrolysis (Shen et. al. 2020). These three processes differ in the use of raw material; more precisely as the raw material changes, the nature of biochar also changes. Scheme 2 represents various synthetic routes for biochar preparation.

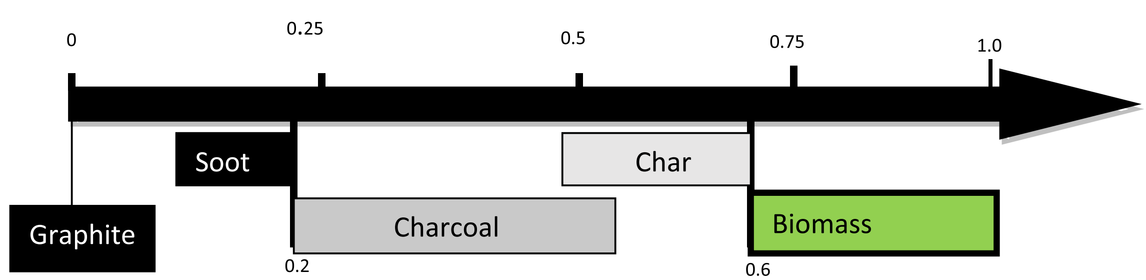


Scheme 2 Synthetic routes for biochar preparation

Hydrothermal carbonization

This method is used to produce structured carbon like charcoal, biochar, etc., from biomass.(Yusuf et al. 2020) As in the case of a fossil fuel where it is formed at high temperature and pressure over thousands of years using biomass, the same as in the case of hydrothermal carbonization, but the product is achieved in a shorter duration of time. For hydrothermal carbonization, a mixture of biomass like animal waste and/or plant waste/litter is taken along with water under a pressure vessel which is heated at the temperature range of 180–250 °C and pressure of about 10 bars or more(Ischia and Fiori 2021).

Although there is no such clear-cut classification available for hydrothermal carbonization, based on acting temperature it can be broadly classified into two categories. One



Scheme 1 Oxygen and carbon ratio for different carbon varieties (from Jones and Chaloner, 1991; Goldberg, 1985)

is high temperature (300–800 °C) and the other is the low temperature (< 300 °C). High-temperature range is used for the synthesis of graphitic carbon material, carbon nanotube, and activated carbon material, whereas in the case of low-temperature, effective carbon content elevates and the content of oxygen and mineral decreases in the carbonization process. (Salvador et al. 2007; Yoganandham et al. 2020)The product obtained by hydrothermal carbonization is called hydrochar instead of biochar. Although the properties and the condition followed during hydrothermal carbonization make hydrochar different from biochar, they are prepared from the same raw material (Fregolente et al. 2019). Hydrochar prepared by the hydrothermal carbonization has relatively low organic content, and less mobility of heavy metals and this is what makes hydrochar ideal for soil amendment (L. Wang et al. 2019). Adding hydrochar to soil improves water retention capacity, nutrient holding capacity, etc. (Maniscalco et al. 2020), and hence, it can be concluded that the biochar formed via hydrothermal carbonization would be best fitted for soil amendment and partially in water treatment purposes (Niinipuu et al. 2020).

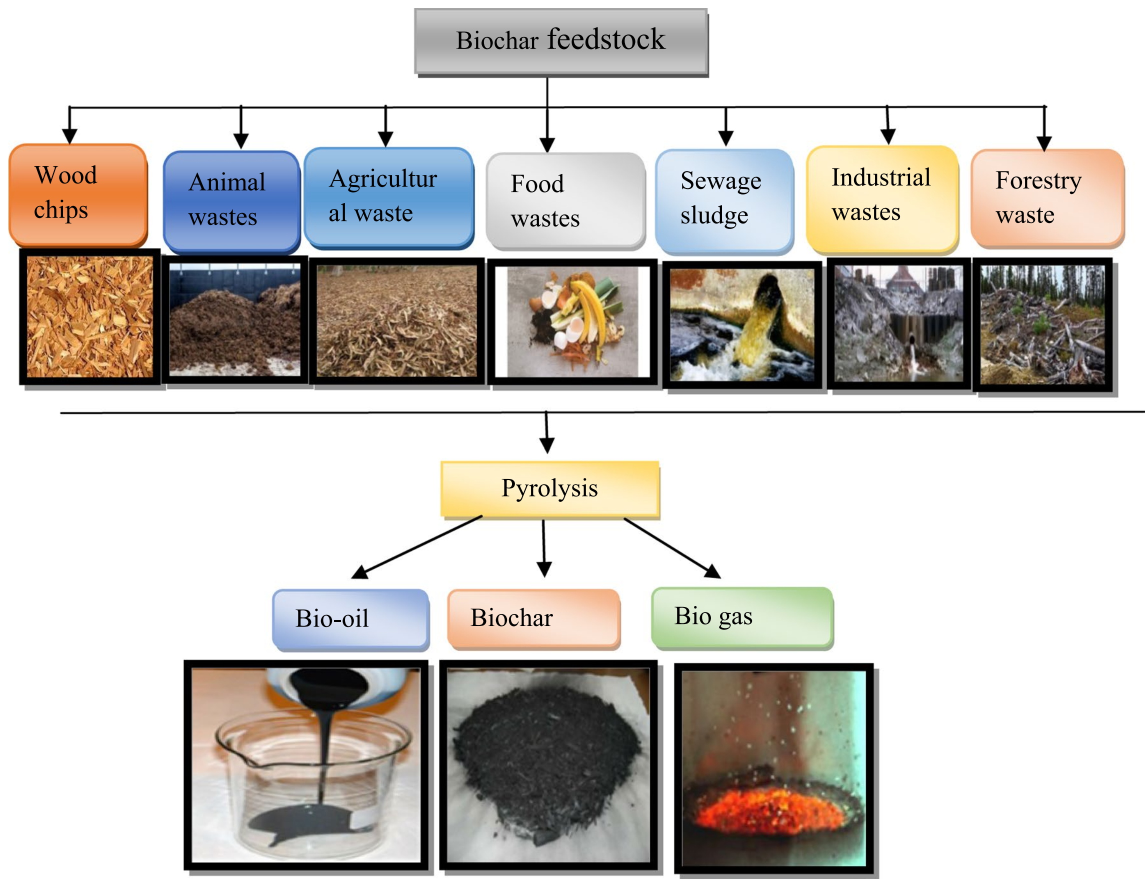
Hydrothermal liquefaction

In the case of hydrothermal liquefaction employing thermal de-polymerization, wet biomass is converted into a variety of final products including bio-oil and biochar. At temperatures ranging from 250–550 °C and pressure 5–25 MPa, wet biomass is exposed for a set time. During hydrothermal liquefaction, several chemical processes happen on biomass such as aromatization, dehydration, re-polymerization, hydrolysis, and fragmentation (Khan et al. 2020). This leads to the formation of biochar along with some other by-products. (H. Liu et al. 2017) Biochar thus produced depends on several factors such as feedstock, temperature, pressure, residence time, etc. (Sun et al. 2017). Though at high temperatures, residence time has been found to have limited effects. Based on different studies, it was noted that the main constituents of biomass are lignin, cellulose, and hemicellulose which plays the important role in the formation and properties of biochar. Out of this three, lignin is the major contributor. At a very high temperature, lignin gets degraded, and hence, it does not lead to the conversion of biomass feedstock into biochar. In most of the studies, it has been seen that the biochar which is produced by hydrothermal liquefaction differs in the physical properties like specific surface area and volume of biochar as compared to those which are produced by the pyrolysis. On the other hand, biochar obtained from hydrothermal liquefaction are good at heavy metal adsorption and also acts as a biological catalyst. (Muppaneni et al. 2017) It has been observed that alcohol such as methanol, butanol, etc. improves the quality of biochar in the case of hydrothermal liquefaction. (Ponnusamy et al. 2020) On using water as a solvent, bio-oil is most likely to form, as water does not support polymerization reaction leading to biochar. Alcohol shows a significant advantage as a solvent in the following ways they support better reaction condition and helps to release hydrogen which is important for stabilization purpose.(Cui et al. 2020) So, from the above discussion, it can be concluded that biochar formed by hydrothermal liquefaction can act as a biocatalyst for heavy metal adsorption.

Pyrolysis

Pyrolysis is a process in which carbons are formed using different biomass feedstock under high temperatures and inert conditions. It is interesting to highlight here that bio-oil which is formed by pyrolysis can be upgraded into high-quality fuel which has a lot of applications. (Shen et al. 2020) Biochar obtained from pyrolysis has applications in many fields such as catalyst, super capacitor, soil amendment, carbon sequestration, removal of dye from wastewater, climate change mitigation, and many more. Scheme 3 highlights the feedstock, and how they are converted into biochar after carrying out pyrolysis along with two by-products namely bio-oil and biogas. (Srivastava et al. 2020) The broad category of feedstock is there out of which wood feedstock contains chipped, shaved, bark, peeled, etc., agriculture waste feedstock includes corn, wheat straw, rice straw and husk, potato, coconut husk, soybean, sugarcane bagasse, cotton, orange, grape, peanut, and rapeseed/straw. Similarly animal waste and industrial waste include paper mill sludge, cattle, and dairy manure, horse/pig manure, swine manure, poultry manure and litter, fish scales, bio-solids, and so on. (Ippolito et al. 2020) Pyrolysis is an industrially preferred method over hydrothermal carbonization and hydrothermal liquefaction because it can be used for a broad range of biomass and waste, for the production of biochar. (Elkhalifa et al. 2019), and hence, the following discussion is primarily focused on pyrolysis. It is noteworthy that pyrolysis temperature affects the quality of biochar and possible applications originating thereof (Zhang et al. 2020a, b). Fast, intermediate, and slow pyrolysis has been demonstrated well (Asensio et al. 2013; Meier et al. 2013).

In the above topic, we have discussed different techniques used to synthesize biochar and it has been concluded that the yield of the product form after different techniques depend upon residence time, and temperature. Table 1 represents the yield of the product based on different physical parameters. It can be concluded from Table 1 that as the rate of pyrolysis increases, the corresponding yield of biochar increases, and the yield of bio-oil decreases. Comparing slow and fast pyrolysis, the residence time can be set as desired. For slow pyrolysis, biochar feedstock should be treated for a longer residence



Scheme 3 Representative feedstock along with products and byproducts of pyrolysis

Table 1 The yield of biochar, bio-oil, and syngas under various conditions

Technique	Temperature	Residence time	Bio-oil (%)	Biochar (%)	Syngas (%)	References
Fast pyrolysis	Moderate temperature–600 °C	Short hot vapor residence time	75	12	13	Asensio et al. 2013; Meier et al. 2013
Intermediate pyrolysis	Low moderate temperature (300 °C)	Hot vapor residence time	50	25	25	Asensio et al. 2013; Meier et al. 2013
Slow pyrolysis	Low moderate temperature,	Long residence time	30	35	35	Asensio et al. 2013; Meier et al. 2013
Gasification	High temperature (> 700 °C)	Long vapor residence time	5	10	85	Asensio et al. 2013; Meier et al. 2013
Hydrothermal carbonization	Elevated temperature (200–250 °C)	Elevated pressure	Not readily available	Not readily available	Not readily available	Asensio et al. 2013; Meier et al. 2013
Flash carbonization (350–650 °C)	(350–650 °C)	residence time below 30 min	Not readily available	50	50	Asensio et al. 2013; Meier et al. 2013

time and at a low temperature. In this case, the amount is also high compared to fast pyrolysis and intermediate pyrolysis. Intermediate pyrolysis is generally taken into consideration when a balanced ratio of bio-oil, syngas, and biochar is needed. In fast pyrolysis, bio-oil becomes the major product whereas in slow pyrolysis biochar is the major product.

Structure, elemental composition, and physicochemical properties of biochar

The composition and structure of a substance important parameters to determine its characteristics and designing an application. Likewise, the structural feature and composition of biochar are one of the most important reasons for its dynamic application in diverse fields.

Structural characteristics of biochar

Biomass is transformed into carbon-rich microporous material through pyrolysis and carbonization. The material has a well-developed porous structure and a high degree of aromatization. (Lehmann & Joseph 2017) The condition of pyrolysis and carbonization is closely related to the property of biochar. (W. Chen et al. 2019a, b) The nanoporous size of rice husk biochar possesses a volume of 2.1 $cm^3 g^{-1}$ which is about 12.35 times greater than the biochar obtained from sludge. (W. Chen et al. 2019a, b) According to different researchers, the temperature of pyrolysis is also a very important factor affecting the biochar structure. It has been seen that upon increasing the temperature, the aromatization and also the nanoporous size of the biochar increase. However, on increasing the temperature above 700 °C, some of the microporous structures seem to destroy, and when the temperature is further increased to 800 °C, the carbon skeleton structure of the biochar may get unstable.(Intani et al. 2018).

Elemental composition of biochar

Biochar generally consists of elements including C, H, O, N, S, P, K, Ca, Mg, Na, and Si, of which carbon has the highest content (above 60%), followed by H and O, with the minerals/elements mainly exists in ash.(Intani et al. 2018) The carbon in biochar is mainly aromatic, and it is deposited in an irregular stack of stable aromatic rings. Nitrogen is specifically present on the surface of biochar within a C–N heterocycle. But the available nitrogen content is invariably very low in the biochar. Similarly, the content of P is low in biochar. The availability of P varies with the pyrolysis temperature; it varies inversely with the pyrolysis temperature. Content of K, Ca, Mg, and Na is different in different kinds of biochar, metal ion having low valence are more available than the high-valence metal ions such as Al, Ca, and Mg in biochar. In a general sense, the elemental composition and activity of biochar are related to raw materials, conditions of the pyrolysis process, and pH.(Y. Yao et al. 2018).

Physicochemical properties of biochar

pH

Biochar is generally basic, as this is mainly related to the inorganic metal carbonates and phosphates, and the ash which has been formed during pyrolysis and carbonization. (Yuan et al. 2011) This is also influenced by the factors like raw material and carbonization temperature. If the pyrolysis temperature is changed, the pH generally increases as the temperature increases, this is due to the decomposition of acidic functional groups, such as carboxyl and phenolic hydroxyl, and the volatilization of organic acids. (Zhao et al. 2015).

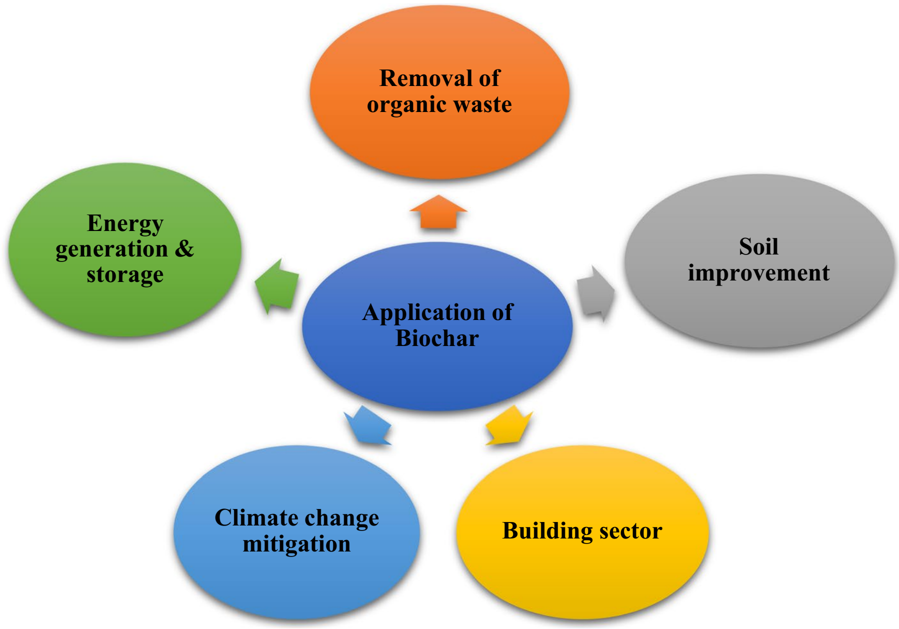
Specific surface area

Various studies suggest that the specific surface area of biochar generally lies within the range of 1.5–500 m^2/g. (Li et al. 2018) Researchers have reported that sugarcane biochar has a comparatively higher pore size as compared to coconut shell biochar. Sugarcane biochar has a pore size of 0.1 m^2/g and a specific surface area of 253.2 m^2/g whereas coconut shell-derived biochar has a pore size of 0.1 m^2/g and specific surface area of 25.8 m^2/g (Kajina and Rousset 2018). As the temperature increases, the surface area also increases within a certain range. (Ahmad et al. 2017) At relatively low temperatures the volatiles, tars, and other products, from the thermal decomposition of biomass fill the internal pore structure of biochar, and therefore reduce the specific surface area to some extent. Upon increasing the temperature, these substances decompose which allows the volatile gases to escape which in turn further reduces the pore size but dramatically increases in the number of pores in the biochar. On increasing the temperature to the critical value, the surface area decreases as the temperature increase, which might be due to the destruction of microporous structures and the enlargement of micropores.

Water-holding capacity

Biochar derived from different sources exhibits different water-holding capacities. As the temperature increases, the degree of aromatization and hydrophobicity of biochar also increases or is enhanced, resulting in the decreased number of functional groups containing O and N, and the water-holding capacities of biochar decline steadily (Yu et al. 2013). Water holding capacity in biochar has been shown to affect soil quality. It has been seen that most of the biochar are hydrophobic in nature having few polar components. Such observation indicates that such biochar having a large polar group enhances water retention efficiency. (Batista et al. 2018).

Scheme 4 Some representative applications of biochar



Stability

The stability of biochar is the main reason why it is used as an efficient alternative for reducing greenhouse gases. Biochar eventually decays so as any other organic matter, but the major difference is that it decays much more slowly, and may leave some unwanted materials. One of the primary reasons for the stability of biochar in soils is their chemical recalcitrance which is due to the presence of aromatic structures of varying properties that are subject to the current investigation. (Leng et al. 2019) High stability can also be explained by a high degree of carboxylate esterification and aromatization structure, high carbon content, low solubility, high stability, high boiling point, and strong resistance to physical, chemical, and biological decomposition. (W. Chen et al. 2019a, b) The stability of biochar is an important concern for dye removal in-field application.

Application of biochar

Scheme 4 shows some major applications of biochar. A broad range of environmental applications made biochar a suitable candidate for water treatment, energy generation, soil quality up-gradation, and many more. As this paper is focused on the major applications of biochar in the removal of organic dyes from water by adsorption technique, a brief description of the dye and adsorption phenomenon is presented below (Scheme 4).

Dyes

Dyes are molecules that connect themselves to the fabric surface to impart a permanent color (Yagub et al. 2014). Nowadays, dyes are used in various industries such as textiles, food, paint, paper, pulp, leather treatment, jute, wool, and personal care products. They possess an aromatic structure and are recalcitrant to biodegradation due to their xenobiotic nature. Discharge of waste dyes to water bodies results in considerable environmental and health problems. (Ramalingam and Jonnalagadda 2017; Song et al.; Mishra et al. 2019) It drastically decreases oxygen concentration in the waterbody and restricts the passage of light through the waterbody. Dyes can remain in the environment for an extended period because of high thermal and photo-stability against biodegradation. The greater environmental concern with dyes is their absorption and reflection of sunlight entering the water. High concentrations of dyes in water bodies stop the re-oxygenation capacity of the receiving water and cut-off sunlight, thereby upsetting biological activity in aquatic life and also influencing the photosynthesis process of the aquatic plants or algae. The polluting effects of dyes on the aquatic environment can be due to their prolonged exposure in the environment, accumulation in sediments especially in fishes or other aquatic life forms, decomposition of pollutants in carcinogenic or mutagenic compounds, and also low aerobic biodegradability. (S. Khan & Malik 2014)Many dyes and their breakdown product are carcinogenic and mutagenic, hence toxic for living creatures. (Altintig et al. 2018) The presence of very small amounts of dyes in the water is highly visible, and seriously affects the quality and transparency of water bodies such as lakes, rivers, and others, leading to damage to the aquatic environment.

Method for treating effluents

Several chemicals, biological, and physical methods have been developed for the removal of dyes from the water bodies. This review is focused on the removal of dye using biochar as an adsorbent. Adsorption is considered to be one of the best techniques. It offers advantages such as easy operation technique, high separation efficiencies, and cost-effectiveness.(Afroze & Sen 2018; Dey et al. 2020; Qaiyum et al. 2022; Mohanta et al. 2020; Ali 2012; Manippady et al. 2020).

Biochar as an adsorbent

Being environmentally friendly and extremely versatile, biochar becomes a potential material to treat dye-containing wastewater. However, successful removal of dyes depends on several operational factors such as solution pH, adsorbent dose, working temperature, the concentration of dye, agitation speed in batch, etc.

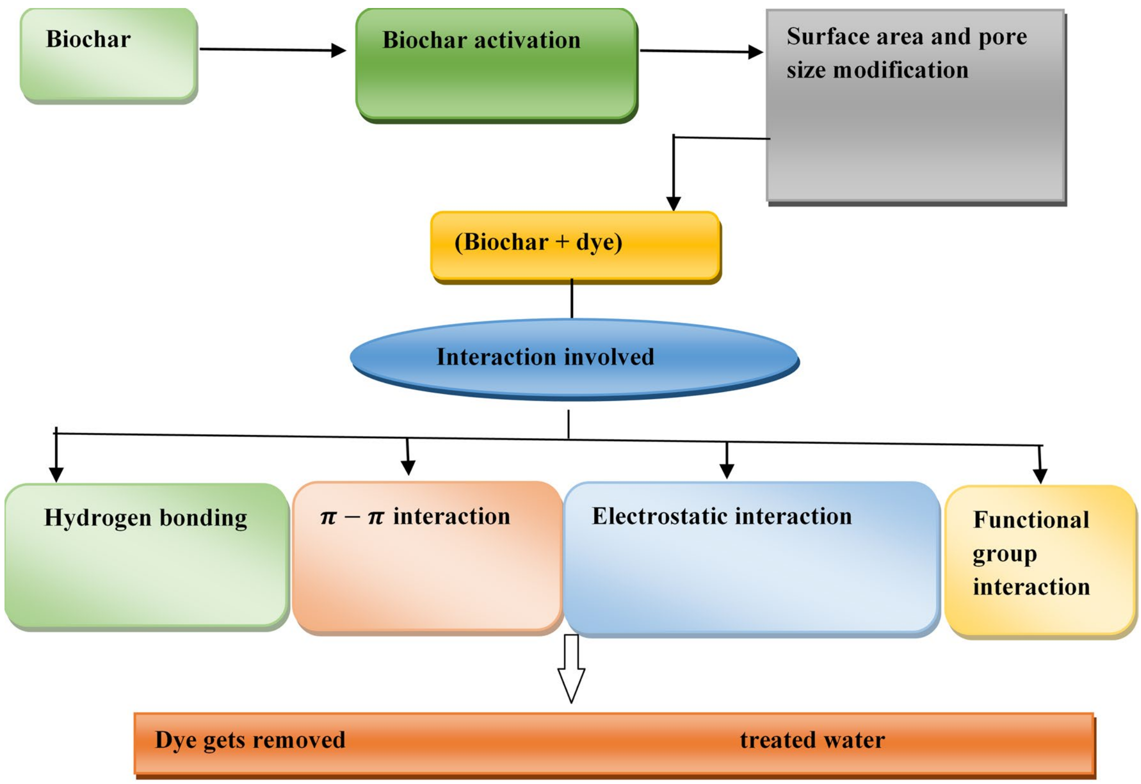
Effect of operational parameters

Biochar works well in a specific condition as an adsorbent. Some factors which play important role in determining the efficiency of biochar are the concentration of dye and nature of biochar, working temperature, and solution pH.(H. Wang et al. 2020).

In a study related to the removal of Methylene Blue (MB) by using rice straw as an adsorbent, in this case, corresponding biochar was obtained at temperatures of 300, 500, and 700 °C. This was done to know the effect of pyrolysis temperature on the adsorption capacity of dye. It has been seen that at elevated temperature pore size is large and hence higher surface area can be seen. Hence in this case pore size increased from 0.051–0.064 to 0.171–0.299 cm^3/g as the temperature increased from 300–700 °C in the case of rice straw. In the same study, pH was taken in the range of 2.0–10.0, and in this pHzpc was found to be 6.9 for the rice straw. From different studies, it has been seen that theoretically charge of the biochar surface is positive if the case is below pHzpc, but if the pH is more than pHzpc the biochar surface turns out to be negative. So, in this case, the adsorption of MB increase as the solution pH increases. Maximum uptake has been observed at pH 7.0 which was up to 91–95%, in the case of rice husk. It can be explained by electrostatic attraction between the positively charged dye and negatively charged biochar surface. As the solution pH increases the number of –COO- anion and –OH functional groups on the biochar surface also increases and hence there is an increase in the negatively charged sites. (A. Ahmad et al. 2020a) In a similar research work based on Remazol Black B and *Caulerpa scalpelliformis* (marine seaweeds) biochar as an adsorbent, it has been seen that pH plays an important role and if it is not optimized properly, it can influence the percentage of dye removal. As the biochar surface consists of lignocelluloses which contain amine group, carboxyl group, and sulfate so as the pH decreases removal efficiency will increase. The presence of these functionalities will increase the electrostatic interaction between biochar and the dyes and in turn, will increase the removal efficiency. In this case, also it has been seen that increase in the temperature of pyrolysis will increase the sorption capacity and hence increase the removal percentage. But carrying out pyrolysis at a high temperature of 45 °C will increase the cost also so the reaction has been carried out at 35 °C which is room temperature. (Gokulan et al. 2021).

From the above studies, it can be concluded that the nature of dye plays an important role in adsorption efficiency. It was also discussed that pH and adsorption are interdependent and a large number of factors are responsible for different trends. Scheme 5 represents dye adsorption using biochar involving several interactions. Activation of biochar leads to an increase in surface area and pore size which in turn acts as a better adsorbent. Possible modes of interaction have also been presented.

In a study related to anionic dye methyl orange (MO) with date palm fronds biochar as an adsorbent, it has been seen that the adsorption capacity of dye decrease with an increase in the amount of biochar dosage but after a limit of dosage it shows no decrease on an increasing amount of the biochar. In this case, the maximum adsorption capacity was found to be 63.5 mg/g. It can be explained by the fact that at a low adsorbent dosage adsorption capacity is high because the ratio of dye to adsorbent molecule increases and this, in turn, increases adsorption capacity. If we keep on increasing biochar dosage keeping dye concentration constant, this may result in overlaying of the binding site, and in this case, dye availability will be less for active sites so, this will also result in low adsorption capacity. (Zubair et al. 2020a) similar study based on rice husk biochar as an adsorbent it has been seen that the biochar dosage range lies between 0.5–5.0 g/100 mL and in this case, it has been seen that maximum adsorption capacity was observed at 5.0 g/100 mL. In this case, the removal efficiency was found to be 96.92% and hence this case increase in dye removal has been observed with an increase in biochar dosage. In the case of magnetic wakame biochar as an adsorbent taking methylene Blue as a dye, the removal took place with an adsorption capacity of 117.58 mg/g.(X. Yao et al. 2020) From the above study it can be concluded that operation



Scheme 5 Dye adsorption mechanism onto biochar

parameter plays an important role to know the adsorption process.

Adsorption kinetics

For understanding the rate of adsorption and mechanism, kinetic studies have been conducted by many researchers. Widely used models are pseudo-first-order, pseudo-second-order, and intra-particle-diffusion models. Based on correlation coefficient R^2, the best-fitted model is generally selected (J. Wang & Guo 2020).

The Study of adsorption kinetics help to identify the physicochemical interaction between the dye and the biochar as an adsorbent, along with predicting the adsorption mechanism. In a study related to date palm fronds, biochar as an adsorbent and methylene orange as a dye; different kinetic studies have been performed like pseudo-first-order, second-order, and Elovich intra-particle-diffusion and based on kinetic studies it has been derived that pseudo-second-order kinetics was best fitted one. (Zubair et al. 2020a) again a study carried out with corn husk biochar pseudo-second-order was found to be best fitted.(Mishra et al. 2019)In a similar kinetic study performed for the adsorption of methyl orange dye on pomelo peel waste, it has been seen that out of pseudo-first-order and pseudo-second-order kinetics the R^2 value for pseudo-second-order kinetics was found to be more than is $R^2 = 0.984$ and in the case of pseudo-first-order it was found to be 0.927, slightly less which shows that pseudo-second-order fits more. Based on the kinetic model, it can be stated that a chemical reaction is taking place. These two-model mentioned above are not efficient to explain variation in the rate of adsorption in every case, hence intra-particle-diffusion is used to explain the kinetics of adsorption. (B. Zhang et al. 2020a, b) In a study related to *Eucalyptus camdulensis* biochar for removing crystal violet, it has been seen that pseudo-second-order was the best-fitted one which describes chemisorptive behavior of adsorption of dye on the biochar. In this case, it has been observed that the beginning uptake rate of dye increased from 16 to 40.6 mg-g^{-1} min^{-1} for crystal violet dye. Here non-linear approach of Elovich kinetic models has also been found to be the best fitted one. (Amin et al. 2021a)In the study based on algae *D. antarctica* based biochar where the researcher took methylene blue as a dye, pseudo-first-order kinetics have been used to explain the progress of the complete adsorption process and to know about the initial phase whereas pseudo-second-order has been used to know the type of adoption taking place that is chemisorption. Then based on different kinetic data it has been concluded that pseudo-second-order and Elovich have a high connection and hence they can be used to describe the mechanism of adsorption of methylene blue dye on biochar. (Guarín et al. 2018).

Thus, from the above discussion, it can be concluded that the pseudo-second-order kinetics is the most followed kinetics which shows in the majority of cases chemisorption is the key adsorption that is happening between adsorbent and adsorbate. Apart from these kinetic studies helps researchers to know the progress of the adsorption process, the type of adsorption process, and the initial phase, and most important deduce the mechanism. Although, it is not always possible to deduce the mechanism by kinetic studies as dye gets adsorb on the biochar by hydrogen bonding interaction too. So, it may not be possible to get complete information regarding the mechanism just by performing the kinetic studies. (Tran 2020).

Table 2 illustrates different kinetic studies studied in adsorptive removal of dye using biochar. This comparative table also shows that the majorly of the processes followed by the kinetic model are pseudo-second-order.

Adsorption isotherm studies

Adsorption isotherm provides useful information about: (i) an equilibrium relation between adsorbate and adsorbent which can be used in understanding equilibrium; (ii) an idea about the biochar-dye interactions; iii) the affinity between biochar and dye; (iv) the maximum adsorption capacity of the biochar in a specific condition; (v) the amount of biochar which should be used for the removal of a certain quantity of dye from an effluent; and vi) the effect of the experimental conditions on the equilibrium.

To ascertain the best-fitted model, various isotherms such as Langmuir, Freundlich, Dubinin-Radushkevich, Redlich-Peterson, and Temkin isotherms have been investigated. Biochar prepared from activated peanut taking up remazol orange RGB as a dye, the isotherm study has been performed at different dye concentrations such as 20,50,75,100 150 mg/L, the temperature was set to 50 °C and the optimized pH is 3. Various isotherm study has been performed such as Langmuir, Freundlich, Temkin, and Pyzhev equations. Depending upon different evaluated parameters, it has been concluded that both Freundlich and Langmuir are found to be best fitted. Langmuir led to the conclusion that adsorption is even, homogeneous and Freundlich indicates that adsorption is heterogeneous. Corresponding R^2 values for Freundlich, and Langmuir are found to be 0.987, and 0.959 respectively. Since the correlation coefficient value of the Freundlich isotherm is closer to unity, Freundlich is more accepted.(Acemioğlu 2019) For chitosan-tapioca peel biochar which was used for the removal of Malachite Green, the correlation coefficient was found higher for Langmuir isotherm as compared to Freundlich isotherm so Langmuir isotherm was considered the best-fitted one. For Langmuir isotherm, the adsorption efficiency was found to be 53.35 mg/g (Vigneshwaran et al. 2021). In a similar study related to weed biochar where methylene blue has been taken as a dye, Langmuir isotherm fitted the best. In this case, it has been observed that with the increase in temperature adsorption density increased. Besides, there seems to operate a chemical interaction between dye and adsorbent. (Güzel et al. 2017) In a study based on municipal solid waste as an adsorbent when the isotherm studies have been performed Temkin model is closely fitted. (Agarwal et al. 2015) From the above discussion, it can be concluded that an isotherm study is very important to know the type of interaction taking place between dye and adsorbent. Table 3 summarizes some selected isotherm constants related to dye removal using biochar prepared from the different feedstock. Based on the kind of feedstock taken and the mechanism involved in the process of adsorption, different isotherms are followed.

Mechanistic interpretation of adsorption onto biochar

The adsorption mechanism of a dye onto biochar involves electrostatic interaction, weak hydrogen bonding, and ion exchange. Besides, nitrogen functional groups may initiate

Table 2 Correlative kinetics parameters for different dyes adsorption onto biochar

Adsorbent	Adsorbate	Application kinetic model	Reference
Soybean dreg	Methylene blue	Pseudo-second-order	(Ying et al. 2021)
Cornstalk Biochar	Methylene blue	Pseudo-second-order	(Nizam et al. 2021)
Rice Straw	Basic Red 46	Pseudo-second-order	(Sackey et al. 2021)
Cornstalk biochar	Methylene blue	Pseudo-second-order	(Ranzi et al. 2018)
Corncob biochar	Brilliant green (BG) dye	Pseudo-second-order	(Giri et al. 2020)
Algae D. Antarctica biochar	Methylene blue	Pseudo-second-order	(Guarín et al. 2018)
Calciumrich biochar	Congo red	Pseudo-second-order	(Dai et al. 2018b)
wood residues biochar	Indosol Black NF1200 dye	Pseudo-second-order	(Kelm et al. 2019)
Lychee seed	Methylene blue	Pseudo-second-order	(Sahu et al. 2020)

Table 3 Adsorption isotherm constants for various dye adsorbent onto biochar

Adsorbent	Adsorbate	Isotherm models studied	References
Cow Dung biochar	Methylene blue	Langmuir	(A. Ahmad et al. 2020)
Sludge and rice husk biochar	Acid Orange II	Langmuir, Freundlich	(S. Chen et al. 2019a, b)
Bael shell (Aegle marmelos)biochar	Patent Blue (PB)	Freundlich isotherm	(Roy et al. 2018)
Alginate-kelp biochar	Crystal violet	Langmuir, Freundlich, and Redlich-Peterson	(Ohemeng-Boahen et al. 2019)
Bamboo biochar	Acid black 172	Freundlich	(Yang et al. 2014)
Corn straw-derived biochar	Malachite green	Langmuir	(Eltaweil et al. 2020)
Wodyetiabifurcata biochar	Methylene blue	Freundlich and Sips	(Santos et al. 2019)

n-π type interaction. In general, dye adsorption onto biochar involves several steps. The first step is regarded as physical adsorption wherein dye settles on the biochar surface. In the second step, dyes get deposited on the biochar's surface and the third and last step involves the condensation of dyes into the pores of the biochar (adsorbent).(Fagbohungbe et al. 2017) The first stage involves the initiation of adsorption, hence regarded as a clean zone. The second stage is regarded as a mass transfer zone. In the third stage, equilibrium is reached and hence called an exhausted zone. During the completion of the process, the exhausted zone increases whereas the clean zone decrease steadily.(Zubair et al. 2020a, b) With increasing adsorbate concentration, the mass transfer zone gets affected significantly. This trend is followed until and unless the adsorbent surface gets saturated, that point is called the breakthrough point. Table 4 presents the adsorption capacities of various biochar-based adsorbents for the removal of different dyes. From Table 4 it has been seen that calcium-rich biochar from crab shells shows the highest adsorption capacity of 12,501.98 mg/g whereas oil palm waste-derived biochar shows the least adsorption capacity of 24.00 mg/g. Mentha plant biochar is also a frontline with an adsorption capacity of 322.58 mg/g.

Regeneration and reuse of biochar

The adsorption capacity of the biochar surface is limited; in other words there is a fixed number of sites available for the adsorption and hence protract exposure of biochar with dye results in the establishment of equilibrium between the biochar and dye. Hence there is a need arises to regenerate and reuse biochar or simply decompose it. Once the biochar surface gets saturated with the adsorbate, desorption has been performed with solutions of $NaNO_3$, KNO_3, and HNO_3 at different concentrations. The low pH of the desorbing solution is used to replace heavy metal ions efficiently.(Sounthararajah et al. 2015)Several techniques can be used to regenerate fixed-bed columns that are partial pressure reduction, a heat treatment that can be done using an inert gas, and changing chemical states such as pH. The solvent which has been demonstrated to regenerate modified biochar is acetic acid, NaOH, EDTA, HCl, and NaCl. The efficiency of regenerated biochar by different organic solvents has been examined in several studies. It was found that methanol, ethanol, and acetone show high regeneration capacity by separating dyes from biochar. (Y. di Chen et al. 2018). Regenerated materials have been tested for multi-cycle reuse and found promising.

Table 4 Adsorption capacities of various biochar-based adsorbents for the removal of different dyes from wastewater

Adsorbent	Adsorbate	Dose (g/L)	Contact time (min)	Adsorption capacity (mg/g)	pH	Ref
Mentha (mint) plant biochar	Malachite green	3.0	45	322.58	10	(Rawat& Singh, 2018)
Oil palm waste-derived biochar	Methylene blue	5.0	90	24.00	2	(Baloo et al. 2021)
Magnetic biochar	Acid orange 7	2.0	200	110.27	2–10	(Santhosh et al. 2020)
Chitosan Beads	Tartrazine	0.72	120	30.03	3	(Pal & Pal 2019)
Pecan nutshell	Reactive Red 141	0.05	240	130	3	(Zazycki et al. 2018)
Lignin-derived porous biochar	Methylene blue	123.8	240	248.96	11	J. Liu et al. 2021)
Fe2O3 biochar nanocomposite	Methylene blue	0.5	30	20.53	8	(Chaukura et al. 2017)
Calcium-rich biochar from Crab Shell	Malachite green	0.5	150	12,501.98	7	(Dai et al. 2018a)
Modified (biochar) from pea shells	Malachite green	0.5	120	277.77	–	(Darama & Çoruh, 2020)

The setback of using biochar as an adsorbent

Till now the ability of biochar for dye removal is discussed, but it is important to know the challenges involved also to proceed with the further experiment to avoid certain experimental errors. Some polyaromatic hydrocarbon (PAH) may be formed during the preparation of biochar which may be detrimental to the environment.(Liang et al. 2021) Biochar may also augment growth factor change in plants and crop production when disposed of in soil.(Spokas et al. 2012) Biochar works well with some specific conditions of dosage, temperature, pH, etc. Hence an extra optimization step needs to be performed for the removal of biochar from the wastewater which in turn increases treatment cost. In a few studies, it has been seen that the efficiency of biochar after prolonged use gets decreased.(Oladipo and Ifebajo 2018) Biochar derived from certain sources contains traces of heavy metals which may increase the risk of additional pollution.(Odinga et al. 2020; Q. Zhang et al. 2020a, b) At a certain temperature, the heavy metals may start diffusing in the surrounding environment which is wastewater. It has been observed that at high operational temperatures heavy metals start volatilizing. At temperatures beyond 500 °C volatility of cadmium increases more as compared to other heavy metals. This is a point of concern as cadmium is a major source of pollution. Despite having a plethora of applications of biochar in a different fields, it still possesses some threat to environmental pollution if not used appropriately. Suitable methods need to be adopted to restrict such occurrences. Moreover, the safe disposal of spent biochar should be considered an integral part of any upcoming studies. Adsorption is a contaminants transferring process and hence used biochar can be hazardous waste. Depending on the type of impurity biochar is loaded with- different techniques are used for regeneration or desorption. Specifically, if the used biochar is loaded with phosphate, nitrate, ammonium, and no other hazardous pollutants, it can be used as a fertilizer which in turn uplifts the fertility of the soil. Whereas if the biochar is used for the removal of organic waste like the removal of dye from wastewater has to handle with intense care. Based on different studies, it has been concluded that if U(VI) is adsorbed in the process so for desorbing loaded biochar should undergo a four-time sorption cycle by the use of 0.05 $molL^{-}1$ HCl. (Z. bin Zhang et al. 2013) Results based on different studies indicate that biochar which is made up of food waste can be used again and again without much loss in the capacity of adsorption in the case of dye. Also, if biochar has undergone several sorption cycles and exhibits less adsorption is due to its high toxicity. This toxic biochar and exhausted biochar should be treated with intense care by following standards of hazardous waste treatment for avoiding further pollution. Nowadays, fly-ash bricks are becoming popular for relatively cost-effective building construction. Exhausted biochar may be mixed in appropriate proportion to reduce the cost further with a goal of waste utilization. Although more study in the field of stability factors, major secondary pollution, and economical feasibility is still needed, the search is on but requires more research.

Economic potential

Biochar has huge application in the removal of dye from wastewater but before applying it on a broad scale it is important to optimize key parameters such as biochar feedstock, the temperature of pyrolysis, availability of industrial-scale reactor, method of regeneration, and a lifetime of the biochar to enhance the economic feasibility of the entire process. (Oni et al. 2019) It was observed that the average harvesting and collection cost of biomass made up of wood like loblolly pine and eucalyptus approximated $24.80/ton. Dragging and transportation costs are depended on the distance covered for the delivery and the density of biomass which is estimated as $0.26/mile for switchgrass and $0.64/mile for poplar wood(Kung et al. 2013). It has been observed by (Y. Dai et al. 2019) that during the production of biochar through slow and fast pyrolysis, the cost came out to be 18.30 and 8.14 US$/ton. Also, based on the international survey conducted by the International Biochar Initiative (IBI) in the year 2013, it has been reported that at sellers' companies, internationally the average biochar price lies in the range of 80.00 US$/ton to 13,480.00 US$/ton. Based on the recent report made by (Y. Dai et al. 2019), the International Biochar Initiative and the European Biochar Certificate set up a standards chart for the development of biochar. Although research based on the market price of biochar is at its initial state, further research is required so that the analysis of biochar can be done in a better way to economic benefits so that it can be applied at the industrial scale for the removal of dye from wastewater and in other potential application.

Biochar: holistic approach to economic and environmental sustainability

Biochar is a resource material that is regarded as waste before going through any thermochemical process, but changing the frame of reference can be regarded as a potential solution to waste management which can be implemented in rural areas to manage agricultural waste. It can boost the source of income and help in developing that area by assisting small scale and medium scale industries with the production of energy. Agricultural and animal feedstock in huge quantities can be efficiently converted to biochar and can be commercialized. This will help in developing a model where one industry can act as a feedstock or input for the other industry. It will bring positive consequences at a different level and help in developing a circular economy. Biochar can also be used for the preparation of bricks in association with fly ash. This will reduce the cost of construction provided the quality is not compromised. Strategies may be made to maintain coordination between the economic as well as the technical aspect. An integrated system has to be developed which will bring balance between the way it has to be used, energy optimization, and controlled drain or discharge.

Conclusion and future Perspective

From the exhaustive discussions presented above, it can be concluded that biochar is an outstanding alternative as an adsorbent for the removal of dye from wastewater. Out of various techniques for preparing biochar, pyrolysis is regarded as the most preferred one to process various types of feedstock such as agricultural waste, algae biomass, sludge, plant residue, animal waste, etc., for the production of biochar. Biochar is eco-friendly adsorbing material by the virtue of its large surface area, presence of surface functional group, and porous nature. It shows the high capability of removal of dye from wastewater which involves different mechanisms including but not limited to electrostatic interaction, weak hydrogen bonding, ion exchange precipitation, surface adsorption, and pore-filling. Performance depends on the different physicochemical parameters including the temperature of pyrolysis, pH, and biochar dosage. Biochar also has the potential to minimize the bioavailability and mobility of pollutants and this can be implemented when the concentration of the contaminant is high. Hence, this review suggests that biochar can be used as a low-cost and environment-friendly adsorbent that can also be used for a socioeconomic benefit which will further lead to environmental and economic sustainability.

Different studies regarding the effect of different feedstock on the quality of biochar and physicochemical properties affecting the adsorption efficiency of biochar suggest that these are still in their initial phase. Following are some areas where more focus should be given in the future:

1. Chemically activated biochar shows high performance as compared to nano-activated biochar, although detailed mechanisms needs to be investigated further for broad-scale application.
2. A model is required for the adsorption mechanism of modified biochar. As it would be good to modify the biochar surface according to the application using a different process like surface oxidation, amination, sulfonating, and modification of pores structure. By doing this, selective biochar materials can be made which can considerably enhance the adsorption efficiency of biochar.
3. Before implementing the use of biochar on a large scale-regeneration, the standard method of operation for the removal of dye pollutants from wastewater, and cost-effectiveness should be monitored carefully to assess the cost of production and usage.
4. Pre-treatment of biochar for removing toxicity or toxic elements and successive biological way of treatment needs more research before implementing it on large scale.
5. For the fast removal of dye from wastewater optimization of adsorption dosage and standard method of biochar production will be helpful.
6. Heavy metals, aromatic hydrocarbon, and metalloids are associated with the biochar which is supposed to be toxic. So, before moving further to use it on a broad aspect negative effect which is associated with the use of biochar it has to be taken into consideration.
7. Regeneration and reusability of biochar need focused comparative research so that biochar can be implemented on large scale without producing potential secondary pollutants. To avoid this knowledge gap, biochar made from different feedstock should undergo security checks under different circumstances and should be explored on a broad time scale.

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