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REVIEW ARTICLE

Efficient Dye Removal Strategies: Exploring the Role of Biochar

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ABSTRACT: The surge in industrial activities, notably in sectors such as textiles, leather processing, and paper manufacturing, has led to a considerable rise in synthetic dye discharge into the environment, posing significant threats to ecosystems and human health. Traditional wastewater treatment methods have struggled to effectively address dye pollution due to the complex nature of these pollutants. In response, biochar has emerged as a promising solution, offering unique physicochemical properties that make it an excellent adsorbent for dye removal. This review explores the role of biochar in dye removal, focusing on its surface properties, production methods, and adsorption mechanisms. Biochar's extensive surface area, porosity, and surface functional groups play crucial roles in facilitating dye adsorption. Various production methods, such as pyrolysis, hydrothermal carbonization, and superheated steam torrefaction, influence biochar properties and effectiveness in dye removal applications. Surface modification techniques enhance biochar's dye removal capacity and regeneration potential, enabling its reuse in wastewater treatment. Moreover, the surface charge of biochar influences electrostatic interactions with dye molecules, affecting adsorption efficiency. Understanding biochar's surface charge is essential for optimizing dye removal processes. Overall, biochar holds promise as a sustainable and efficient adsorbent for mitigating dye pollution, offering valuable insights for environmental remediation efforts.

Keywords: Biochar; Dye removal; Surface properties; Adsorption mechanisms; Regeneration; Surface charge; Surface area

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1. INTRODUCTION

In recent years, industries such as textiles, leather processing, and paper manufacturing have experienced rapid expansion, leading to a significant increase in the discharge of synthetic dyes into the environment [1, 2]. This influx of dyes poses a serious threat to aquatic ecosystems and human health [3, 4]. Synthetic dyes are known for their persistence, toxicity, and non-biodegradability, making them particularly challenging to address once they enter water bodies. Traditional wastewater treatment methods, including chemical, physical, and biological approaches, have struggled to effectively treat dye-containing wastewater due to the complex nature of these pollutants. Currently, there is a surge of ongoing research directed towards the effective removal of dyes from wastewater [5–7].

In response to the urgent need for sustainable and efficient methods to address dye pollution, biochar has emerged as a promising solution. Biochar is a carbonaceous material produced from the pyrolysis of organic biomass under oxygen-limited conditions. This process results in the production of solid (biochar), liquid (oil), and gaseous products. Biochar is a valuable material that can be utilized as a soil additive for nutrient improvement and carbon sequestration, where the carbon can be stored (locked) in the soil, improving soil structure, pH, water and nutrient retention, and mitigating climate change [8]. It can also be used as a biofuel in energy generation directly or converted to biomass briquettes, enhancing its energy and economic value [8]. It possesses unique physicochemical properties, such as high surface area, porosity, and surface functional groups, which make it an excellent adsorbent for a wide range of pollutants, including synthetic dyes [9, 10].

Additionally, biochar is derived from renewable sources

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and can be produced using waste biomass, making it an environmentally friendly option for wastewater treatment [11]. The utilization of biochar for dye removal offers several advantages. Its high surface area and porosity provide ample sites for dye molecules to adsorb, effectively removing them from wastewater [12].

The production of biochar can be achieved through various methods, such as hydrothermal carbonization, superheated steam torrefaction, and pyrolysis using a pilot carbonization kiln [13, 14]. The production process and the type of feedstock used can significantly influence the biochar's properties and its effectiveness in various applications [15]. For instance, biochar produced from sugarcane bagasse through a pyrolysis or gasification process has been used as catalysts for the biodiesel production process [16]. Additionally, chemical activation of biochar derived from pine needles and coconut shells has been studied to optimize the production process and improve the material's characteristics for specific applications [17].

Several methods have been developed for producing biochar, each with its advantages and limitations. In this section, we provide a brief overview of common methods for producing biochar, including pyrolysis, gasification, and hydrothermal carbonization. We discuss the principles underlying each method, key process parameters, and the characteristics of the resulting biochar products. Understanding the different methods for producing biochar is essential for optimizing its properties and tailoring its application to specific environmental challenges, such as dye pollution in water bodies.

Pyrolysis: This is a thermo-chemical process of biomass conversion to a carbon neutral or better fuels and materials from biomass. It is a thermal decomposition of organic material in a controlled (insufficient) oxygen at a high temperature, thereby producing solid (biochar), liquid (oil), and gaseous products. Biochar produced during this process is a valuable material that can be utilized as a soil additive and in carbon sequestration, where the carbon can be stored (locked) in the soil [18].

Hydrothermal Carbonization (HTC): This is a process that converts wet biomass into biochar and biocrude oil in a high-pressure and high-temperature environment. It is a more efficient method for converting wet biomass into biochar compared to pyrolysis, as it does not require drying of the feedstock [19].

Gasification: This is a process that converts biomass into a gaseous product, which can be used as a fuel, and a solid product, which is biochar. It is a more complex process compared to pyrolysis, as it involves the partial oxidation of biomass in a high-temperature environment [20].

Torrefaction: This is a mild form of pyrolysis that is used to produce biochar from biomass at lower temperatures compared to pyrolysis. It is a more energy-efficient method compared to pyrolysis, as it uses less energy to heat the biomass. The resulting biochar has a higher energy density compared to biochar produced through pyrolysis [21].

2. PROPERTIES OF BIOCHAR RELEVANT TO DYE REMOVAL

The effectiveness of biochar as an adsorbent for dye removal is intricately linked to its unique physicochemical properties. Understanding these properties is essential for optimizing the performance of biochar-based adsorption processes in treating dye-contaminated wastewater. In this section, we explore the key properties of biochar that play a crucial role in its efficacy for dye removal. These properties include surface area, porosity, surface functional groups, surface charge, and structural characteristics (Fig. 1). By elucidating the relationship between biochar properties and dye adsorption behavior, we can enhance our understanding of the mechanisms underlying dye removal processes and design more efficient and sustainable strategies for mitigating dye pollution in water bodies.

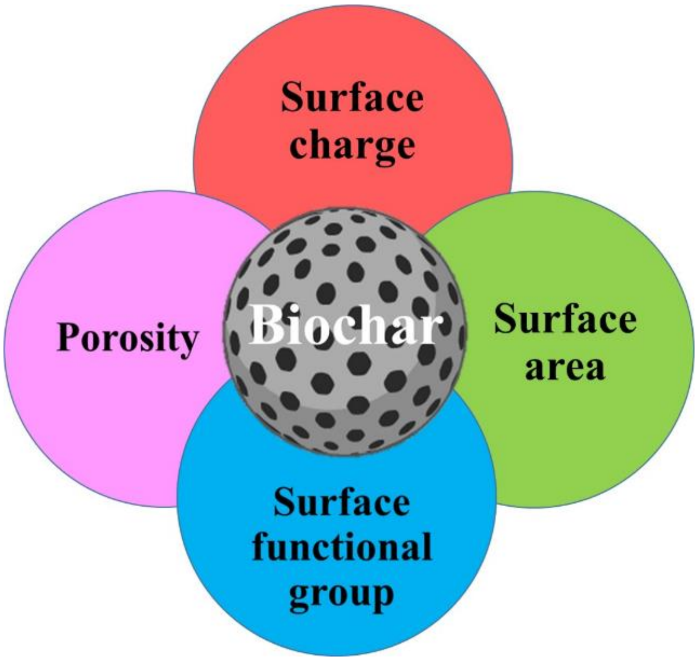

Fig. 1. Properties to improve the biochar efficiency.

Numerous studies have highlighted the direct correlation between biochar surface area and its adsorption capacity for organic dyes. The extensive surface area of biochar provides many active sites and pore structures, facilitating the adsorption of dye molecules from aqueous solutions. Research by Yao et al. [22] demonstrated that biochar with higher surface area exhibited superior adsorption performance for various organic dyes compared to biochar with lower surface area. This finding underscores the significance of surface area in enhancing the adsorption capacity of biochar for dye removal. Similarly, studies by Wang et al. [15] and Zhang et al. [23] validated these findings, showing that biochar with larger surface area effectively removed a wide range of dye pollutants from wastewater. Furthermore, investigations into the effect of surface area on dye removal kinetics have elucidated the role of surface area in governing the rate of adsorption. Sterenzon et al. [24]

observed that biochar with higher surface area exhibited faster dye adsorption kinetics, attributed to its increased accessibility of active sites for dye molecules. This suggests that surface area not only influences the adsorption capacity but also impacts the efficiency and kinetics of dye removal processes. Given the crucial role of surface area in biochar, researchers consistently seek methods to enhance it. Truong et al. [25] employed $KHCO_3$ as an effective activator to increase the surface area of biochar derived from Sargassum hemiphyllum. Their study showed the use of $KHCO_3$ escalated the surface area of biochar from 976 to 2024 m^{2}g^{-1}. The researchers also utilized a method involving low-temperature pyrolysis and high-temperature copyrolysis with potassium hydroxide ($KHCO_3$) to increase the surface area of the magnetic biochars (NMPBs) [26]. Similarly Liu et al. [27] uses the active reagents to expand the specific surface area to increase the amount of adsorption. Researchers shown that after the modification treatment, the specific surface area of the two altered biochars expanded, both exhibiting a mesoporous distribution (Fig. 2). The pore size generated by WSC was larger, while the specific surface area of WSC was smaller compared to that of WPC. The micropore surface areas and average pore sizes of the NMPBs were higher than those reported for porous carbon derived from copyrolysis with hydroxide and biomass.

Porosity is another important property of biochar that affects its adsorption capacity. Moreover, the mesoporous and microporous structure of high-surface-area biochar has been found to enhance dye adsorption by providing additional adsorption sites and diffusion pathways. Recent studies have demonstrated that biochar with hierarchical pore structures and high surface area showed enhanced dye adsorption performance due to improved accessibility and diffusion of dye molecules into the internal pores [28, 29]. The KOH activated biochar has shown the increased poracity and hence the amount of dye removal [30]. The use of active agents is a trend modify the pore size and hence the surface area (Fig. 3). The nitrogen-doped porous biochar in the study had a micropore volume of 0.14 cm^3/g, which contributed to its high adsorption capacity of 173.9 mg/g for the Reactive Orange 16 dye [31]. Similarly, the activated biochar pyrolyzed at 750 °C had a total pore volume of 0.65 cm^3/g, which contributed to its high adsorption capacity of 65.9 mg/g for the cationic dye [24].

A comprehensive literature survey reveals the critical importance of surface functional groups in biochar for efficient dye removal in wastewater treatment. Surface functional groups, such as hydroxyl (-OH), carboxyl (-COOH), and phenolic (-Ph) groups, play a significant role in facilitating the adsorption of dye molecules onto the biochar surface. Numerous studies have demonstrated that surface functional groups significantly influence the adsorption capacity and selectivity of biochar for organic dyes. For instance, Hasan et al. [32] and Ghazy et al. [33] found that biochar with a higher abundance of hydroxyl groups exhibited enhanced adsorption performance for cationic dyes due to electrostatic interactions between the hydroxyl groups and the dye molecules. Similarly, biochar modified with carboxyl groups showed improved adsorption efficiency for anionic dyes through electrostatic attraction and π-π interactions [34–36].

Liu and colleagues [37] demonstrated that conventional carbon microspheres (CMS), after amino modification (AF-CMS), exhibited significantly enhanced efficacy in capturing almost 100% of both methyl orange (MO) and tartrazine (TTZ).

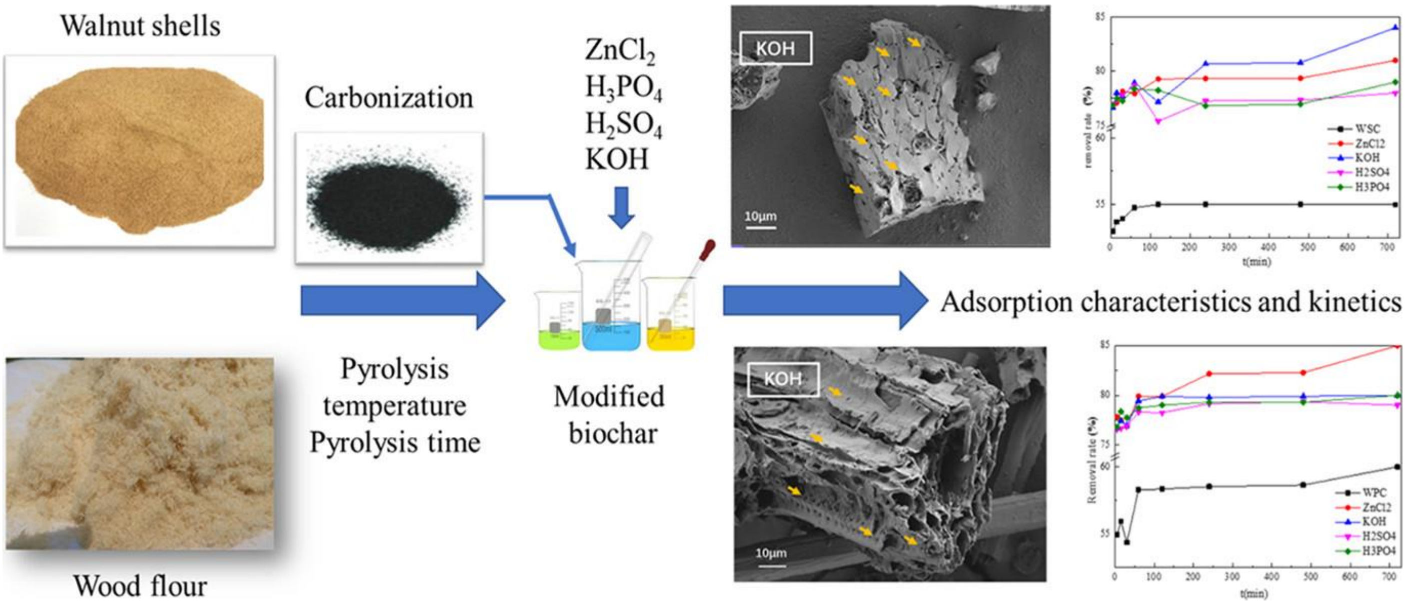

Fig. 2. Biochar synthesis and surface area modification to increase the absorption rate. Reprinted with permission from ref. [27], Liu, C., Wang, W., Wu, R., Liu, Y., Lin, X., Kan, H. and Zheng, Y., **2020.** Preparation of acid-and alkali-modified biochar for removal of methylene blue pigment. *ACS omega*, *5*(48), pp.30906-30922. Copyright © ACS Publications

This remarkable improvement in performance can be ascribed to the electrostatic attraction between the positively charged amine groups on AF-CMS and the anionic dyes. Furthermore, research by Zhang et al. [38] highlighted the importance of surface functional groups in controlling the surface chemistry and reactivity of biochar for dye adsorption. They found that biochar with a higher density of phenolic groups exhibited superior adsorption capacity for aromatic dyes, attributed to the formation of π-π interactions between the phenolic groups and the aromatic rings of the dye molecules. Additionally, the surface functional group modifier like KOH and chitosan (CHKBC) exhibited an enriched composition of functional groups such as -COOH, -NH_2, and -OH, leading to a substantial increase in the maximum adsorption of MB by the biochar from 8.83 mg g^{-1} to 62.04 mg g^{-1}, a 7.03-fold increase [39].

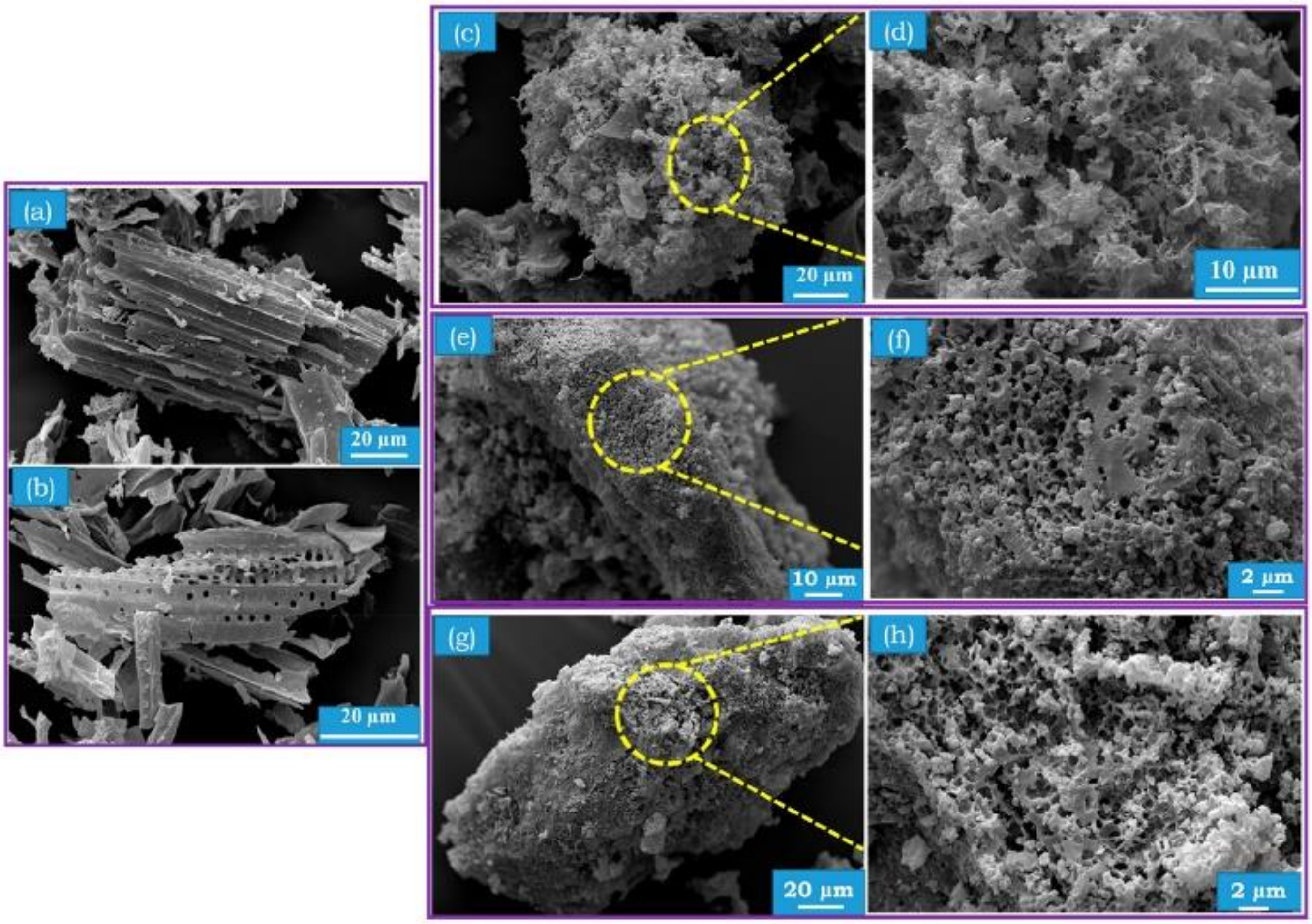

Fig. 3. SEM micrographs of the base biochar without activation (a,b) and with activation (with KOH) (c-h). Reprinted with permission from ref. [30], Priyanka, Vashisht, D., Ibhadon, A.O., Mehta, S.K. and Taylor, M.J., **2024**. Enhanced Wastewater Remediation Using Mesoporous Activated Wheat Straw Biochars: A Dye Removal Perspective. *ACS Sustainable Resource Management*, 1(2), pp.355-367. Copyright © ACS Publications.

Surface modification of biochar serves not only to augment its dye removal capacity but also to play a vital role in the regeneration and reusability of biochar-based adsorbents. Yang et al. [40] demonstrated that functional groups on the biochar surface can undergo chemical reactions with dye molecules during adsorption, leading to the formation of stable complexes. This enables the desorption of dye molecules from the biochar surface under certain conditions, allowing for the regeneration of the adsorbent and its subsequent reuse in wastewater treatment processes. The functional groups also influence adsorption mechanisms differently for various contaminants, affecting regeneration differently. For instance, functional groups rich in electrons promote π-interactions and hydrogen bonds during dye adsorption, leading to higher regeneration efficiency [41].

In wastewater treatment processes, biochar serves as an effective agent for removing dyes. This effectiveness stems from the surface charge characteristics of biochar, which are predominantly determined by its functional groups and the pH conditions of the environment. These surface charges enable biochar to engage in electrostatic interactions with dye molecules present in the wastewater. Essentially, biochar acts as a sort of magnet, attracting and binding dye molecules to its surface. The specific functional groups on the biochar's surface influence the nature of these interactions. For instance, functional groups like carboxyl (-COOH) or hydroxyl (-OH) can impart negative charges to the biochar surface under certain pH conditions, facilitating attraction to positively charged dye molecules.

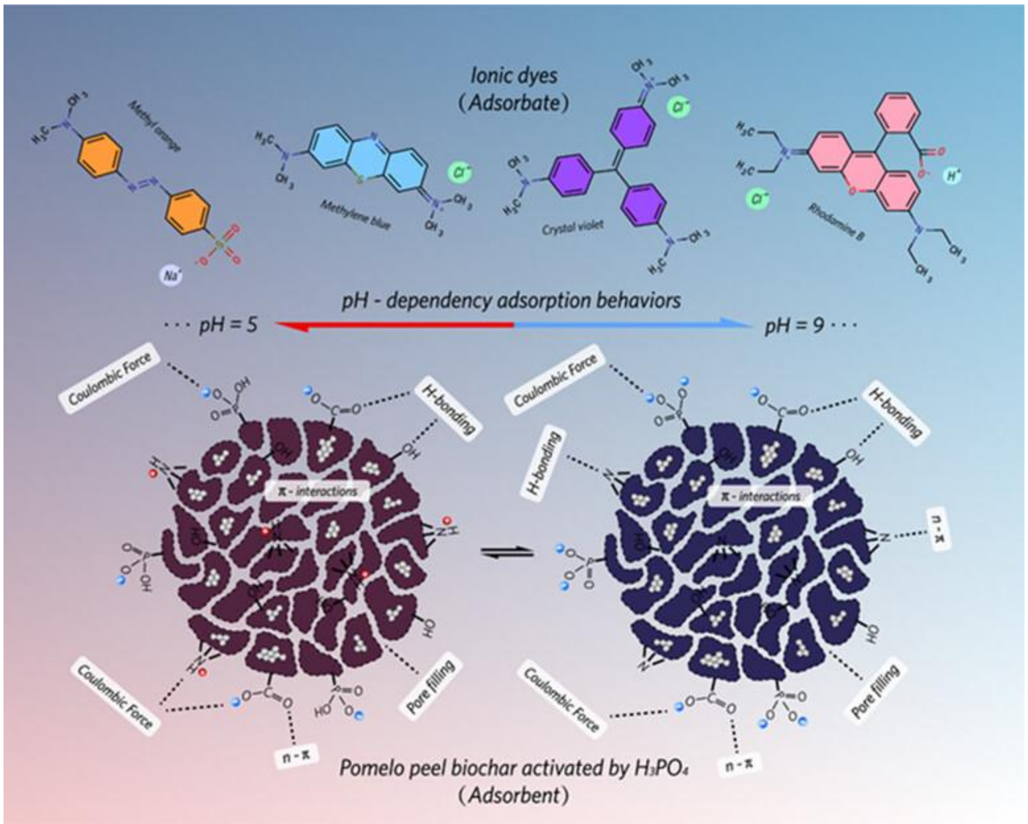

Fig. 4. Effect of pH on the absorption capacity of biochar. Reprinted with permission from ref. [42], Wei, F., Zhu, Y., He, T., Zhu, S., Wang, T., Yao, C., Yu, C., Huang, P., Li, Y., Zhao, Q. and Song, W., **2022.** Insights into the pH-dependent adsorption behavior of ionic dyes on phosphoric acid-activated biochar. *ACS omega*, *7*(50), pp.46288-46302. Copyright© ACS Publications.

Conversely, in acidic conditions, protonation of these functional groups can result in a positively charged biochar surface, enhancing the adsorption of negatively charged dye molecules through electrostatic attraction. This interplay between the surface charge of biochar and the characteristics of dye molecules ultimately determines the adsorption capacity and efficiency of the process. By understanding and optimizing these factors, wastewater treatment systems can leverage biochar effectively to remove dyes, thereby contributing to cleaner water resources and environmental sustainability.

The surface charge of biochar, primarily influenced by functional groups and pH conditions, plays a crucial role in electrostatic interactions with dye molecules, ultimately affecting adsorption capacity and efficiency [42]. Studies shown that adsorption of ionic dyes with single-polarity charges like methyl orange (MO), methylene blue (MB), and crystal violet (CV), the electrostatic force predominantly determines the pH-dependent character. However, for RhB, factors such as electrostatic force, self-aggregation, and H-bonding collectively contribute to its pH-dependent adsorption behavior, resulting in a synergistic effect (Fig. 4). Likewise, favorable adsorption of cationic dyes such as MB and CV occurs under alkaline conditions. Conversely, it exhibits enhanced adsorption of anionic dyes like MO under acidic conditions. Several studies have highlighted the impact of surface charge on the adsorption behavior of biochar towards different types of dyes [43]. For example, Xu et al. [44] investigated the adsorption of cationic dyes onto biochar and found that the positively charged surface of biochar facilitated the electrostatic attraction and adsorption of cationic dye molecules. Conversely, the adsorption of anionic dyes and observed that biochar with a negatively charged surface exhibited enhanced adsorption capacity for anionic dye molecules through electrostatic interactions [45]. Similarly, Ullah et al. [41] demonstrated the surface charge of adsorbent materials plays a crucial role in the adsorption process. The activated biochar (ABC600) had a pHpzc value of 3.0, suggesting it may have a negative charge above this pH and a positive charge below it. Thus, at pH values higher than pHpzc, cationic dye adsorption is favored, while at pH values lower than pHpzc, anionic dye adsorption is more likely to occur. The study emphasized the significance of pH-dependent surface charge in regulating the adsorption behavior of biochar. The nitrogen-doped porous biochar in the study had a positive surface charge at pH 2.0, which contributed to its high adsorption capacity of 173.9 mg/g for the Reactive Orange 16 dye [46]. Similarly, the activated biochar pyrolyzed at 750 °C had a positive surface charge at pH 2.0, which contributed to its high adsorption capacity of 65.9 mg/g for the cationic dye [47].

3. RECENT ADVANCES IN BIOCHAR-BASED DYE REMOVAL

Recent studies have focused on optimizing the adsorption processes of biochar for efficient dye removal [48, 49]. Modification of biochar properties, synthesis of composite materials, and optimization of adsorption processes are crucial aspects in enhancing the efficiency and applicability of biochar-based adsorbents for pollutant removal from various environmental matrices. Several studies have explored enhancing biochar properties through innovative methods. For instance, the research on milkvetch-derived biochar involved decorating it with ZnO-Ce nanoparticles, leading to enhanced photocatalytic performance for reactive blue 19 dye removal [50]. This modification strategy demonstrates a novel approach to improving biochar's effectiveness in dye removal processes.

Likewise, the simple chemical modification is also popular for the biochar modifications. This mainly includes acid modification, alkaline modification, oxidation agent modification, and modification with metal salts. Acid modification aims to eliminate impurities like metals and add acid functional groups to biochar surfaces using acids like hydrochloric, sulfuric, nitric, phosphoric, oxalic, and citric acid [49, 51]. Alkaline modification seeks to boost surface area and oxygen-containing functional groups using agents like potassium hydroxide and sodium hydroxide [52, 53]. Furthermore, for oxidative biochar modification, potassium permanganate and hydrogen peroxide are commonly used oxidizing agents. These agents play a crucial role in introducing functional groups onto the biochar surface, thereby altering its physicochemical properties [54–56].

The modification of biochar using metal salts or metal oxides can certainly alter its characteristics significantly. By incorporating metals or metal oxides into biochar, the sorption capacity for heavy metals can be enhanced, leading to improved adsorption, catalytic performance, and magnetic properties [57–59]. This modification process involves mixing the metals or metal oxides with raw materials before pyrolysis or soaking biochar in metal solutions under specific conditions, resulting in changes in physicochemical properties and functional groups on the biochar surface [57–59]. The presence of metal oxides in biochar can enhance its sorption capacity for pollutants, facilitate their removal from water and sewage, and improve interactions such as electrostatic attraction and surface complexation, making biochar an effective material for wastewater treatment technologies [58].

Apart from the abovementioned methods of modification, biochar materials were also employed to enhance the surface area of biochar. Additionally, biochar modification using organic solvents has been documented. Methanol, for instance, facilitates esterification between carbonyl groups and municipal solid waste-derived biochar, resulting in a notable increase in adsorption capacity for compounds like tetracycline [60]. Ammonia gas modification introduces nitrogen-containing groups onto the biochar surface, as demonstrated by Xiong et al. [61]. Moreover, steam and gas purging modifications involve two distinct processes: first, the pyrolysis of the feedstock, followed by the modification of biochar through the purging of carbon dioxide or ammonia gas [62].

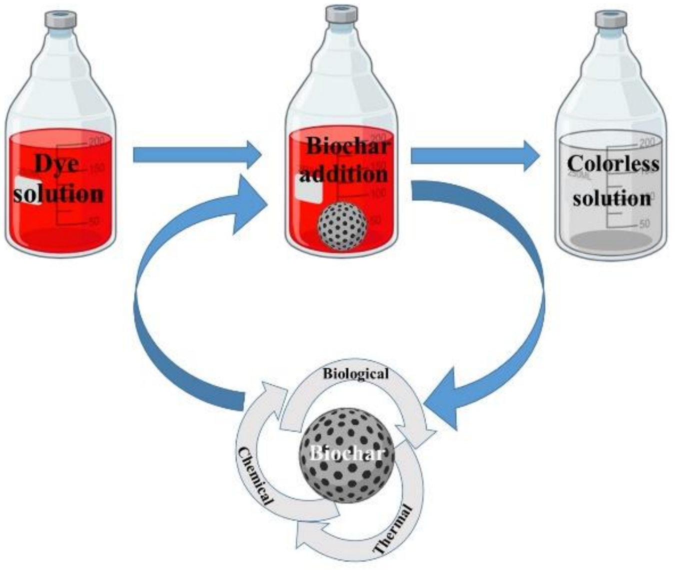

Fig. 5. Recovery and reuse of the biochar of effective use.

4. CHALLENGES AND FUTURE PERSPECTIVES

The challenges and future perspectives of biochar as a biosorbent for water remediation are multifaceted. The effectiveness of biosorption processes heavily relies on the choice of biosorbent, which in turn is influenced by various factors. Researchers emphasize the importance of selecting biosorbents that are abundant and freely available in nature, encouraging the exploration of biochar as a promising option due to its availability [63]. Despite its potential as a cost-effective and environmentally friendly alternative for pollutant removal, some researchers have questioned its commercial viability due to complexities in physicochemical and biological factors involved in pollutant removal. Consequently, there is a growing emphasis on enhancing biosorption capacity, selectivity, kinetics, and the possibility of regeneration or re-use of biosorbents.

The significant challenge facing the practical application of biochar for dye removal is the regeneration of spent biochar, which is critical for sustainable and cost-effective operations [64,65]. Additionally, the scalability of biochar-based dye removal processes presents a hurdle, requiring efficient and large-scale production methods to meet industrial demands [66]. Moreover, the cost-effectiveness of biochar production and utilization impacts its economic viability for dye removal on a larger scale [50].

Future research should prioritize the development of effective regeneration techniques for spent biochar to enhance its reusability and sustainability in dye removal processes [67, 68]. Regeneration techniques for spent biosorbents play a crucial role in reducing production costs and energy consumption, contributing to sustainable waste management practices. Addressing scalability issues necessitates research into optimizing biochar production methods and scaling up manufacturing processes to meet industrial needs [50, 69]. Exploring innovative and cost-effective approaches for biochar production and application can overcome economic barriers, making biochar-based dye removal more commercially viable [69]. Various techniques for recovering and regenerating spent adsorbents, such as magnetic separation, filtration, thermal desorption, chemical desorption, supercritical fluid desorption, advanced oxidation processes, and microbial-assisted regeneration, are discussed [70] (Fig. 5). Furthermore, research into advanced biochar materials, composites, or nanocomposites can enhance the efficiency and effectiveness of biochar in dye removal processes, improving overall performance and sustainability. Modification techniques, such as ionizing radiation, offer environmentally friendly alternatives to chemical modification, enhancing fibre compatibility without compromising original features. Moreover, continuous market research is essential to understand industrial requirements and drive innovation in biochar-based dye removal. By addressing these challenges and focusing on future research directions, the practical application of biochar for dye removal can be optimized, leading to more sustainable, efficient, and cost-effective solutions in water treatment and environmental remediation.

5. CONCLUSIONS

In conclusion, the review highlights the urgent need for sustainable and efficient methods to address dye pollution in water bodies, which poses significant threats to aquatic ecosystems and human health. Biochar has emerged as a promising solution due to its unique physicochemical properties and environmental advantages. The review explores the key properties of biochar relevant to dye removal, emphasizing the importance of surface area, porosity, surface functional groups, surface charge, and structural characteristics in enhancing its adsorption capacity. Recent advances in biochar-based dye removal, including modification techniques and synthesis of composite materials, have shown promising results in improving the efficiency and applicability of biochar-based adsorbents. However, several challenges need to be addressed to realize the full potential of biochar in water remediation, including regeneration of spent biochar, scalability issues, and economic viability. Future research should focus on developing effective regeneration techniques, optimizing production methods, exploring innovative approaches for biochar synthesis, and advancing biochar materials to overcome these challenges and pave the way for more sustainable, efficient, and cost-effective solutions in dye removal and environmental remediation.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests.

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