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Evaluating the role of hydrochars as sustainable adsorbents for pollutant removal

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ABSTRACT

Hydrothermal carbonization (HTC) produces biomass-derived hydrochar, a promising adsorbent for environmental remediation. Lignocellulosic biomass serves as the primary feedstock, and adsorption performance depends on biomass structure and HTC conditions, especially carbonization temperature. This review highlights hydrochar's adsorption capabilities and modification strategies, including physical treatments to increase surface area and chemical treatments to introduce oxygen-containing functional groups. Heteroatom doping and acid-base modifications notably enhance the removal of metal ions and dyes. Hydrothermal treatment is key to producing tailored hydrochars for specific applications. Future research should focus on combining physico-chemical modifications, deepening understanding of adsorption mechanisms, and broadening hydrochar applications. These efforts will advance the use of biomass hydrochars as effective, sustainable adsorbents for pollution control while addressing waste management.

Keywords: Hydrothermal carbonization, biomass-derived adsorbents, environmental remediation, sustainable hydrochar, surface modification.

1. Introduction

Hydrothermal carbonization (HTC) is an innovative and efficient thermochemical process that converts various biomass feedstocks into hydrochar, a carbon-rich material with significant potential for environmental applications, especially in pollution remediation. It occurs in a sealed, water-filled reactor under moderate temperatures (180-250°C) and self-generated pressure (Petrović et al., 2024; Gong et al., 2025). During the process, at elevated temperatures and pressures biomass reacts with water, breaking down and reorganizing into a more carbon-dense structure. HTC mimics natural coal formation but accelerates it, making it an efficient method for waste treatment and biofuel production. Recent comparative reviews emphasize that HTC, compared to pyrolysis, offers better control over hydrochar surface chemistry and functional group retention, making it especially suitable for adsorptive applications (Yang et al., 2023). This process is particularly attractive due to its versatility in utilizing a diverse range of feedstocks, including agricultural residues such as corn cob, grape pomace, Miscanthus, and Paulownia leaves, as well as organic waste like spent mushroom substrate (Petrović et al., 2016; Kojić et al., 2022; Koprivica et al., 2023; Ercegović et al., 2024). The ability to use diverse feedstocks,

combined with relatively mild processing conditions, makes HTC an economically viable and sustainable method for biomass valorization. The properties of produced hydrochar, particularly its effectiveness as an adsorbent for environmental pollutants (Figure 1), are significantly influenced by both the nature of the biomass and the specific conditions of the HTC process, such as temperature, pressure, and reaction time. Biomass structural differences directly impact the surface chemistry and morphological properties of the resulting hydrochar (Petrović et al., 2024). As a result, hydrochars derived from different feedstocks will have distinct adsorptive performances. Therefore, understanding biomass composition and HTC parameters is essential for optimizing hydrochar performance in pollution remediation. To improve the adsorptive properties of hydrochars, various modification strategies have been explored, which can be broadly categorized into physical and chemical treatments (Algethami et al., 2023; Petrović et al., 2024; Gong et al., 2025). Physical modifications primarily focus on increasing the surface area and porosity of the hydrochar, as these are critical factors for enhancing its capacity to adsorb contaminants. On the other hand, chemical modifications aim to introduce or enhance specific functional groups on the surface of the hydrochar, such as oxygen-containing groups. These modifications can significantly improve interactions with a wide range of pollutants, including metal ions and organic dyes (Kojić et al., 2022; Petrović et al., 2024; Gong et al., 2025).

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Fig. 1. Schematic representation of the production and environmental application of hydrochars

Given concerns about environmental pollution, particularly regarding heavy metals and persistent organic pollutants such as dyes, the use of biomass-derived hydrochars as adsorbents offers a sustainable and cost-effective solution (Petrović et al., 2024). The ability to modify the properties of hydrochar through control of the HTC process and subsequent modifications creates opportunities for developing highly specialized adsorbents, tailored for targeted applications in water treatment and pollution control. This paper aims to provide a short overview of the performance, modifications, and potential applications of biomass-derived hydrochars, emphasizing the role of hydrothermal treatment in producing optimized materials for efficient and sustainable environmental remediation.

2. Influence of process parameters on hydrochar adsorption properties

Hydrothermal temperature and residence time have a significant impact on the adsorption performance of biomass-derived hydrochar, with temperature being a crucial factor in determining its structural and chemical properties. The decomposition of hemicellulose (around 180 °C), cellulose, and lignin (above 200 °C) determines the pore structure and functionality of the resulting hydrochar (Petrović et al., 2016). As temperature rises, water acts more effectively as a reaction medium, promoting biomass breakdown and porosity development (Kojić et al., 2022).

The adsorption capacity typically increases with temperature, peaking between 200-220 °C for cellulose- and lignin-rich biomass like coffee waste and oil palm shells (Budiman et al., 2019; Santana et al., 2022). Beyond this range, pore collapse may occur, reducing surface area and performance. For instance, Gong et al., (2025) reported a drop in specific surface area of *Ulva pertusa* hydrochar from 44.5 m²/g at 210 °C to 4.89 m²/g at 250 °C. Similarly, Georgiou et al. (2021) found that miscanthus hydrochar produced at 180 °C showed the best adsorption for Cu²+ (310 mg/g) and NH₄+ (71 mg/g), due to a favorable balance of oxygen-containing groups. At higher temperatures, intensified dehydration and decarboxylation reduce key functional groups like -OH and -COOH, which are essential for adsorption (Petrović et al., 2024). While moderate heating promotes their formation, excessive heat leads to their loss, increasing hydrophobicity and diminishing performance.

Thus, optimizing hydrothermal conditions is crucial to balance porosity and surface functionality for maximum adsorption efficiency.

3. Influence of modification process onto hydrochar adsorption performance

3.1. Physical Modification of Hydrochar

Physical modification of hydrochar involves heat treatment at high temperatures (700-900 °C) using gases like air, CO_2 , or water vapor. Steam activation implies a reaction of water vapor with the hydrochar's surface, creating micropores and increasing the surface area. For instance, CO_2 modification also increases surface area, but it can reduce oxygenated surface groups, imparting alkaline properties. For example, CO_2 modification of sewage sludge hydrochar increased methylene blue adsorption capacity up to 122.4 mg/g, and surface area from 6.3 m²/g to 215.7 m²/g (Khoshbouy et al., 2019).

3.2 Chemical Modification of Hydrochar

Chemical modification greatly enhances hydrochar's adsorption performance by introducing or altering surface functional groups (Petrović et al., 2024). These modifications can be done during HTC process, by adding reagents like AlCl₃, FeCl₃, KOH, or H_3PO_4 , or afterward through post-treatment (Petrović et al., 2024; Gong et al., 2025).

In-situ additions improve porosity and active site formation, while post-HTC treatments with acids, bases, or metal salts (e.g., ZnCl2, FeCl₃) further develop pore structure and functional group density (Kojić et al., 2022; Petrović et al., 2023). Acidic agents (e.g., HNO3, HCl) introduce oxygen-containing groups (e.g., -COOH, -OH, -NO2), which enhance surface polarity, porosity, and affinity toward dyes and heavy metals (Gong et al., 2025). According to molecular simulation studies, surface functional groups not only govern adsorption behavior but also significantly influence hydrochar's hydrophilicity and water retention properties, which can affect its handling, application efficiency, and regeneration potential (Ha et al., 2024). For instance, HNO₃treated orange peel hydrochar improved methylene blue adsorption from 59.6 mg/g to 107 mg/g (Nguyen et al., 2019). Alkaline (KOH, NaOH) and oxidative (H2O2) treatments also enhance porosity and functionality, boosting removal of heavy metals, dyes and ammonium (Koprivica et al., 2022; Khoshbouy et al., 2019; Nguyen et al., 2021). Additionally, metal salt modifications (e.g., K2FeO4, MgCl2) can trigger structural rearrangements, further improving adsorption capacity and selectivity (Petrović et al., 2024). For example, K₂FeO₄-modified hydrochar adsorbed more tetracycline (from 56.4 to 119.7 mg/g) (He et al., 2023), while Mg-doped hydrochars showed uniform pores and strong dye removal (Petrović et al., 2023). Ca-modified hydrochar had high stability and affinity for Pb2+ and Cd2+ (Kojić et al., 2021), and N-doping enabled simultaneous Cu²⁺ and Cr⁶⁺ removal via structural reconstruction (Kim et al., 2023). These surface modifications not only enhances chemical functionality but also significantly transforms the physical structure of hydrochar-pore size, distribution, and morphology-resulting in materials with improved adsorption efficiency and pollutant selectivity.

4. Application of hydrochars in pollution remediation

4.1. Application of Hydrochar in Heavy Metal Removal

Heavy metal pollution in wastewater is a critical environmental issue due to the non-biodegradable nature, toxicity, and persistence of these contaminants. Common heavy metals such as Cr^{6+} , Pb^{2+} , Cd^{2+} , and Cu^{2+} pose serious risks to aquatic ecosystems and human health. Consequently, the development of cost-effective and efficient adsorbents for heavy metal removal has become a significant focus in wastewater treatment research.

Numerous studies have demonstrated the effectiveness of hydrochars in adsorbing heavy metals (Table 1). For instance, hydrochars derived from miscanthus biomass; produced through HTC with the addition of acetic acid, followed by pyrolysis in order to prepare three-dimensional hierarchical porous carbons, exhibit high adsorption efficiency for Pb2+ (Ercegović et al., 2024). In another study, hydrochars obtained from Paulownia leaves underwent alkaline activation using NaOH, also exhibited improved Pb2+ adsorption capacity, achieving a maximum of 174.75 mg/g. Alkaline activation alters the surface structure of the material, generating additional functional groups that improve metal ion binding (Koprivica et al., 2023). Similarly, hydrochars produced from spent mushroom substrate were modified through CaCl2 activation followed by pyrolysis, demonstrating high potential for removing Pb2+ and Cd2+, with maximum capacities of 297 mg/g and 131 mg/g, respectively (Kojić et al., 2022). Hydrochars obtained from grape pomace were activated with KOH, resulting in a significant increase in Pb^{2+} adsorption capacity, from 27.8 mg/g to 137 mg/g (Petrović et al., 2016). The use of KOH to activate hydrochars produced from grape pomace enhances their properties by creating more surface area and functional groups that facilitate stronger metal binding (Petrović et al., 2016). Moreover, Kim et al., (2023) found that NH₄Cl modification of hydrochar enhanced its adsorption capacity due to an increase in deprotonated imine groups on the N-doped hydrochar surface, providing more binding sites. These results highlight the versatility of hydrochars in removing heavy metals from aqueous media and show the importance of modification methods in enhancing their performance. The adsorption kinetics of hydrochars typically follows a pseudo-second-order model, indicating that the adsorption process is primarily controlled by the rapid binding of ions to the surface of the adsorbent (Koprivica et al., 2022; Petrović et al., 2023; Ercegović et al., 2024).

4.2. Application of Hydrochar in the Removal of Organic Pollutants

Hydrochars derived from various biomass sources have shown significant potential for removing organic pollutants from wastewater, alongside their ability to adsorb heavy metals (Behera et al., 2024). Mg-based pyro-hydrochars synthesized from waste grape pomace, corn cob, and Miscanthus demonstrated strong methylene blue (MB) adsorption capacities, with Mg-GP achieving highest capacity of 289.65 mg/g (Petrović et al., 2023), through mechanisms like electrostatic interactions, hydrogen bonding, π - π interactions, and

 $\textbf{Table 1.} \ \ \text{Different hydrochars as heavy metal sorbents}$

ion-exchange. Similarly, hydrochars derived from coffee beans, enhanced by oxygenated functional groups formed during HTC, showed promising MB adsorption, suggesting their potential for both environmental and agronomic applications (Santana et al., 2022). Activated hydrochars from wastewater sludge, particularly those treated with KOH, exhibited even higher MB adsorption capacities, with a maximum of 588.2 mg/g (Khoshbouy et al., 2019). He et al., (2023) investigated removal of tetracycline using potassium ferrate modified hydrochar. Moreover, nitric acid modification of hydrochars derived from glucose and orange peels significantly improved their MB adsorption capacity, enhancing electrostatic and hydrogen bonding interactions (Nguyen et al., 2019). Finally, hydrochars modified with hydrogen peroxide (H2O2) from paper waste sludge demonstrated increased ammonium (NH4+) adsorption, making them effective for removing cations from contaminated water and offering a sustainable, eco-friendly solution for wastewater treatment (Nguyen et al., 2021). Together, these findings highlight the promise of modified hydrochars from diverse biomass sources as cost-effective and reusable adsorbents for organic pollutant removal in wastewater treatment.

4.3 Regeneration, stability, and real-water performance of hydrochars

The reusability of hydrochars represents a critical factor for their practical application in water treatment. Recent findings confirmed that co-hydrothermally derived hydrochars (H-180 and H-215) maintained a stable removal efficiency of methylene blue even after five regeneration cycles, thus demonstrating satisfactory operational stability (Cavali et al., 2025). Moreover, systematic assessments have indicated that thermal and solvent-based approaches are the most effective regeneration strategies to recover the adsorption capacity of hydrochars for heavy metal removal, ensuring both economic feasibility and environmental sustainability (Khanzada et al., 2024). In addition, recent study on Mg-doped pyro-hydrochars confirmed excellent adsorption stability and reusability during methylene blue removal, with only a slight decrease in capacity after five regeneration cycles using ethanol washing, highlighting the potential for sustainable cyclic use of these materials in dye remediation (Petrović et al., 2023).

Conclusion

This study provides a brief literature review focused on the potential of HTC for producing biomass-derived hydrochar materials suitable for environmental remediation. The findings highlight that both the structural characteristics of the feedstock and the specific hydrothermal conditions, especially carbonization temperature, play a crucial role in determining the adsorption efficiency of hydrochars. Furthermore, physical modifications and chemical modifications have been shown to significantly enhance adsorptive performance. Overall, the review emphasizes the importance of HTC as a versatile and effective process for tailoring biomass-based adsorbents to meet specific environmental challenges.

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Hydrochar	Modification	Pollutant	Capacity, mg/g	Ref
Grape pomace	КОН	Pb^{2+}	137	Petrović et al., 2016
Spent mushroom substrate	$\mathrm{CaCl}_{_{2}}$	Pb^{2+} Cd^{2+}	297 131	Kojić et al., 2022
Paulownia leaves	NaOH	Pb^{2+}	174.75	Koprivica et al., 2023
Corncob	$\mathrm{NH_4Cl}$	$\begin{array}{c} Cu^{2+} \\ Cr^{6+} \end{array}$	77.72 103.74	Kim et al., 2023
Watermelon seed	$\mathrm{FeCl}_{_{2}}\mathrm{,}\mathrm{FeCl}_{_{3}}$	Cd^{2+}	347.2	Algethami et al., 2023
Miscanthus	Acetic acid+pyrolysis	Pb^{2+}	155.6	Ercegović et al., 2024

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