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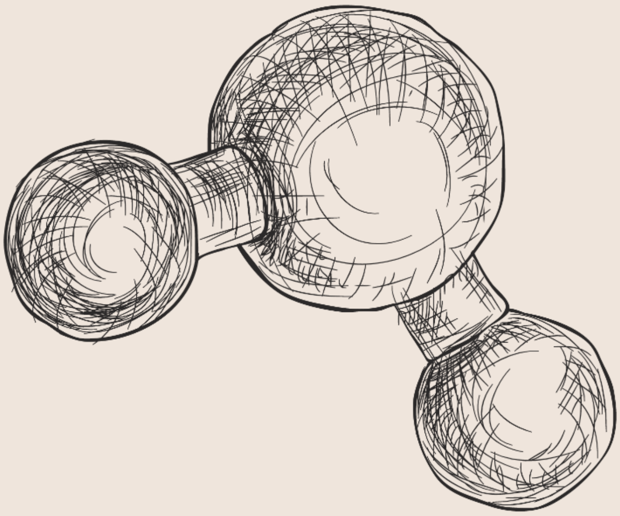
Cutting-Edge Research in Chemical and Material Science

Volume II



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PREFACE

In recent decades, the fields of chemical and material science have experienced unprecedented growth, driven by rapid advancements in technology and a deeper understanding of fundamental principles. These developments have paved the way for innovations that were once the domain of science fiction, such as nanotechnology, advanced composites, and smart materials. The synergy between chemistry and material science has led to breakthroughs that impact a wide range of industries, from electronics to pharmaceuticals, and from energy to environmental science.

Cutting-Edge Research in Chemical and Material Science is a collection of the latest research contributions from leading scientists and engineers worldwide. This book aims to present a comprehensive overview of the current trends, challenges, and opportunities in these dynamic fields. Each chapter delves into a specific aspect of chemical and material science, offering insights into both the theoretical underpinnings and practical applications of new technologies and materials.

The book is structured to cater to a diverse audience, including researchers, industry professionals, and students. The topics covered span a broad spectrum, from the synthesis and characterization of novel materials to the exploration of their potential applications in various industries. The contributors have been carefully selected to ensure that each chapter represents the forefront of research in their respective areas, providing readers with valuable perspectives on future directions in the field.

We hope that this book will serve as a valuable resource for those seeking to stay abreast of the latest developments in chemical and material science. Whether you are a seasoned researcher or a newcomer to the field, the content within these pages will offer you a deeper understanding of the complexities and possibilities that define this exciting area of study.

Finally, we would like to extend our gratitude to the contributing authors, whose expertise and dedication have made this book possible. We also thank the editorial team for their meticulous work in bringing this project to fruition. It is our sincere hope that this book will inspire further innovation and discovery in chemical and material science, contributing to a future where these fields continue to shape our world in profound ways.

Editors

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A REVIEW ON POTENTIAL ENVIRONMENTAL APPLICATIONS OF HYDROCHAR THROUGH HYDROTHERMAL CARBONIZATION

Karan Sathish and Shweta Saraswat

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Abstract:

Hydrothermal carbonization (HTC) is an efficient thermochemical process that converts wet biomass into hydrochar, a carbon-rich material with diverse environmental applications. This review explores the role of hydrochar in soil amendment, solid biofuel production, carbon sequestration, pollutant adsorption, and as a catalyst support. Hydrochar enhances soil fertility, water retention, and reduces greenhouse gas emissions. Its potential as a renewable biofuel and carbon capture medium highlights its importance in sustainable energy. Additionally, hydrochar's unique physicochemical properties make it an effective adsorbent for pollutants and a viable catalyst support in chemical reactions. However, its lower stability compared to biochar poses challenges for long-term carbon sequestration. This review synthesizes recent advancements and emerging applications of hydrochar, underscoring its potential in environmental management and energy solutions. Further research is needed to optimize HTC conditions and improve hydrochar's efficiency in various applications.

Keywords: Hydrothermal Carbonization, Hydrochar, Soil Amendment, Carbon Sequestration, Pollutant Adsorption.

1. Introduction

Hydrothermal carbonization (HTC) is a thermochemical process that effectively converts wet biomass into hydrochar by utilizing the inherent moisture content of the feedstock. The HTC process typically occurs at temperatures ranging from 180°C to 260°C in a water-saturated environment, resulting in the production of hydrochar and process wastewater. The reaction sequence involves hydrolysis, dehydration, decarboxylation, aromatization, condensation, and polymerization, ultimately yielding a carbon-rich solid material with enhanced energy density and stability (Hoekman *et al.,* 2011; Libra *et al.,* 2011). HTC's ability to process a wide variety of high-moisture feedstocks, such as MSW, lignocellulosic biomass, and non-lignocellulosic waste, makes it a versatile technology for sustainable waste management.

The utilization of hydrochar offers a promising solution for managing biomass residues, especially those containing high levels of moisture, reaching up to 80% (Catalkopru *et al.,* 2017). Extensive endeavors have been undertaken to generate energy-rich hydrochars from diverse sources such as digestate, lignocellulosic biomass, and manure. Conditions during HTC operation, such as the type of feedstock, operation temperature, and time, determine the hydrochar's quality (Saqib *et al.,* 2019). According to Berge *et al.* (2013), hydrochar is structurally more similar to coal than biochar made through dry pyrolysis. Their applications could be found in soil amendments (Reibe *et al.,* 2015), energy storage, supercapacitors, and batteries (Li/Na ion batteries) (Jayaraman *et al.,* 2017), CO_2 and H_2 gas storage (Sevilla *et al.,* 2011), carbon sequestration (Naisse *et al.,* 2015) and pollutants removal (Zhang *et al.,* 2019). A schematic representation and a summary of the major environmental applications of hydrochar are illustrated in Figure 1, while Table 1 provides further details on these applications.

In recent years, there has been a significant increase in research focused in multiple fields on hydrothermal carbonization (HTC) and hydrochar. This research has unveiled numerous emerging applications for hydrochar, including its use as solid fuel, soil amendment, electron storage material, hydrogen storage medium, carbon capture agent, carbon sequestration medium, and for various forms of adsorption such as dye adsorption, toxin adsorption, heavy metal adsorption, and nutrient recovery from wastewater.

2. Soil amendment and remediation

Hydrochar is well known for its ability to boost soil fertility and water holding capacity while reducing greenhouse gas (GHG) emissions. When hydrochar is added to soil, its bulk density is reduced and its total pore volume is increased, allowing the soil to hold onto more water (Abel *et al.* 2013). Because there is only a small amount of polar functionality on the surface of freshly formed hydrochar, it generally exhibits a hydrophobic character. However, over time, after being incorporated into the soil, the hydrochar undergoes oxidation due to interactions with ambient oxygen, which results in the formation of phenolic and carboxylic functional groups on the hydrochar's surface (Cheng *et al.* 2008). The water holding capacity, cation exchange capacity and nutrient retention capacity would significantly increase as a result of the presence of these capabilities on the surface (Rillig *et al.* 2010; Kambo & Strength, 2014). Although only sandy soils, which have a low available water capacity (AWC), show this improvement in water storage (Abel *et al.* 2013). High AWC soils, like those with high organic matter contents, did not exhibit a significant change in their physical characteristics.

Since it's necessary for plants to absorb the nutrients, they must first be sorbed into the pores on the outermost layer of the char material (Yao *et al.* 2013).Although the majority of hydrochars, particularly those made from plant biomass, have low nutrient contents and can't be used as fertiliser on their own, they can be added to soil to improve the effects of fertiliser by lowering the amount lost via surface run-off (Bargmann *et al.* 2014).However, crop yield responses to hydrochar application in the soil could be beneficial or harmful. There is a wealth of information available about using biochar to enhance soil; On the use of hydrochar for this application, there isn't much information, though. At a 20% hydrochar loading made from beetroot chips, Rillig *et al.* (2010) observed favourable effects on the colonisation of arbuscular mycorrhiza fungi and pore germination in soil.

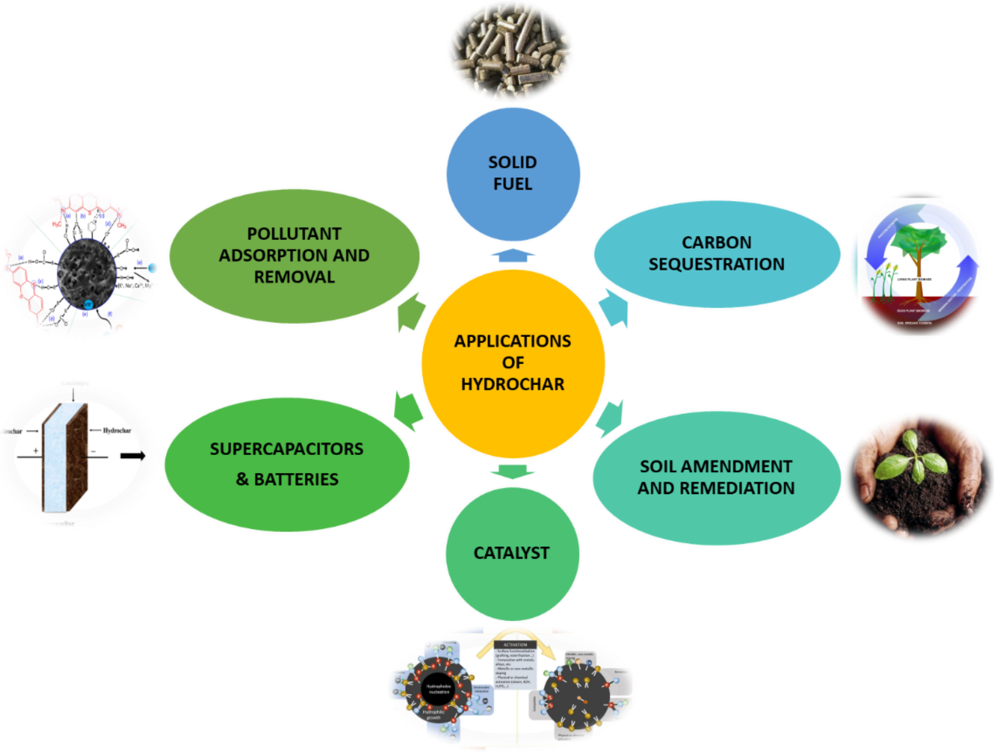

Figure 1: The schematic representation of major environmental applications of hydrochar

Table 1: Summary of potential environmental applications of hydrochar

Feedstock	HTC conditions	Modifications	Application	Remarks	Reference
Poultry litter	Temperature of 180, 220, and 250 °C	-	Soil amendment- Hydrochar rates of 0.5, 1 and 2% on lettuce seedlings	Improved plant growth up to three-fold, improved soil water retention, and decreased nitrate leaching	Mau *et al.* 2020
sewage sludge	Temperature 200 °C and 260 °C; 0.5 h, 3 h	-	Soil amendment- Calcic Cambisol at hydrochar doses of 5 t ha^{-1}.	Improved biomass production about 70%	Paneque *et al.* 2019
Sawdust	Temperature 260 °C	-	Soil amendment- Microbial-aged hydrochar at two application rates (5%, 15%) on rice field	Increased rice grain yield by 16.6–19.3% and reduced N_2O emissions	Hou *et al.* 2020
Glucose	Temperature 180°C, 4 h	Concentrated H_2SO_4 (98wt%) at 423 K under a N_2 flow for 8h.	Catalyst -Esterification	Excellent catalyst and increases accessibility of the active sites.	Li & Zeng, 2017
Alkali lignin	Temperature 200°C, 18 h	zero-valent iron encapsulated	Catalyst -Phenol removal	In 20 minutes at room temperature, Fe@HC-800 could totally break down phenol.	Ma *et al.* 2018
Eucalyptus bark	Temperature 220–300 °C, 2–10 h	-	Solid Fuel	Hydrochar had a calorific value between 20.2 and 29.2 MJ/kg that was equivalent to coal.	Gao *et al.* 2016
Food waste + yard waste	Temperature 220- 260 °C, 60-240 min	-	Solid Fuel -Biofuel pellets production	Compared to food waste hydrochar alone, pellets made from a mixture of food and garden waste hydrochar had higher energy (46.4 MJ/m^3) and mass density (1679 kg/m^3).	Sharma & Dubey,2020

Coffee Husk	Temperature 180 ◦C, 6 h	KOH 700 ◦C, 4 h	Methylene blue removal	Due to the significant amount of oxygen-containing functional groups in activated carbon, there was a substantial absorption of the Methylene blue dye.	Tran *et al.* 2021
Rice Straw	Temperature 200 ◦C, 70 min	Microwave Assisted HTC	Cu^{2+} and Zn^{2+} removal	Heavy metal adsorption is facilitated by the presence of oxygen-containing functional groups, a rough surface, and a greater pore volume.	Li *et al.* 2019
Micro Algae	Temperature 180°C ,10 h	K_2CO_3 Activation	Pollutant adsorption - CO_2 Capture	Polar surface of heteroatom-containing species and Ultra-micropores adsorb more CO_2.	Guo *et al.* 2017
Orange peel	Temperature 200 ◦C, 20 h	H_3PO_4 300–750 ◦C, 1.5 h	Diclofenac Salicylic acid Flurbiprofen removal	Activated hydrochar contains higher surface area and hydrogen bonding	Fernandez *et al.* 2015
Maize silage	Temperature 230°C and 180°C, 15 and 75 min	-	Carbon sequestration potential	A soil and CO_2 efflux isotopic analysis revealed that within a year, about half of the C applied was reemitted as CO_2.	Baronti *et al.* 2017
Waste tea	-	KOH and combusted at 500 ºC for 2 h	Carbon sequestration -Remove CO_2 in biogas	Modified activated carbon has higher adsorption due to hydrogen bond and dispersion interactions	Rattanaphan *et al.* 2019

3. Catalyst support

Recent research has emphasized the potential utilization of biomass-derived carbon catalyst reactions, where the carbon can be synthesized through the HTC technique, resulting in hydrochar with active polar oxygenated functionalities (Titirici & Antonietti, 2010). Hydrochar exhibits the ability to modify its physical and chemical composition, making it suitable for enhancing sorption potential by incorporating charged surface functions. This utilization of hydrochar for catalytic applications can contribute to a circular economy, reduce the cost of biocatalysts, and promote sustainable manufacturing practices. The introduction of acidic catalysts is a crucial step to enhance the presence of acidic sites on carbon. This can be achieved by treating the carbon with chemical agents such as H_3PO_4, H_2SO_4, HCl, or $HClSO_3$, which improve its acidic properties (Abdulkareem-Alsultan *et al.,* 2016; Soltani *et al.,* 2016). Hydrochar-derived carbon materials represent a select group that possesses at least two of these characteristics, such as the case with sulfonic groups (-SO_3H) functionalized hydrochar catalysts (Zailan *et al.,* 2022). Sulfonated amorphous carbon, which consists of -SO_3H groups in its structure, exhibits higher catalytic activity compared to other solid acid catalysts, making it feasible for applications like biodiesel production (Chen & Fang, 2011). The porosity of the carbon material plays a significant role in anchoring the sulfonic groups, thereby influencing the catalytic activity of the sulfonated catalysts. Reducing the particle size of the carbon catalyst can enhance the effectiveness and stability of the sulfonation process by improving contact between the carbon particle surfaces and H_2SO_4 (Tamborini *et al.,* 2016).

4. Solid bio fuel

Hydrothermal carbonization (HTC) involves the conversion of raw biomass into a solid residue that can serve as a substitute for coal in energy production. During the HTC process, the polymeric components present in the biomass undergo depolymerization, breakdown, and degradation. Different polymeric materials found in biomass exhibit varying higher heating values, with ash having the lowest value, followed by extractives, lignin, cellulose, and hemicellulose (Falco *et al.,* 2013). Through the HTC process, the removal of cellulose and hemicellulose leads to an increase in lignin concentration within the biomass. This lignin acts as a natural binder, promoting densification of the HTC residue, making it suitable for coal-like applications. Additionally, the carbon-to-oxygen (C/O) ratio also increases during HTC, resulting in an elevated higher heating value of the final product, i.e., the HTC residue. The hydrophobicity of the HTC residue is improved due to the increased lignin content or reduced hemicellulose content, which contributes to extending its shelf life by preventing biodegradation (Reza *et al.,* 2012).

Oumabady *et al.* (2020) conducted optimization of the hydrothermal carbonization (HTC) process to produce hydrochar from the sludge of an effluent treatment plant in a paper mill. The HTC char derived from the sludge exhibited a fixed carbon content of 15.6% and a heating value of 18.4 MJ/kg. It also displayed lower oxygen-to-carbon (O/C) ratio of 43.7% and hydrogen-to-carbon (H/C) ratio of 35.05%, indicating coalification of the sludge. The resulting HTC coal from the sludge had a higher heating value (HHV) of 22.3 MJ/kg and proved to be a viable option for generating heat energy in paper mills when blended with regular coal at a 1:1 ratio. In another study by Wang *et al.* (2018), the co-hydrothermal carbonization (co-HTC) technique was employed to produce hydrochar with a higher heating value using a combination of sludge and food waste. The researchers varied the carbonization temperature to determine the optimal HTC temperature for achieving the highest heating value. They observed that with the inclusion of 50% or 70% food waste, the heating efficiency of the hydrochar improved from 9.6 to 19 and 23 MJ/kg at 230°C, respectively. Furthermore, the co-HTC process enhanced the heating value, increased the carbon content, and decreased the ash content of the hydrochar. The synergistic effect between the two feedstocks in the co-HTC process likely contributed to the formation of stable fixed carbon, resulting in improved thermal stability of the hydrochars.

5. Carbon sequestration

Carbon capture and storage, also referred to as carbon sequestration, is the procedure used to store the hydrochar made from biomass in the soil. It is the same as removing net amounts of anthropogenic CO_2 off the atmosphere when the carbon remains stored in the soil. When carbon sequestration is done on purpose, it creates a carbon-negative or carbon-neutral environment, offsetting anthropogenic CO_2 emissions. Due to the motivating CO_2 mitigation method, the idea of carbon sequestration attracted a lot of attention globally (Lee *et al.* 2010). Pyrolysis, a process that converts biomass into a more stable form, leads to the production of biochar, which has been recognized as an effective means of carbon sequestration to mitigate climate change (Zhang *et al.,* 2014). If hydrochar is found to possess similar recalcitrant properties, it could potentially be utilized for similar purposes.

Research suggests that hydrochar is less effective than biochar in mitigating climate change due to its lower persistence in soils. Studies, such as the one conducted by Malghani *et al.* (2013), have shown that the addition of 1% by weight of hydrochar to soils resulted in a reduction in N_2O emissions but an increase in CH_4 and CO_2 emissions. Furthermore, within 100 days of adding 50% hydrochar, emissions increased due to the rapid breakdown of hydrochar. Similarly, studies by Kammann *et al.* (2012) and Schimmelpfennig *et al.* (2014) investigated the carbon sequestration potential of hydrochar made from different feedstocks such as ryegrass, peanut hulls, and Miscanthus giganteus. These studies also observed increased emissions of CO_2 and CH_4 when hydrochar was applied. The less stable carbon content of hydrochar, coupled with its increased degradability and promotion of microbial activity compared to biochar, were identified as contributing factors to the increase in CO_2 emissions. Overall, the findings suggest that hydrochar's lower stability and higher degradability compared to biochar contribute to its reduced efficiency in mitigating climate change, as it may lead to increased greenhouse gas emissions, particularly CO_2 and CH_4.

6. Supercapacitors and batteries

Hydrochars have potential applications in electrochemical devices such as supercapacitors and batteries. Both supercapacitors and batteries serve the purpose of providing energy, with supercapacitors excelling in high power density and batteries offering a high energy density (Winter & Brodd, 2004). The unique characteristics of hydrochar, including its smaller surface area, polarity, porosity, aromaticity, and stability, have attracted attention for utilization in these specific applications. According to Kammann *et al.* (2012), rechargeable batteries exhibit weaker cycle stability, an increased discharge/charge rate, and a lower energy density than supercapacitors made from hydrochar. Liu *et al.* (2020) used a microwave-assisted hydrothermal activation approach to activate hydrochar made from corn straw. The hydrochar structure was transformed from micropore structures to hierarchical pores throughout the activation duration of 40 to 100 min. i.e., a transition from amorphous to sheets that resemble graphene. In comparison to pyro chars made from maize, hydrochars shown greater capacitance (98 F/g), power, energy density (340 W/kg), and electrochemical performance (96 W h/kg). They also had a larger specific surface area (1781 m^2/g).

The superior performance of supercapacitors relies on the presence of hierarchical porous carbon structures (micro/meso/macro) that facilitate the transport of ions, leading to maximized capacitance (Li *et al.,* 2021). Researchers have explored the synthesis of functional porous carbon from waste eucalyptus bark using hydrothermal treatment combined with KOH activation for applications such as toluene adsorption and aqueous symmetric supercapacitors. The study demonstrated that the material achieved a maximum specific capacitance of 263.2 F/g, exhibited excellent capacitance retention even after 10,000 cycles, and possessed high energy and power densities of 10.5 Wh kg^{-1} and 159.5 W kg^{-1}, respectively (Li *et al.,* 2021). Recent investigations have shown that the specific capacitance of hydrochar can be enhanced by introducing heteroatom doping, which contributes to additional pseudocapacitance (Liu *et al.,* 2019). The improved performance was attributed to the presence of Fe oxides, a significant specific surface area (1509.5 m2/g), high electrical conductivity, and the carbon sphere architecture, which facilitated efficient ion and electrolyte diffusion (Xu *et al.,* 2021). Furthermore, apart from its application in supercapacitors, hydrochar possesses excellent mechanical properties, a large surface area, electrical conductivity, and easy accessibility, making it suitable for utilization as an electrochemical storage device.

7. Pollutants adsorption and removal

When comparing hydrochar to biochar, hydrochar generally possesses a smaller surface area. However, its adsorption capacity surpasses that of biochar due to the prevalence of oxygen-rich functionality and the abundance of chemically active functional groups, such as ketones, COOH groups, and hydroxyl, on its outermost layer (Qambrani *et al.,* 2017). The efficiency of hydrochar in adsorbing pollutants is influenced by its physicochemical characteristics, experimental conditions, and the nature of the pollutants. The surface functional groups responsible for adsorbing specific pollutants tend to increase with higher hydrochar content (Fang *et al.,* 2015). By utilizing hydrochar as an adsorbent, contaminated water can be treated and purified, effectively removing toxins, heavy metals, and dyes. The adsorption mechanism of hydrochar is depicted in Figure 2.

Hydrochar has emerged as an effective and economically viable adsorbent material for treating water contaminated with dyes (Maniscalco *et al.,* 2020). Numerous studies have investigated the adsorption performance of hydrochar with different types of dyes, with a tendency for better adsorption of cationic dyes (such as methylene blue, rhodamine b, and methyl green) compared to anionic dyes (such as methyl orange and acid red 1) (Tran *et al.,* 2017). Various post-modification treatments have been explored to enhance the adsorption capacity of hydrochar, and multiple mechanisms have been proposed to explain dye uptake, including pore filling facilitated by specific surface area, mesoporosity, and pore volume, electrostatic attraction and hydrogen bonding due to charged interactions between the adsorbate and adsorbent, presence of oxygen-containing functional groups, π-π interactions, and ion exchange. For instance, Ronix *et al.* (2017) produced hydrochar from coffee husks and tested its adsorption efficiency for removing methylene blue dye from aqueous solutions. The highest adsorption efficiency achieved was 34.9 mg/g of hydrochar after a 4-hour reaction at 210°C. In another study by Tran *et al.* (2017), spherical hydrochar was used as a control to compare the adsorption performance of glucose-activated hydrochar, which was prepared by enriching spherical hydrochar with triethylenetetramine for adsorption applications. The additional modifications to the spherical hydrochar led to significant increases in the maximum adsorption capacities (Qmax) for methyl green 5 and acid red 1, with reported enhancements of 1200% and 640%, respectively.

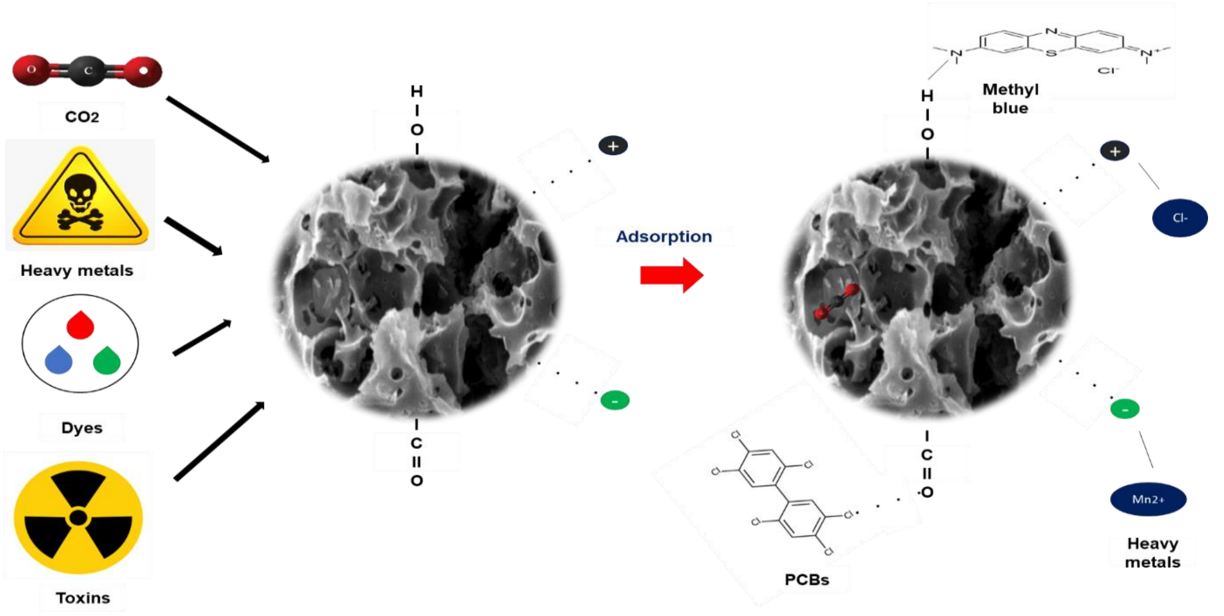

Figure 2: The pollutants adsorption mechanism of hydrochar

The eco-friendly removal of heavy metals (such as Pb^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+}) from water is a pressing need, and hydrochar treatment is regarded as a sustainable solution. Regmi *et al.* (2012) employed switchgrass in the hydrothermal carbonization (HTC) process to produce hydrochar and activated hydrochar for extracting copper and cadmium from aqueous solutions. Their study revealed that KOH-activated hydrochar exhibited 100% adsorption of copper and cadmium within 24 hours, surpassing the performance of hydrochar and commercially available activated carbon. In a separate study conducted by Nadarajah *et al.* (2021), rice straw hydrochar modified with $FeCl_3$ exhibited an 11%

increase in BET surface area and 4% higher removal of Pb^{2+} and Cu^{2+}. This improvement may be attributed to changes in the band intensities of oxygen-containing functional groups, which contribute to surface complexation and spontaneous endothermic adsorption. It can be concluded that hydrochars produced through HTC demonstrate good potential for removing heavy metals from water. However, the efficiency of heavy metal removal can be further enhanced by modifying the hydrochars using acids, alkaline substances, and oxidizers, which increase the presence of oxygen-containing functionalities. These functionalities play a crucial role in facilitating the surface complexation reaction with heavy metal ions, thereby effectively eliminating them from water (Xia *et al.,* 2019).

Conclusion:

Hydrochar, derived from the hydrothermal carbonization of biomass, exhibits versatile environmental applications. It offers potential in areas such as soil amendment, pollutant adsorption, energy storage, and carbon sequestration, presenting a promising solution for sustainable waste management. While hydrochar shares some similarities with biochar, its distinct physicochemical properties and functional groups enable it to perform uniquely in various environmental roles. Despite its lower stability compared to biochar, hydrochar's potential for enhancing soil properties, capturing carbon, and adsorbing pollutants underscores its value as a multifunctional material for addressing environmental challenges.

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A REVIEW ON ADVANCEMENTS IN HYDROCHAR CHARACTERIZATION: INSIGHTS INTO PHYSICAL, CHEMICAL, MORPHOLOGICAL AND FUNCTIONAL GROUP PROPERTIES

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Abstract:

Hydrothermal carbonization (HTC) has emerged as an effective technology for converting wet waste into hydrochar, a carbon-rich material with promising applications in environmental management. This process leverages high moisture content and specific reaction conditions to transform various feedstocks into hydrochar. The effectiveness of hydrochar is determined by its physical and chemical characteristics, which are analyzed through proximate and ultimate analysis, Fourier-transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM). These characterizations reveal insights into hydrochar's surface area, pore structure, elemental composition, and functional groups, which are crucial for optimizing its use in pollutant adsorption, soil amendment, and carbon sequestration. This review synthesizes current knowledge on the HTC process and hydrochar properties, emphasizing the importance of continued research to enhance the material's application potential and contribute to sustainable waste management solutions.

Keywords: Hydrothermal Carbonization, Hydrochar, Characterization, Morphological Characterization, Functional group Characterization.

1. Introduction

Wet waste conversion technology known as hydrothermal carbonization (HTC) has recently gained popularity and been thoroughly investigated (Funke and Ziegler, 2010; Kambo and Dutta, 2014; Saqib *et al.,* 2019). The HTC uses a sequence of reactions, including hydrolysis, dehydration, de-carboxylation, aromatization, condensation, and polymerization, to take advantage of the waste's high moisture content and turn it into a carbon-rich material, called hydrochar (Hoekman *et al.,* 2011; Libra *et al.,* 2011). HTC is typically carried out in a closed vessel with surplus water (more than 70% by weight) at temperatures between 180 and 260°C (Basso *et al.,* 2016). It yields the waste into two fractions: process wastewater and hydrochar (HC), a solid substance with added carbon. The process of hydrochar produced from HTC are summarized in Fig. 1.

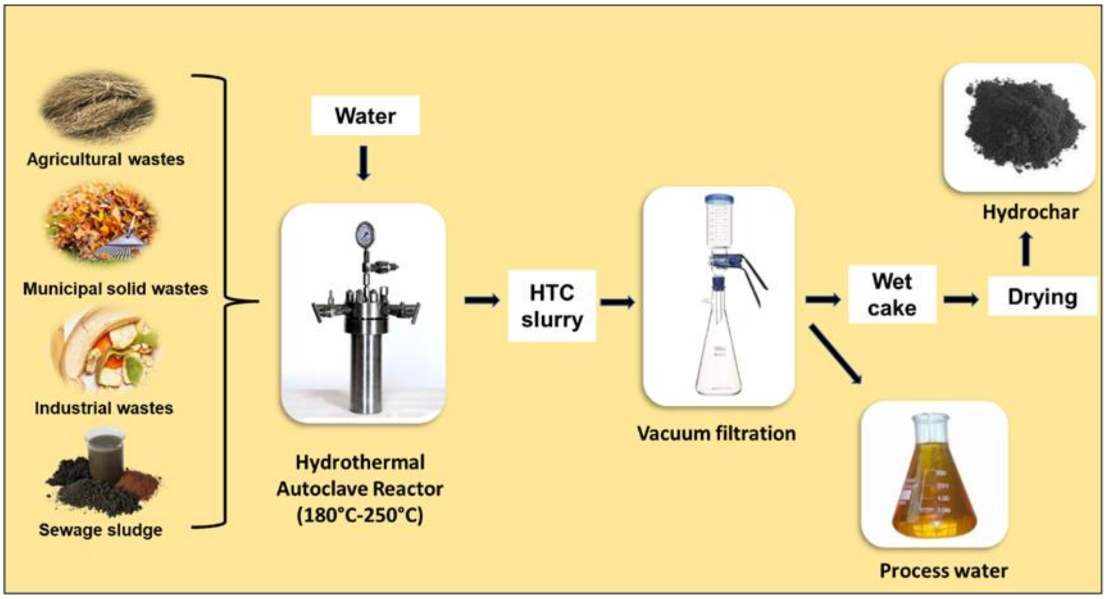

Figure 1: Schematic diagram of hydrochar production from HTC process

Due to HTC's high adaptability to wet waste, a variety of high moisture-containing feedstocks, such as MSW, specific lignocellulosic biomass, e.g. paper mill sludge, microalgae, fruit waste and peels, and non-lignocellulosic waste, have been studied to produce hydrochar. (Zhai *et al.,* 2016; Chen *et al.,* 2017;). The HTC process also results in hydrochar that is more grindable, more energy dense, and hydrophobic in addition to using water to its advantage. (Sharma *et al.,* 2019; Kambo and Dutta, 2014). As evident in Figure 2, the tremendously increased trend in research on HTC and hydrochar from 2009 to 2022. When heated under subcritical conditions, the moisture found in wet biodegradable waste functions as an organic solvent and catalyst. As aromatic compounds demonstrate excellent stability in this environment, hydrothermal pre-treatment is especially advantageous for enhancing the aromaticity of solids (Funke and Ziegler, 2010).

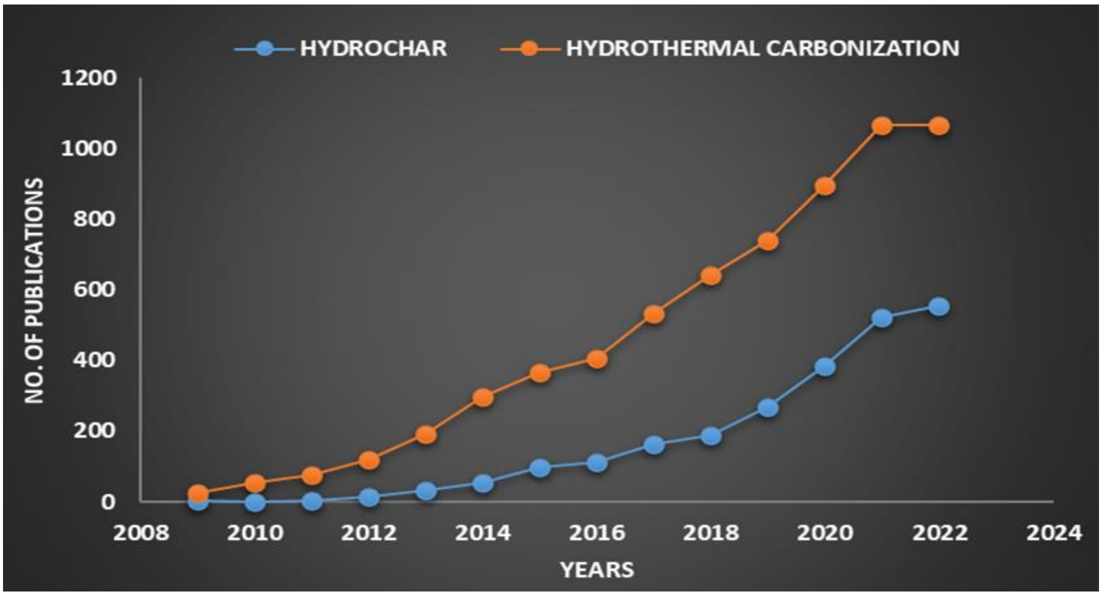

Figure 2: The increasing trend of number of publications including HTC and hydrochar from 2009 to 2022 (Source: Web of Science, 2023)

The performance of hydrochar in environmental applications is largely determined by its physical and chemical properties. Physical characterization involves assessing surface area, pore structure, and particle size distribution, all of which influence the material's effectiveness in applications like pollutant adsorption. Scanning electron microscopy (SEM) is commonly used to analyze these properties, providing insights into hydrochar's surface morphology (Chen *et al.,* 2017). Chemical characterization focuses on determining the elemental composition and identifying functional groups on the hydrochar surface, which are crucial for its interaction with environmental contaminants. Fourier-transform infrared spectroscopy (FTIR) is used to analyze these aspects (Sharma *et al.,* 2019; Kambo and Dutta, 2014). These characterizations are essential for optimizing hydrochar for specific uses and understanding its long-term stability in environmental applications. This review paper aims to provide an information on proximate and ultimate analysis, atomic ratio, surface, and functional group characterization of hydrochars.

2. Characterization of hydrochar

2.1 Proximate and ultimate analysis and atomic ratio characterization

To ensure that hydrochar is used effectively as a fuel and a component of the sample, the hydrochar must undergo both a preliminary and a final examination. The products' Volatile Matter (VM), ash, and Fixed Carbon (FC) contents were measured as part of the proximate analysis. In many cases, the difference in weight between hydrochars and the ashes produced in a muffle furnace at specific temperatures is utilized to calculate the quantities of ash and VM. By subtracting the amounts of VM and ash from 100% based on dry weight, the FC content is determined (Fu *et al.,* 2019). Nevertheless, it is possible to achieve an increased fraction of FC and ash content in the hydrochar, indicating that a significant amount of carbon is retained in the hydrochar. Generally, HTC conducted at high temperatures yields a lower solid mass output. The drawbacks of raw biomass, such as its propensity to ignite easily at low temperatures (around 250 °C) and undergo rapid weight loss when used as solid fuel, can be mitigated by hydrochar with higher fixed carbon content and reduced VM content (Xu, 2014). The FC and ash contents primarily depend on the characteristics of the feedstock.

According to Qambrani *et al.* (2017), chars with greater FC concentrations were more stable in the environment as well as resistant to biological breakdown. One can argue that chars created at a high temperature from carbohydrate-rich substances (such cooked rice and breadcrumbs) would be preferable from the perspective of carbon sequestration. Through cation exchange and electrostatic interaction, the ash concentration of biochars was crucial to the adsorption process (Zhu *et al.,* 2018). With rising peak temperatures, hydrochars' volatile matter levels dropped. This resulted from the breakdown of organic materials, the release of volatiles, and the subsequent transformations of those volatiles (Kambo and Dutta, 2015). The final study of hydrochar revealed that it is made up of many elements, including N, P, K, C, H, O, and S. For all feedstocks, the temperature was inversely correlated with the carbon content and directly correlated with the oxygen and hydrogen contents (Qian *et al.* 2013).

Table 1: Differences in the proximate and ultimate analysis and atomic ratio of hydrochar from different raw feedstocks.

Temperature (°C)	Residence time (h)	Biomass/ water (Kg/Kg)	Hydrochar yield (db, %)	Proximate analysis (%)			Atomic ratio		Ultimate analysis (%)				Reference
				VM	Ash	FC	H/C	O/C	C	H	O	N	
200 ∘C	1	0.7/2	50.0 ± 2.4	91.4 ± 0.6	2.7 ± 0.18	5.9 ± 0.22	-	-	58.4	6.4	29.7	2.8	Gupta *et al.* 2021
	3	0.7/2	47.8 ± 3.6	91.5 ± 2.8	6.2 ± 0.04	2.3 ± 0.21	-	-	55.2	6.5	28.9	3.2	
	5	0.7/2	53.7 ± 5.2	92.3 ± 0.9	5.5 ± 0.19	2.2 ± 0.09	-	-	58.4	6.1	27.4	2.6	
	8	0.7/2	48.5 ± 4.5	92.8 ± 0.1	6.0 ± 0.78	1.2 ± 0.78	-	-	63.5	7.2	20.7	2.6	
220–300	2–10	0.005/0.05	46.4–40.9	71.2–60.1	2.7–5.9	26.1–34	1.36–0.83	0.68–0.23	9.5–72.72	5.59–5.05–	44.91–22.23	-	Gao *et al.* 2016

160–200	2–24	0.004/0.04	45.60–78.50	83.01–63.24	5.11–8.89	11.28–27.80	1.37–1.03	0.81–0.40	45.10–60	5.18–5.19	49.20–32.48	0.5–0.1	Sharma *et al.* 2019
180	10 (mins)	0.25/0.375	71.29	84.59	1.58	9.12			47.42	6.60	42.32	0.41	Zhang *et al.* 2020
220	20		66.40	79.60	2.08	15.26			51.36	6.53	38.88	0.51	
280	30		46.71	60.11	2.60	35.97			66.45	6.08	23.41	1.01	
180	30 min	20/180	66.18	22.18	68.47	9.15	1.99	0.15	21.23	3.51	4.27	1.64	Peng *et al.* 2016
220	30 min	20/180	60.58	18.81	72.02	9.17	1.97	0.13	19.62	3.22	3.27	1.32	
260	30 min	20/180	56.23	27.26	62.46	10.28	1.94	0.23	24.27	3.92	7.28	1.56	
300	30 min	20/180	53.00	16.79	70.97	12.24	1.84	0.07	21.94	3.36	2.13	1.12	
260	60 min	20/180	58.51	23.14	65.17	11.69	1.80	0.14	24.49	3.68	4.51	1.59	
260	90 min	20/180	59.37	24.78	61.98	13.24	1.86	0.25	24.13	3.73	8.04	1.52	
260	6 h	20/180	63.32	22.61	69.74	7.65	1.95	0.20	19.90	3.24	5.35	1.24	

220	30 min	10/100	76.6	69.8	6.2	24.0	1.01	0.37	62.47	5.28	31.09	0.90	Liu *et al.* 2013
250	30 min	10/100	65.7	67.9	5.0	27.1	0.93	0.30	67.10	5.20	26.43	0.98	
300	30 min	10/100	65.0	53.6	4.3	42.1	0.97	0.21	73.22	5.09	20.21	1.13	
350	30 min	10/100	55.78	56.6	4.9	38.5	0.74	0.21	73.37	4.52	20.58	1.17	
240	30–24	-	-	-	24.94–29.16	-	1.16–1.03	0.45–0.21	44.26–46.46	4.26–3.98	24.01–13.31	2.5–3.07	Gao *et al.* 2013
220	10	-	55.54	68.67	23.27	8.06	1.29	0.25	50.64	5.44	17.05	3.16	Zhang *et al.* 2018
200	30 min	30/100	-	69.07	26.31	3.54	1.17	0.82	41.95	4.99	46.02	6.20	Zhao *et al.* 2013
190-260	1-12	-	65.73-56.45	-	5.20-6.61	-	1.22 - 0.98	0.38-0.13	57.44-72.11	5.85-5.87	29.00-12.16	2.51-3.25	Chen *et al.* 2017
197	30 min	-	-	59.4	30.5	10.1	1.43	0.58	35.2	4.2	27	3.1	Areeprasert *et al.* 2014

The H/C and O/C atomic ratios generally decrease as the peak temperature increases. This observation is supported by Crombie *et al.* (2013), who used the H/C ratio as an indicator of aromaticity and stability. Hydrothermal carbonization (HTC) significantly alters the elemental composition of hydrochar, as evidenced by changes in the H/C and O/C ratios, which provide information about the degree of carbonization, deoxygenation, and aromatic content. Higher H/C ratios indicate lower concentrations of aromatic compounds in the hydrochar (Tekin *et al.,* 2014). A study by Lehmann and Joseph (2009) found that hydrochars produced at lower HTC temperatures with higher O/C ratios exhibit higher amounts of oxygenated surface functional groups such as hydroxyl, carboxylate, and carbonyl groups. These functional groups contribute to a higher cation exchange capacity (CEC), which is advantageous for sorbing positively charged pollutants like heavy metals and retaining nutrients in soils (Uchimiya *et al.,* 2011; Inyang *et al.,* 2014). Dehydration processes can lead to simultaneous decreases in the H/C and O/C ratios, as well as the removal of carboxyl groups (Sevilla & Fuertes, 2009). Chemical dehydration is the primary mechanism responsible for the significant water loss from biomass during the HTC process, while both chemical and physical processes contribute to dehydration during hydrothermal carbonization (Funke & Ziegler, 2010). Table 1 summarizes the differences in proximate and ultimate analysis, as well as aromatic ratios, of hydrochar derived from various raw feedstocks using the HTC process.

2.2 Surface functionality characterization

The surface functional groups present in hydrochars play a crucial role in pollutant removal by influencing sorption processes (Qambrani *et al.,* 2017) and electron transfer mechanisms. The structural properties of hydrochar can vary significantly depending on the type of feedstock and the processing conditions employed. Due to the complex composition of hydrochar and the diverse variations in hydrothermal conditions and feedstocks used in hydrothermal carbonization (HTC), researchers often employ Fourier-transform infrared (FTIR) spectroscopy to analyze the surface functional groups of both raw biomasses and hydrochar. FTIR spectra provide valuable insights into the mechanistic analysis of hydrochar evolution, and numerous studies have utilized this method to examine the structural changes in hydrochar produced from different biomass sources under various HTC settings. Examples include coconut fiber and dead eucalyptus leaves (Liu *et al.,* 2013), miscanthus (Calucci *et al.,* 2013), barley straw (Sevilla *et al.,* 2011), pinewood (Liu *et al.,* 2010), and sewage sludge (Zhang and Ok, 2014).

The findings suggest that pyrolysis and hydrothermal carbonization at temperatures above 400°C can lead to the loss of hydroxyl, carboxyl, and carbonyl functional groups due to dehydration and decarboxylation processes. Oxygen-containing functional groups also tend to decrease after hydrothermal carbonization, attributed to dehydration and decarboxylation. At high temperatures, peaks corresponding to lignin and cellulose become stronger and wider, indicating the transformation of single aromatics into polyaromatics (Fu *et al.,* 2019). Hydrochars and biochars produced from food wastes at lower temperatures (300°C) tend to retain more functional groups, which can aid in contaminant immobilization, nutrient retention, and water retention (Qambrani *et al.,* 2017). The prevalence of oxygenated functional groups on the surface of hydrochar is evident from the presence of ester, carboxyl, and carbonyl groups (Sevilla and Fuertes, 2009). The decrease in H/C and O/C ratios during hydrothermal carbonization is consistent with the weakening of O-H stretching vibrations in hydroxyl and carboxyl groups, indicating dehydration compared to the feedstock (Zhao *et al.,* 2013; Wang and Li, 2015). Oxygenated functional groups play a significant role in the simplicity and effectiveness of hydrochar production during hydrothermal carbonization. For example, Gao *et al.* observed that the rate of decarboxylation increased with residence time during hydrothermal carbonization of discarded eucalyptus bark, resulting in a decrease in C=O stretching vibrations in ketone, amide, and carboxylic groups in the hydrochar (Gao *et al.,* 2013). Furthermore, FTIR analysis has been employed to investigate the presence of nitrogen (N) functional groups in sludge and associated hydrochar (Zhao *et al.,* 2013).

Indeed, X-ray photoelectron spectroscopy (XPS) is a valuable technique for analyzing the surface functionality of hydrochar. In XPS wide-scan spectra, hydrochars derived from lignocellulosic materials typically exhibit prominent peaks for carbon (C1s) around 285 eV and oxygen (O1s) around 530 eV (Manya, 2012). The hydrochar produced from sewage sludge (SS) also showed higher atomic ratios of oxygen to carbon (O/C) on the outer surface compared to the inner core. For example, a study by He *et al.* (2016) using XPS analysis demonstrated that hydrochar produced at 260 °C had higher O/C ratios, while hydrochar produced at 300 °C exhibited higher carbon-oxygen (C-O, C=O) and carbon-nitrogen (C-N) functionalities. These results support the presence of oxygen-rich functional groups on the surface of hydrochar particles. The findings align with the FTIR spectra, which indicate the presence of both aromatic and aliphatic carbon, as well as a higher concentration of oxygenated functional groups on the hydrochar surface, as reflected by XPS analysis.

2.3 Morphological characterization

SEM is commonly employed for the examination of hydrochars' morphology under different HTC conditions, as it generates micrographs that depict the physical attributes and surface structure of the materials. Generally, hydrochar possesses a more rugged surface compared to the smooth surface of raw biomass. The degradation of easily collapsible polymers, such as hemicellulose, can lead to the formation of a rough and porous surface on the solid residue, along with the release of organic substances during HTC. Consequently, these minuscule particles may undergo further melting or give rise to carbonaceous spheres. While the surface of the original materials appeared flat and continuous, the hydrochar surface exhibited uneven and rough regions, accompanied by the development of novel microspheres in diverse shapes and sizes. According to Sevilla and Fuertes (2009), the HTC conditions for reaction and the variety of feedstock employed have an impact on the creation of microspheres. It demonstrated that the cellulose present in the plant wall underwent breakdown. Although HTC was carried out at relatively low temperatures, the primary structure was preserved; as a result, greater carbonization temperatures are needed for lignin degradation during the HTC process (Xiao *et al.* 2012). The hydrochar's porous microstructure suggests that during the HTC, organic materials were broken down. Simultaneously, the SEM revealed micrometer-sized particles dispersions on the surface in an array of shapes, including fluffy sponges, honeycombs, and spherical particles. The creation of these particles was mostly ascribed to the presence of carbohydrates (Gai *et al.* 2016).

Sharma *et al.* (2020) conducted an SEM analysis of hydrochar produced through co-hydrothermal carbonization (Co-HTC) of yard debris and food waste at a temperature of 220°C. The surface of the food waste (FW) hydrochar was observed to be covered with numerous small, individual carbon spheres, some of which were interconnected, forming larger microspheres. On the other hand, the yard debris (YD) hydrochar exhibited a porous structure without any noticeable microspheres. According to Sevilla and Fuertes (2009), the formation of larger microspheres through the cross-linking of smaller carbon spheres suggests the occurrence of polymerization and condensation reactions during HTC. The results of the YD+FW sample indicated that the hydrochar generated from a mixed feedstock through Co-HTC differed from hydrochar produced through HTC using a single substrate. This distinction arises from the fact that during Co-HTC, food waste contributes resources such as carbohydrates and nitrogen, which behave differently compared to HTC using a single substrate. Wang *et al.* (2018b) explained that in one-substrate HTC, the lignocellulosic components (lignin, hemicellulose, and cellulose) are carbonized without a supply of carbohydrates, resulting in a distinct hydrochar structure. The SEM of hydrochar made from rye straw was studied by Falco *et al.* (2011) at temperatures ranging from 160° to 240°C. Similar to cellulose, particle production occurred on the raw straw fibres' surface. This contrasts with the hydrochars made from glucose, which had a largely homogenous distribution. Due to the existence of greater temperature resistant lignin, the body of fresh straw was able to preserve its original structural framework, and the cellulose could also go through reactions that resembling pyrolysis.

Conclusion:

hydrothermal carbonization (HTC) represents a promising technology for converting wet waste into valuable hydrochar, offering a sustainable approach to waste management and resource recovery. The effectiveness of hydrochar in environmental applications, such as pollutant adsorption and soil amendment, is largely influenced by its physical and chemical properties, which vary depending on the feedstock and HTC conditions. Characterization techniques like proximate and ultimate analysis, FTIR, XPS, and SEM provide crucial insights into the composition, surface functionality, and morphology of hydrochar. These findings highlight the importance of optimizing HTC parameters to enhance the hydrochar's stability, carbon content, and functional groups, making it more suitable for specific environmental applications. As research continues to evolve, HTC and hydrochar hold significant potential for contributing to environmental sustainability and carbon sequestration efforts.

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ALTERNATIVE METHODS FOR SECOND-ORDER ODES WITH CONSTANT COEFFICIENTS

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Abstract:

This article provides details methods for solving second-order (ODE) ordinary differential equations with constant coefficients. This article presents the general form of second-order differential equations and constant coefficients. The article formerly discusses the characteristics of the equation roots, which define the solution forms. In This article we discuss different and real roots, complex conjugate roots, and repetitive roots and presents the overall solution for each case and given examples to show the procedure. A brief outline of second-order differential equation applications in engineering and physics concludes the paper. This paper is intended to clearly and concisely guide students and scholars attentive in this significant topic.

Keywords: Differential Equations of Order Two, Constant Coefficients, Homogeneous Linear Differential Equations Real & Distinct Roots, Complex Conjugate Roots and Repeated Roots.

1. Introduction:

Second-order ordinary difference coefficients, the class of coefficients in which the coefficients remain constant is one that is encountered frequently in a wide variety of aspects and physical fields. As a result, these coefficients are extremely important in providing knowledge about physical phenomena and the conditions in the tribes about them. These coefficients are found in many domains, including quantum mechanical, electromagnetism and mechanics [1]. The task of finding solutions for these parameters is an important task for a large number of dolls and students studying in various subjects.

The drive of this article is to present a thorough and precise examination of the techniques used in solving equations belonging to this special class. We begin by presenting the identical form of a second-order differential equation, where the coefficients are constant through the equation. This equation is recognized as a homogeneous linear equation. the significance of constant coefficients and their significant role in solving these equations. Next, we existent the characteristic equation and its roots, which provide valuable facts about the properties of the solutions. We will examine three possible situations, the presence of exact and distinct roots, the existence of complex conjugate roots, and the occurrence of repetitive roots. We find general solutions for every one case. We present specific examples to demonstrate the practical implementation of the technique [2].

One of the initial works on this theme was by Leonhard Euler in the 18th era. Euler developing a general technique for solving LDE (linear differential equations) of any order, including the 2^{nd} orders equation coefficients with constant (Euler, 1748).

2. Literature review:

One of the initial influences to the subject was the 18th period work of Leonhard Euler. Euler developing a technique for solving second-order linear differential equations (LDEs) of any degree with constant coefficients. The Euler method developing in 1748 for solving (LDEs) linear differential equations of any degree including second-order complications with constant coefficients, i.e. constant ones (Euler, 1748).

3. Constant homogeneous linear ODE coefficients

Specifically, we examine the situation of a second-order homogeneous linear differential equation in which all of the coefficients are constant and real.

Now to place it another way, we only intend to look at equations that have the structure that is described below:

The General form of the linear differential equation with constant coefficients is

$$b_0 \frac{d^2y}{dx^2}+b_1\frac{dy}{dx}+b_2y=0 \text{ ……………….} (i)$$

As a result, we are going to look for solutions to equation (1) in the form of $y=e^{mx}$, where we will choose the constant m in such a way that e^{mx} satisfies the equation. $Since\ y=e^{mx}$,

$$\Rightarrow y'=me^{mx}\ and\ y''=m^2e^{mx}$$

These value using in equation (i)

$$b_0\, m^2e^{mx}+b_1me^{mx}+b_2e^{mx}=0$$

$$b_0\, m^2+b_1m+b_2=0$$

After solving equation (i)we find three cases

- The roots of given auxiliary equation are real and distinct.
- The roots of given auxiliary equation are equal.
- The roots of given auxiliary equation are Imaginary.

3.1 Case-I: Distinct and Real Roots-

If m_1, m_2 be the different roots of equation (2) then $y = e^{m_1 x}$ and $y = e^{m_2 x}$

Be the independent solutions of (i)Therefore the general solution of $equation$ (i) is.

$$y = C_1 e^{m_1 x} + C_2 e^{m_2 x}$$

Where C_1 and C_2 be the arbitrary constants.

Example: Solve the differential equation $\frac{d^2y}{dx^2} - 3\frac{dy}{dx} - 4y = 0$

Solution: the given equation is

$$\frac{d^2y}{dx^2} - 3\frac{dy}{dx} - 4y = 0$$

Given equation can be written as $D^2y - 3Dy - 4y = 0$

or $(D^2 - 3D - 4)y = 0$

For auxiliary equation D is replace by m

$m^2 - 3m - 4 = 0$

$$or\ m^2 - 4m + m - 4 = 0$$

$\Rightarrow m(m-4) + 1(m-4) = 0$

$\Rightarrow (m-4)(m+1) = 0$

$\Rightarrow m = 4\ \&\ m = -1$

The roots are distinct and real . Thus the roots are e^{4x} and e^{-x}

solutions to the equation are given and can be express the general solution

$y = C_1\, e^{4x} + C_2\, e^{-x}$ Where C_1 and C_2 be the arbitrary constants.

3.2 Case-I: Repeated and Real Roots-

If m and m be the repeated roots of equation (2) then $y = e^{mx}$ and $y = e^{mx}$ be the independent solutions of (i)Therefore the general solution of $equation$ (i) is.

$$y = C_1 e^{mx} + xC_2 e^{mx}$$

$$y = (C_1 + xC_2)e^{mx}$$

Where C_1 and C_2 be the arbitrary constants.

Example- the differential equation $\frac{d^2y}{dx^2} - 2\frac{dy}{dx} + y = 0$

Solution: the given equation is $\frac{d^2y}{dx^2} - 2\frac{dy}{dx} + y = 0$

Given equation can be written as $D^2y - 2Dy + y = 0$

$or\ \ (D^2 - 2D + 1)y = 0$

For auxiliary equation D is replace by m

$m^2 - 2m + 1 = 0$

$$or\ \ m^2 - m - m + 1 = 0$$

$\Rightarrow m(m-1) - 1(m-1) = 0$

$\Rightarrow (m-1)(m-1) = 0$

$\Rightarrow m = 1{,}1$

The roots of differential equation are real and equal. Thus the roots are $e^x\ and\ e^x$ solutions to the equation are given and can be express the general solution

Then Complementary function C.F = $(C_1 + xC_2)e^x$

Hence it's general solution $y = (C_1 + xC_2)e^x$, where $C_1\ and\ C_2$ the arbitrary constants.

3.3 Case-I: Conjugate Complex Roots-

If auxiliary equation has a non-repeated complex number roots of equation (ii) of the form $a + ib\ and$ $a - ib\ be\ the$ conjugate complex roots and it also a $non-$ repeated $root's$. Science the coefficients in the given equation are real. Therefore, the corresponding part of the general solution is $given\ by$

$$y = \{ke^{(a+ib)x} + k'e^{(a-ib)x}\}, \text{where } k\ be \text{ the arbitrary constants.}$$

$$y = \{ke^{(a+ib)x} + k'e^{(a-ib)x}\}$$

$$y = ke^{ax}(e^{ibx}) + k'e^{ax}(e^{-ibx})$$

$$y = ke^{ax}(Cosbx + i\ Sinbx) + k'e^{ax}(Cosbx - i\ Sinbx)$$

$$y = e^{ax}[(k + k')Cosbx + i(k - k')\ Sinbx)$$

$y = e^{ax}[C_1Cosbx + C_2Sinbx]$,

$$where\ C_1 = (k + k')\ and\ C_2 = (k - k')$$

Example.: $y'' - 6y' + 25\,y = 0$

Solution: Given equation can be written as

$(D^2 - 6D + 25)y = 0$, for auxiliary equation put $\emptyset(m) = 0\ and$ D is replace by m

$m^2 - 6m + 25 = 0$ ie. Quadratic equation in terms of m.

$$ie.m = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$or\ m = \frac{6 \pm \sqrt{36-4(25)}}{2}$ or $m = \frac{6 \pm \sqrt{-64}}{2}$

$$\Rightarrow\ m = \frac{6}{2} \pm \frac{i\sqrt{64}}{2}\ or\ m = 3 \pm i4$$

Here the roots be the conjugate complex numbers in form of $a + ib$ where $a = 3\ and\ b = 4$.

Complementary function $y_c = e^{3x}(C_1 Cos 4x + C_2\ Sin\ 4x)$

Hence it's general solution

$y = e^{3x}(C_1 Cos 4x + C_2\ Sin\ 4x)$

4. Non Homogeneous linear differential equation with constant coefficient-

In this case, the coefficients 0, 1, and 2 are constants, but the non-homogeneous term *F(x)* in general a non-constant function of *x*. that not always remains constant. It is possible to write the general solution of the equation that was presented earlier as follows: $y = y_c + y_p$, where y_c is the general solution of the homogeneous equation that corresponds to it (i),with $F(x)$ replaced by zero. The complementary function, which is referred to as y_p is a solution that does not contain any arbitrary constants. In contrast, a specific integral is a solution to equation (i) that does not include any arbitrary constants. This type of solution is referred to as a particular integral.

4.1. Case-I: If $F(x) = x$, ie. polynomial in x then

$$y_c = \frac{1}{f(D)} x = \{f(D)\}^{-1} x$$

This binomial expansion in terms of $\{f(D)\}^{-1}$ and multiplying term by term. Sometimes this expansions using partial fraction method.

Example. Solve: $\frac{d^3y}{dx^3} - \frac{d^2y}{dx^2} - 6\frac{dy}{dx} = 1 + x^2$

Solution: Given equation can be written as

$(D^3 - D^2 - 6D)y = 1 + x^2$, for auxiliary equation put $\emptyset(m) = 0\ and$ D is replace by m

$m(m^2 - m - 6) = 0$ or $m(m^2 - 3m + 2m - 6) = 0$

$$or\ m\{m(m-3) + 2(m-3)\} = 0\ \Rightarrow m(m-3)(m+2) = 0$$

$$\Rightarrow m = 0, 3\ \&-2$$

Complementary function $y_c = C_1 + C_2\ e^{3x} + C_3\ e^{-2x}$

Particular Integral $y_p\ = \frac{1}{(D^3 - D^2 - 6D)}\ (1 + x^2)$

$= \frac{1}{D(D^2-D-6)}(1+ x^2)$

$= -\frac{1}{6D}\frac{1}{\{1-\frac{(D^2-D)}{6}\}}(1+x^2)$

$= \frac{1}{D}\frac{1}{(1-t)}(1+x^2)$ where $t = \frac{(D^2-D)}{6}$

$= \frac{1}{D}(1-t)^{-1}(1+x^2)$

$= \frac{1}{D}(1+t+t^2+t^3+\cdots)(1+x^2)$

$= \frac{1}{D}\{1+\frac{(D^2-D)}{6}+\frac{(D^2-D)^2}{36}+\frac{(D^2-D)^3}{216}+\cdots\}(1+x^2)$

$= \frac{1}{D}\{1+\frac{(D^2-D)}{6}+\frac{(D^4+D^2-2D^3)}{36}+\cdots\}(1+x^2)$

here $Dx^2 = 2x, D^2x^2 = 2, D^3x^2 = 0$ & $D^4x^2 = 0$

$= \frac{1}{D}\{1+\frac{D^2}{6}-\frac{D}{6}+\frac{D^2}{36}+\cdots\}(1+x^2)$

$= \frac{1}{D}\{1+\frac{7D^2}{36}-\frac{D}{6}+\cdots\}(1+x^2)$

$= \frac{1}{D}\{(1+x^2)+\frac{7D^2(1+x^2)}{36}-\frac{D(1+x^2)}{6}+\cdots\}$

$= \frac{1}{D}\{(1+x^2)+\frac{7.2}{36}-\frac{2x}{6}+\cdots\}$

$= \frac{1}{D}\{1+x^2+\frac{14}{36}-\frac{x}{3}+\cdots\}$

$= \frac{1}{D}(\frac{50}{36}+x^2-\frac{x}{3})$

$y_p = \frac{50}{36}x+\frac{x^3}{3}-\frac{1}{2}x^2$

Thus the general solution is

$y = y_c + y_p,$

$y = C_1 + C_2\, e^{3x} + C_3\, e^{-2x} + \frac{50}{36}x + \frac{x^3}{3} - \frac{1}{2}x^2$

Case-II- If $F(x) = \boldsymbol{e^{ax}}$ ie. polynomial in terms of x then

$y_p = \frac{\mathbf{1}}{f(\boldsymbol{D})}\boldsymbol{e^{ax}}$***, provided*** $\boldsymbol{f(a)} \neq \mathbf{0}, y_p = \{f(D)\}^{-1}\boldsymbol{e^{ax}}$

Example. Solve $\frac{d^2y}{dx^2} - 7\frac{dy}{dx} + 12y = e^{5x}$

Solution: Given equation can be written as

$(D^2 - 7D + 12)y = e^{5x}$, for auxiliary equation put $\emptyset(m) = 0$ *and* D is replace by m

$$m^2 - 7m + 12 = 0 \; or \; m^2 - 4m - 3m + 12 = 0$$

or $m(m-4) - 3(m-4) = 0$

$$or\ (m-4)(m-3)=0\ or\ m=4\ and\ 3$$

Complementary function ie. $y_c\ =C_1e^{4x}+C_2e^{3x}$

Particular Integral P.I. ie. $y_p\ =\frac{1}{f(D)}e^{ax}$, provided $f(a)\neq 0$

$$=\frac{1}{(D^2-7D+12)}e^{5x}$$

$$y_p\ =\frac{1}{25-35+12}e^{5x}\ or\ y_p\ =\frac{1}{2}e^{5x}$$

Its general solution will be

$y=y_c+y_p$

$y=C_1e^{4x}+C_2e^{3x}+\frac{1}{2}e^{5x}$

Case-III- If $F(x)=\boldsymbol{e^{ax}}$ ie. Polynomial in terms of x then

$y_p=\frac{1}{f(D)}e^{ax}$, *provided* $f(a)=0, y_p=\boldsymbol{e^{ax}}\{f(D+a)\}^{-1}$*here* $f(a)=0$

Example. Solve $(D-5)^3y=e^{5x}$

Solution: Given equation can be written as

$(D-5)^3y=e^{5x}$, for auxiliary equation put $\emptyset(m)=0\ and$ D is replace by m

$$(m-5)^3=0\ \Rightarrow m=5,5,5$$

Complementary function $y_c=(C_1+C_2x+C_3x^2)e^{5x}$

Particular Integral $y_p\ =\frac{1}{f(D)}e^{ax}$, provided $f(a)\neq 0$, but in this case $f(a)=0$

$$y_p=\frac{1}{(D-5)^3}e^{5x}$$

$=e^{5x}\ \frac{1}{(D+5-\ 5)^3}$

$=\ e^{5x}\ \frac{1}{(D)^3}1$

$or\ y_p\ =\ e^{5x}\ \frac{1}{D^2}x$

$=e^{5x}\frac{1}{D}\frac{x^2}{2}\ =e^{5x}\frac{x^3}{2.3}\ =e^{5x}\frac{x^3}{6}$

$y_p\ =\frac{x^3e^{5x}}{6}$

Hence it's general solution $y=y_c+y_p$

$y=(C_1+C_2x+C_3x^2)e^{5x}+\frac{x^3e^{5x}}{6}$

Conclusion and future focus:

The solution of second-order ordinary differential equations (ODEs) with constant coefficients is of great importance in the fields of engineering and mathematics, physics. It has many applications in physical systems and this equation is prevalent in various fields. This paper provides an overview of the characteristic equation, its roots, and three scenarios involving unique and real roots, complex conjugate roots, and repeated roots. It also plays an important role in examining the implications and practical uses of the answers in evaluating and predicting the behavior of physical systems. This article is important for researchers and students who are exploring this issue to address the concerns related to it.

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A REVIEW ON VARIOUS TYPES OF HYDROTHERMAL CARBONIZATION AND EFFECT OF PROCESS CONDITIONS FOR HYDROCHAR PRODUCTION

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Abstract:

Hydrothermal carbonization (HTC) is a cutting-edge technology for converting wet biomass into hydrochar, offering a sustainable approach to waste management and resource recovery. Operating under subcritical water conditions at temperatures between 180°C and 260°C, HTC facilitates rapid dehydration, decarboxylation, and polymerization reactions, efficiently transforming high-moisture feedstocks, such as municipal solid waste and agricultural residues, into carbon-rich hydrochar. Key parameters, including temperature, residence time, and feedstock composition, significantly influence the quality and yield of hydrochar. Recent advancements, such as microwave-assisted HTC and co-hydrothermal carbonization, have further enhanced the efficiency and functionality of the process, enabling the production of hydrochar with tailored properties for specific applications. This review explores the HTC mechanisms and optimizing process conditions, HTC can be effectively integrated into waste valorization strategies, contributing to environmental sustainability and resource conservation.

Keywords: Hydrothermal Carbonization, Hydrochar, Co-hydrothermal carbonization, microwave-assisted carbonization, Process conditions.

1. Introduction

The rapid urbanization in emerging nations is driving a significant increase in waste generation, posing a formidable challenge to sustainable development. Municipal solid waste (MSW), a major byproduct of urbanization, is particularly concerning due to its substantial wet biodegradable component, which constitutes nearly half of all waste produced and has a moisture content of 70-80%. As global MSW production is projected to rise by 70% to 3.4 billion metric tonnes (BMT) by 2050, the need for effective waste management solutions becomes ever more urgent (Kaza *et al.,* 2018). A significant portion of this waste stems from inefficient agricultural practices, poor storage, and food loss during transport and harvest. Annually, about 3 billion tonnes of food are lost, with an estimated 1.3 billion tonnes decaying in dumpsters of retailers and consumers. This scenario exacerbates environmental degradation and highlights the need for innovative waste conversion technologies.

To tackle the growing waste problem, various biomass conversion technologies have been developed, including biochemical, physicochemical, and thermochemical processes (Chew and Doshi, 2011; Menon and Rao, 2012). Among these, thermochemical processes, such as pyrolysis, gasification, and incineration, are commonly employed to convert wet feedstock into solid carbonaceous products (Sharma *et al.,* 2019). Despite the potential of these methods, biomass conversion often faces challenges due to its low energy content, high moisture content, low density, heterogeneity, and contamination.

Selecting an appropriate conversion method depends on several factors, including biomass properties, pretreatment techniques, and logistics. For instance, toxic substances in biomass can inhibit microbial activity in biochemical processes, necessitating careful selection and treatment of feedstock (Mata-Alvarez, 2015). Additionally, these methods often require long processing times, which can increase costs and waste volume (Karthikeyan and Visvanathan, 2013). In contrast, thermochemical methods do not rely on microorganisms and can process materials more quickly, making them suitable for heterogeneous and low-purity biomass like sewage sludge (Yeoh *et al.,* 2018). One thermochemical process, slow pyrolysis, has gained attention for producing biochar, bio-oil, and syngas, which have diverse applications in energy, water treatment, and soil improvement (Karakas *et al.,* 2017). However, slow pyrolysis can be economically unfeasible for biomass with high moisture content (>60%), as it requires larger storage volumes and controlled drying, limiting its applicability to certain waste types (Khiari and Jeguirim, 2018; Elkhalifa *et al.,* 2019).

Recently, hydrothermal carbonization (HTC) has emerged as a promising solution for converting wet waste. HTC is designed to process high-moisture feedstocks efficiently, making it particularly suitable for the conversion of wet biodegradable waste. This technology has gained significant attention and has been extensively studied for its ability to transform organic waste into hydrochar, a carbon-rich material (Saqib *et al.,* 2019). HTC operates under subcritical water conditions, typically at temperatures between 180°C and 260°C, and involves reactions such as hydrolysis, dehydration, decarboxylation, and polymerization. The process produces hydrochar and process wastewater, with hydrochar being the primary product of interest due to its enriched carbon content and versatile applications (Hoekman *et al.,* 2011; Libra *et al.,* 2011). Hydrochar can be used for soil amendment, energy production, and pollutant removal, offering a sustainable alternative to traditional waste disposal methods. This review explores the principles, and advancements, of HTC, emphasizing its role in sustainable waste management and resource recovery.

2. Hydrothermal carbonization (HTC) process

HTC is a novel technique that allows for the thermal conversion of wet biomasses at moderate temperatures and autogenous pressure (Rillig *et al.,* 2010). Under subcritical conditions, water exhibits notable changes in its properties. When its temperature is lowered below 374 °C, its hydrogen bonds weaken, its dielectric constant decreases, and the ionization constants increase, causing the water to dissociate into hydronium (H_3O^+) ions and hydroxide ions (OH^-) (Savage, 1999). During the HTC of biomass, dehydration and decarboxylation reactions are the main chemical processes that occur (Funke and Ziegler, 2010; Saqib *et al.,* 2019). Sealed reactors trapping moisture experience significant thermodynamic changes within the subcritical phase region, which can happen between 140 and 350 °C (Reza *et al.,* 2012). In such conditions, anoxic reactions can take place due to the added water in reaction media and original biomass moisture in the absence of atmospheric air feed. The feedstock's inherent moisture is converted into water vapour via the exothermic reaction, which speeds up the carbonization process (Libra *et al.,* 2011). The inner pressure of the reactor typically increases dramatically and ranges between 2 and 10 MPa as a result of the rapid change in the water phase (Xiao *et al.,* 2012). HTC involves transforming organic wastes that are present near water into bio-oil that has been blended with water (process water), gas that is primarily CO_2, and a product with a high carbon content called hydrochar. At relatively low temperatures (180-250 °C) and autogenous pressure that is maintained for a predetermined residence time, conditions are only somewhat controlled (Rillig *et al.,* 2010; Judy *et al.,* 2011). The primary output of HTC is hydrochar, which is easily removed from the suspension thanks to its strong hydrophobicity and homogenous characteristics (Hoekman *et al.,* 2011). According on the nature of the feedstock and the operating circumstances, HTC products' yields, physico-chemical composition, and surface properties alter (Wang *et al.,* 2018). Understanding the crucial process parameters influencing HTC and the mechanics of the hydrochar generation process is vital to properly study the exceptional features and possible applications of hydrochar. Currently, some of new approaches of HTC, like microwave HTC and Co-hydrothermal carbonization getting high attention among researchers (Figure. 1).

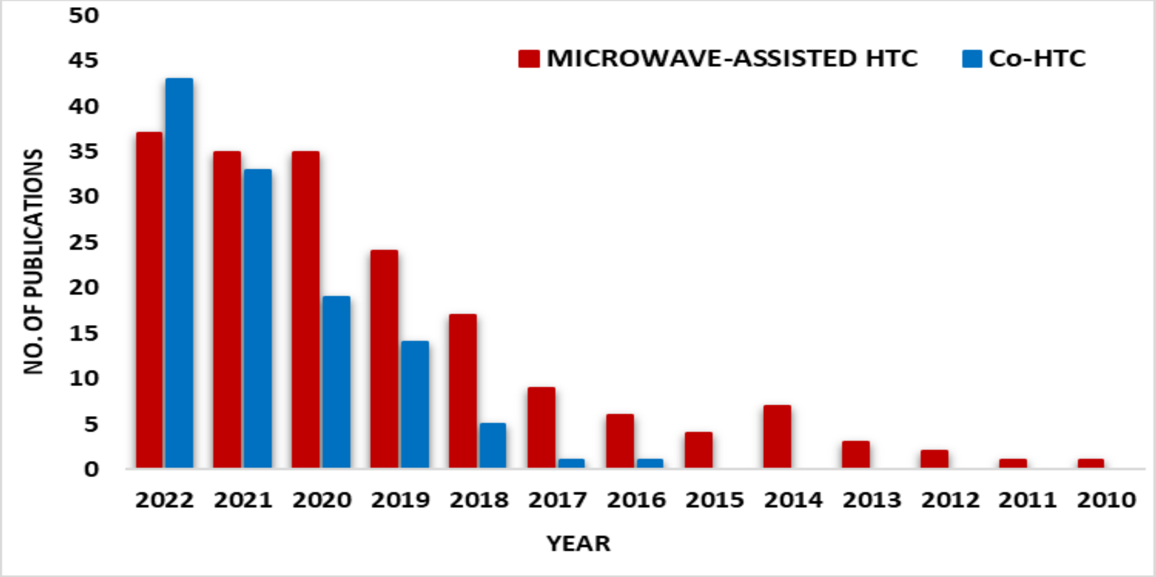

Figure 1: The increasing trend of number of publications in microwave HTC and Co-hydrothermal carbonization from 2010 to 2022 (Source: Web of Science, 2023)

2.1 Conventional and microwave hydrothermal carbonization

From the perspective of the heating way, conventional and microwave-assisted heating HTC is widely used. In the regular HTC, the heater transfers heat energy to the reactor vessel's surface, which subsequently heats the reaction vessel's contents (waste and substrate). By contrast, microwave HTC produces effective internal heating via the direct coupling of the radiation from the microwave with the reaction mixture's ions and/or dipoles. Mechanism of conventional and microwave heating systems clearly explained is Fig. 2. Recently, researchers have been working aggressively to develop a heating method for HTC that uses microwaves rather than the more traditional heater (Dai *et al.* 2017; Bundhoo, 2018). Microwave is a high-frequency electromagnetic radiation (0.3– 300 GHz) with the heating mechanisms of dipole rotation and ionic conduction, corresponding to wavelengths between 1 mm and 1 m (Wang *et al.* 2016). In contrast to the ordinary HTC, the process of converting of electromagnetic radiation into heat energy operates very efficient and produces rapid heating ramps. Another benefit of microwave HTC is that by-product production is suppressed because the target temperature is quickly reached and reaction times are drastically cut. Although the benefits, heating heterogeneous materials using a microwave source may not be uniform. "Thermal runaways" or instability and "hotspots" arise from the uneven heating of heterogeneous feedstock. The material being carbonised can be continually mixed or stirred, nevertheless, to lessen this restriction (Wu *et al.,* 2008). To provide guidance on the practical use of microwave aided HTC, more study can be done using diverse biomass sources with varying compositions.

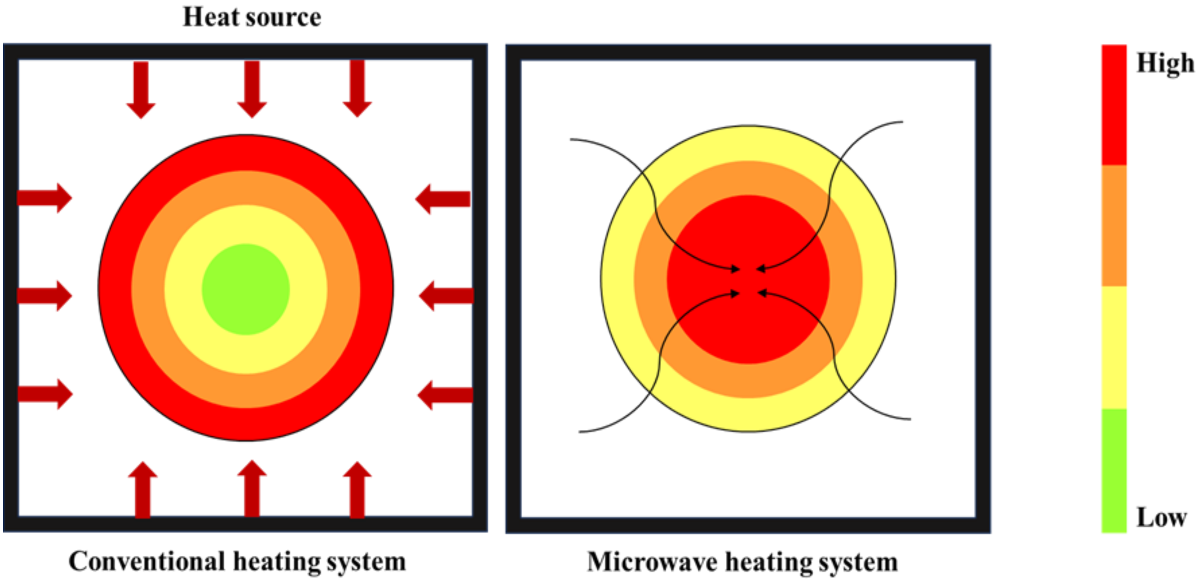

Figure 2: Mechanism of conventional and microwave heating systems

In their comparative study on bamboo sawdust pretreatment, Dai *et al.* (2017) found that microwave and conventional hydrothermal methods have distinct effects on the characteristics of hydrochar. They observed that microwave HTC generally outperformed conventional HTC in terms of higher heating value (HHV) and lower oxygen concentration, except at 150°C. They also concluded that microwave irradiation's hot spot effect led to greater removal of acetyl groups from hemicellulose compared to conventional HTC. However, they noted that hydrochars produced through conventional HTC exhibited better resistance to thermal shock than those generated using microwave heating. Another study by Zhang *et al.* (2018) focused on microwave-assisted HTC of cellulose. They discovered that the reaction time required to produce hydrochar could be significantly reduced by 5-10 times compared to conventional HTC. However, they also observed that higher temperatures and longer residence times resulted in an increase in calorific value but a decrease in hydrochar yield (Elaigwu & Greenway, 2016). Considering the inconsistent outcomes reported and the limited studies available on the efficiency of energy and utilization aspects of microwave-assisted thermochemical conversion techniques, future research should prioritize these aspects to establish the financial feasibility and scalability of this technology (Bundhoo, 2018).

2.2 Co-hydrothermal carbonization

Co-Hydrothermal Carbonization (Co-HTC) is the term for the hydrothermal decomposition of two substrate blends as rather than treating each substrate separately. In accordance with Lang *et al.* (2019), co-hydrothermal carbonization (Co-HTC) offers advantages in terms of producing hydrochar with a lower ash content and higher energy content. This method involves the simultaneous processing of protein-based waste (e.g., sewage sludge, animal manure, and food processing waste) and carbon-rich lignocellulosic waste. By combining these two types of waste materials during the Co-HTC process, the resulting hydrochar exhibits improved properties, making it a promising approach for waste management and energy production. When treated jointly, volatiles from coal and biomass are exposed to one another during the co-HTC process. According to Haykiri-Acma and Yaman (2010), these reactions boost the yield of the char and aid in the synthesis of volatiles from the mixture. According to Saqib *et al.* (2019), the composition of the raw materials used in hydrochar production plays a crucial role in determining the mechanical and fuel properties of hydrochar pellets. Different raw materials can lead to variations in these properties. In the case of co-hydrothermal carbonization (co-HTC) with lignocellulosic biomass, Zhang *et al.* (2017) observed that this process can result in enhanced characteristics of the final hydrochar. Specifically, co-HTC with lignocellulosic biomass led to improvements in carbon content and a decrease in ash content. These findings highlight the positive impact of utilizing lignocellulosic biomass in the co-HTC process for producing hydrochar with desirable features, particularly in terms of its carbon and ash content.

Animal manure and sludge generally have higher ash levels and lower carbon percentages, which can result in hydrochar pellets with poor mechanical strength due to the limited binding forces between carbon microspheres, as stated by Zhai *et al.* (2018). In contrast, fuel pellets produced from the hydrothermal carbonization (HTC) of woody biomass, which contains non-carbonized lignin, exhibit better inter-particle bonding and liquid bridging. Therefore, the co-HTC of lignocellulosic biomass and food waste is desirable for producing high-strength and durable fuel pellets, as highlighted by Saqib *et al.* (2019). Furthermore, the interaction between low-rank coal and woody biomass in co-HTC can lead to the removal of sulphur from coal by utilizing the acid generated from biomass, as reported by Saba *et al.* (2017). Co-HTC also offers the advantage of enhancing the homogeneity of the blend since biomass and coal possess different solid densities.

3. Effects of process parameters on hydrochar production

Hydrochar production is influenced by various process parameters that can impact the yield, quality, and properties of the hydrochar produced. Some key parameters include temperature, residence time, pH, pressure.

3.1 Temperature

The production of hydrochar, which is a carbon-rich material obtained through the hydrothermal carbonization process, can be influenced by temperature in several ways. Temperature plays a crucial role in the chemical reactions and physical transformations that occur during hydrochar production.

The hydrothermal carbonization (HTC) process involves subjecting biomass to high temperatures (180°- 250°C) and elevated pressure (2-10MPa) in the presence of water for several hours. In this process, the critical parameter proposed by Broch *et al.* (2013) is the temperature of the cellulose-water mixture heated in a closed vessel, typically ranging from 250 to 310°C. The primary role of temperature in HTC is to provide the necessary heat for the disintegration and fragmentation of the biomass structure, breaking down its binding components (Akhtar and Amin, 2012). The variation in process yield, which refers to the amount of desired product obtained, is an indicator of the temperature's ability to effectively break down the biomass. At process temperatures below 200°C, the hydrolysis of the feedstock occurs first, followed by the production of char. On the other hand, at temperatures exceeding 200°C, the solid-state reactions become more dominant. The reaction temperature also influences the distribution of carbon in the liquid and solid phases. Lu *et al.* (2013) suggested that as temperatures increase, gas evolution through decarboxylation and organic volatilization increases, leading to a higher retention of carbon in the liquid and solid phases at lower temperatures.

According to Saqib *et al.* (2019), the hydrothermal carbonization of food waste yielded a relatively small amount of solid char. At a temperature of 200°C, the solid char accounted for approximately 7% of the initial biomass. This yield further decreased to 5.95% at 250°C and 5.25% at 300°C. The decrease in hydrochar yield can be attributed to the primary or secondary decomposition of the biomass or the solid residue. As the temperature increases during the hydrothermal carbonization process, the biomass undergoes thermal degradation, resulting in the production of gases and the loss of solid material. This decomposition process contributes to the decrease in the hydrochar yield observed at higher temperatures. The production of hydrochar from sugarcane at two different temperatures such as 180-200°C and 250-300°C through steam activation (temperature 700-800° C). Hydrochar produced at low temperature could not withstand steam activation at 900°C because of the weaker carbon structure due to the presence of larger volatile compounds. (Congsomjit and Areeprasert, 2021). Similar research was conducted on rotten apple, apple juice pomace, grape, and apple chip by Zhang *et al.* (2018) for 15 minutes at 190°C, 225°C, and 260°C. They discovered that as the temperature rose, the bulk yields of the decaying grape and apple pomace also rose. These results appear to defy lignocellulosic biomass trends that mass yields normally decrease with increasing temperature and residence time.

In the hydrothermal carbonization (HTC) process, subcritical water plays a role in dissolving the -(1-4) glycosidic linkages present in hemicellulose, particularly at a temperature of 200°C, as stated by Zhao *et al.* (2013). This dissolution process leads to the breakdown of hemicellulose into sugar monomers, which can further undergo reactions to form furfurals and other substances. As a result of this degradation mechanism, hydrochars produced at temperatures of 240°C and 260°C exhibited very low hemicellulose concentrations, specifically at around 1.0%, as reported by Zhao *et al.* (2013). The degradation of insoluble macromolecular substances, such as hemicellulose, is enhanced with increasing reaction temperature. This enhanced degradation leads to a more efficient conversion of the biomass, resulting in the formation of aqueous and gaseous byproducts, which contribute to the overall HTC process (Cao *et al.,* 2011). However, it's worth noting that excessively high reaction temperatures can also lead to the secondary degradation of hydrochar. This secondary degradation may cause a reduction in hydrochar yield, potentially due to the excessive breakdown and loss of organic components. Therefore, finding an optimal reaction temperature is crucial in order to balance the desired conversion efficiency with the preservation of hydrochar yield.

The bulk density of hydrochar reduced as HTC temperature increased and sample colour gradually changed when HTC temperature above 240°C. It may be due to higher degree of decomposition improves the formation of the porous structure. The observed increase in the BET surface area of hydrochar from 6.28 m2/g to 11.99 m2/g within the temperature range of 220-260°C can be attributed to the higher degree of decomposition during hydrothermal carbonization (HTC). This porosity decreased the particle density which in turn decreased the hydrochar's bulk density (Li *et al.,* 2018).

3.2 Residence time

The duration for which the feedstock remains in the reaction zone, known as residence time, affects the extent of the conversion process. Residence time is another important parameter of HTC that has a comparable influence as temperature. Longer residence times typically lead to increased conversion and higher yields but may also increase energy consumption and processing time.

Increase in residence time decreases the hydrochar yield. At 180 and 220°C temperature clearly shown a reduction in the yield of hydrochar from sugarcane bagasse. The wet yield dropped from 37.0% to 30.1% and 31% at 220°C indicating the reduction of 18.7% and 16.2% respectively, when the residence time was augmented from 30 to 60 and 90 min (Congsomjit and Areeprasert, 2021). Similarly, 86.9% of hydrochar produced from oil palm residues at 30 min of reaction time, which decreased to 63.5 % at 240 min. longer reaction time are thought to generate not only excessive polymerization resulting in condensed compounds, but also decarboxylation reaction which reduces hydrochar production (Ameen *et al.,* 2022).

The hydrochar yield obtained from the hydrothermal carbonization of swine manure exhibits a significant decrease from 56.4% to 53.2% as the reaction or residence time surpasses 30 minutes, after which it remains relatively stable. Prolonged reaction time within a specific range may result in the decomposition of liquid products and the generation of gaseous products (Xiong *et al.,* 2019).

Contrary to the hydrochar yield, the energy content of hydrochar demonstrated an upward trend as the residence time increased. Through the co-hydrothermal carbonization (co-HTC) process, the energy content of the feed increased from 15.2 MJ/kg to a range of 18.1-21.5 MJ/kg, with variations depending on temperature and residence time. The highest energy content was achieved at 250°C and 120 minutes, whereas the lowest energy content was observed at 180°C and 90 minutes (Azaare *et al.,* 2021). The initial carbon content of the raw feedstock (36.49%) exhibited an increase with higher temperatures and longer residence durations. At 250°C and 120 minutes, the carbon content reached its peak (53.84%), while it reached its lowest level (46.36%) at 180°C and 90 minutes. The changes in carbon content can be attributed to the progressive loss of hydrogen and oxygen during dehydration, decarboxylation, and deoxygenation reactions that occurred during the co-

HTC process. These reactions led to a gradual decrease in oxygen and hydrogen contents and an increase in carbon content of the hydrochars as the temperatures and residence times increased (Kang *et al.,* 2012).

Different reaction times during hydrothermal carbonization (HTC) resulted in hydrochar with varying structures and chemical properties. When HTC was performed at lower severity, the hydrochar primarily consisted of cellulose and hemicellulose, which are easily degradable components. These hydrochars could be readily degraded into volatile substances even at low temperatures. Conversely, hydrochar produced through higher severity HTC contained a higher proportion of lignin, which is thermally more stable (Sharma *et al.,* 2020)

3.3 pH

The pH, or acidity/basicity, of the reaction environment can have an impact on hydrochar production, particularly in hydrothermal carbonization (HTC) processes. The pH level influences several aspects of the reaction, including reaction kinetics, hydrochar yield, and properties.

The process operates by utilizing water present in the feedstock as both a catalyst and reaction medium. As the biomass is heated, the water's dielectric properties initiate the hydrolysis of carbohydrates, converting them into organic acids. These acids, in turn, lower the pH and facilitate the hydrolysis of carbohydrate fractions, leading to the production of soluble polymers and the dissolution of carbohydrates in the aqueous phase. These dissolved carbohydrates can undergo subsequent dehydration, fragmentation, polymerization, and condensation reactions (Sevilla and Fuertes, 2009).

The hydrochar produced exhibited higher hydrophilicity, as confirmed by pH testing. The pH value of H250-5-6 in water was measured at 4.41, which is lower than the pH of walnut shell (pH 5.0). This finding suggests the presence of acidic and hydrophilic functional groups on the hydrochar's surface, as well as the formation of organic acids in the liquid phase (Naderi and Vesali-Naseh, 2021). Similar acidic behavior has been observed in various hydrochar samples reported in the literature, as demonstrated by studies conducted by Fang *et al.* (2015) and Saha *et al.* (2019).The pH solid hydrochar generated at 200°C was lower than that of solid hydrochar produced at 260°C. Simple sugars in hemicellulose often breaks into simple organic acid compounds at lower HTC temperature, but lignin begins to degrade at higher HTC temperature producing phenolic substances with just a mildly acidic pH (Reza *et al.,* 2015).

With increasing temperature, the pH of the liquid product initially decreased and then later exhibited a subsequent increase. At a temperature of 210°C, the lowest pH value recorded was 4.80. This decline in pH indicates that a greater amount of organic matter underwent dehydration and decarboxylation, leading to the production of more organic acids with increased reaction severity. Conversely, when the manure-to-water ratio was increased under constant temperature conditions, it had a contrasting impact on the pH. The decrease in pH observed can be attributed to the intensified dehydration and decarboxylation processes of dairy manure, leading to the generation of a greater quantity of organic acids (Wu *et al.,* 2018).

Conclusion:

Hydrothermal carbonization (HTC) is an innovative waste conversion technology that processes wet biomass under subcritical water conditions, typically between 180°C and 260°C. HTC efficiently converts high-moisture feedstocks into hydrochar, a carbon-rich material with versatile applications in energy production, soil amendment, and pollutant removal. Unlike conventional methods, HTC leverages autogenous pressure and water's altered properties in subcritical states to facilitate rapid dehydration and decarboxylation reactions, making it ideal for converting heterogeneous and low-purity biomass. The process is gaining attention for its potential to manage municipal solid waste and agricultural residues sustainably. Variations in temperature, residence time, and feedstock composition significantly impact hydrochar yield and properties. Microwave-assisted HTC and co-hydrothermal carbonization are emerging as advanced techniques, offering improved efficiency and enhanced hydrochar characteristics. Overall, HTC represents a promising solution for sustainable waste management and resource recovery.

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HYDROGEN PRODUCTION TECHNIQUES

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Abstract:

Resources that are not renewable, such as conventional fuels, are running out daily. Environmental issues are also brought on by the byproducts of using these fuels. The world is in danger, which is why finding alternative energy sources is necessary. The energy carrier hydrogen offers the possibility of resolving these issues. Of all the traditional fuels, hydrogen has the largest energy content per weight and is the most abundant element in the world. Hydrogen, is not readily accessible in nature like conventional fuels. The sole byproduct generated in a fuel cell is water. It has the highest energy content and is carbon-free. The main issue with using hydrogen gas as fuel is that it cannot be found in nature, demanding the use of low-cost production techniques. There are two methods for producing hydrogen namely chemical and biological. Chemical methods are of high cost. Conversely, biological methods are inexpensive, environmentally gentle, and sustainable. In this book chapter, the various methods of production of hydrogen are discussed.

1. Introduction

Many uses for hydrogen are currently found in the chemical and refinery industries [1,2]. It can be produced using a range of techniques with the help of a variety of raw materials, including chemicals, water, and fossil and renewable energy [3,4]. It is also well known that burning fossil fuels contributes to environmental issues like air pollution, greenhouse effect, and climate change. The primary cause of global warming is the excessive and irresponsible consumption of fossil fuels, which are generated underground over millions of years, such as coal, oil, and natural gas. Thus, one of the primary issues with the world's energy demand is figuring out how to replace the energy resources that are now in use with ecologically acceptable and sustainable alternatives. It is believed that hydrogen is a desirable, sustainable, and adaptable energy source [5]. It becomes a fuel that is entirely carbon-free when it is made using primary renewable energy. To make this possible, number of technological difficulties must be removed, such as boosting production effectiveness, cutting expenses, and coming up with workable solutions for transportation and storage. Nowadays, hydrogen is nearly exclusively utilized as a fundamental feedstock in the chemical and refining industries. Research is being done on its potential application as an energy storage device in conjunction with renewable energy production [6]. Electric vehicles are currently posing a challenge to the usage of hydrogen as fuel for fuel-cell automobiles. Though fuel cell automobiles are still being developed, large-size batteries for electric vehicles also have their own set of technological and financial challenges.

2. Techniques of the Production of hydrogen

Hydrogen is the most abundant element in the universe. It is the element with only one proton and one electron. In nature, hydrogen is found in mixtures with other elements such as carbon and oxygen. Since it is present with hydrocarbons or water, these materials need to be transformed in order to produce H_2. The synthesis of hydrogen can be done using a variety of energy sources [7]. Such as solar, nuclear, water power, wind, geothermal energy and fossil fuels.

Some are described below

1. Thermochemical

Among large-scale hydrogen production systems, thermochemical water-splitting using heat from nuclear, solar, and other sources is one of the most promising techniques. Research has been done on the Iodine-Sulfur (IS) [8] method for thermochemical hydrogen production processes that employ nuclear heat.

High-temperature solar heat is used by solar thermochemical water-splitting cycles to drive a series of processes that result in the production of hydrogen and oxygen as a useful byproduct. Because the chemicals are recycled, a closed-loop system using only water as input and solar heat is produced. There are two steps in the most basic thermochemical water-splitting cycles. There are two types of metal oxide redox reactions: one exothermic and one endothermic. First, the metal oxide is changed into a reduced-valence metal oxide combined with oxygen.

$$MO_{ox} \rightarrow MO_{red} + \frac{1}{2} O_2 \quad (1)$$

The reduced-valence metal oxide then reacts with H_2O producing H_2, oxygen, and the initial metal oxide.

$$MO_{red} + H_2O \rightarrow MO_{ox} + H_2 \quad (2)$$

The metal oxide is, thus, recycled. These cycles require temperatures well above 1,500°C. A thermochemical water-splitting cycles with more than two steps has been designed to deliver better performances at lower temperatures.

The iodine-sulfur cycle

This process is based on the decomposition of two acids at high temperature, sulfuric acid, which yields oxygen and SO_2, and hydrogen iodide (hydriodic acid:HI), yielding hydrogen and iodine. Iodine and SO_2 react at low temperature in the presence of water to reconstitute these two acids (Bunsen reaction):[9]

$H_2SO_4 \rightarrow H_2O + SO_3$ (400°– 600 °C)

$SO_3 \rightarrow SO_2 + \frac{1}{2} O_2$ (800 – 900 °C)

$2\ HI \rightarrow H_2 + I_2$ (200 – 400°C)

$SO_2 + 2\ H_2O + I_2 \rightarrow H_2SO_4$ (aqueous) +2 HI (aqueous) (25 – 120 °C)

2. Water Electrolysis

Electrolysis is the process of using direct current to split water into hydrogen and oxygen. The most significant technique for producing hydrogen from water is electrolysis. Through the application of an electric current between two electrodes, water is broken down into hydrogen and oxygen. After separation, pure H_2 is created in a quick and easy manner. There are no carbon, nitrogen, or sulfur byproducts produced during or after the operation. Such purity levels offer significant advantages over other methods of production of hydrogen. The usage of primary energy is the fundamental distinction between the hydrogen production technique and steam reforming.

The following reactions take place at the electrodes of an electrolysis cell filled with a suitable electrolyte (aqueous solution of KOH or NaOH or NaCl) upon the application of a potential:

Cathode reaction:

$2\ H_20\ (I) + 2e^- \rightarrow H_2\ (g) + 2\ OH^-\ (aq)$ ... (1)

Anode reaction:

$2\ OH^-\ (aq) \rightarrow \frac{1}{2} O_2\ (g) + H_2O\ (I)$ ... (2)

Overall cell reaction:

$H_20\ (I) \rightarrow H_2\ (g) + O_2\ (g)$ ... (3)

The total theoretical water decomposition potential is 1 .480 V corresponding to hydrogen's enthalpy.

3. **Biological**

   An encouraging alternative to hydrogen generation is biomass. It can be produced in a number of ways, such as by photocatalysis of waste materials and thermochemical conversion. Despite the fact that producing hydrogen from biomass releases CO_2, this is offset by the CO_2 that organisms take in throughout their lives. Furthermore, the increased hydrogen-to-carbon ratio of biomass helps stabilize the atmospheric CO_2 equilibrium through photosynthesis and lessens reliance on hydrocarbons. Biomass gasification uses fixed bed reactors that are heated to about 800 ^{0}C to convert biomass into syngas. Biomass pyrolysis uses fluidized bed reactors at a temperature of about 500 ^{0}C to turn biomass into bio-oil and syngas. In steam reformers, which are normally run around 800 ^{0}C, biomass reacts with steam to produce hydrogen through the process of biomass reforming. In their investigation into biomass-based hydrogen production, Zhang *et al.* [12] developed a novel two-step process of hydrolysis-oxidation at 160 °C and 85 °C, respectively. Methane and carbon monoxide are byproducts of this process, with hydrogen serving as the primary product. Research into appropriate catalysts for the reaction is highly important since it has been found that the conversion of hydrogen from biomass depends mostly on them. The development of hydrogen production from biomass, the affordability of hydrogen, and its use in other technologies like fuel cells are all crucial.

Conclusion:

The conventional method currently in use, regardless of its considerable environmental impact, is to extract hydrogen from coal and natural gas. When combined with new energy sources, electrolysis and thermochemical cycle techniques exhibit significant development potential from an economic and environmental standpoint.

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DEVELOPMENT OF ECO-FRIENDLY BIO-NANOCOMPOSITE FILMS AND ITS APPLICATION IN FOOD PACKAGING INDUSTRY AND WOUND HEALING PROCESS

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Abstract:

Bio-nanocomposites films are advanced materials made by integrating natural and bio-polymer matrices with nanoscale fillers or reinforcements. Preservation and protection of food is crucial due to its significance in human life. While complete prevention of food spoilage is challenging, extending shelf life can be achieved through effective packaging. Biodegradable food packaging films obtained from polymeric material is of increasing demand for the food industry due to pollution and health risk resulting from usage of conventional plastic packaging materials. The functional properties can be overcome by incorporating nano additives like Zinc oxide nanoparticles (ZnO NPs) into the films. ZnO NPs recognized as safe by the US Food and Drug Administration, are utilized for their negligible interaction with food. ZnO NPs containing bio-nanocomposites offers a cutting-edge approach for enhancing regeneration of damaged tissues and increase in collagen deposition. These bio- nanocomposite bandages can improve healing faster and modulate in inflammation of wounds.

The review involves biosynthesis of ZnO NPs using plant extracts and incorporating them into natural polymers to form bio-nanocomposite films. This eco-friendly method is compared to traditional chemical and physical methods. The resulting films exhibit high performance, cost-effective, light-weight and biodegradable characteristics. These bio-nanocomposite films demonstrate antibacterial properties against various pathogens responsible for food packaging and wound healing. The study aims to determine the optimal amount of ZnO NPs required achieving the desired antibacterial activity. Overall, these review focus on development of bio-nanocomposite films for its effective application in food packaging industry and as a wound healing bandages covering infection sensitive wounds.

Keywords: ZnO NPs, GRAS, Bio-Nanocomposite Films, Biopolymer Matrix, Food Packaging, Wound Healing.

1. Introduction:

Nanotechnology refers to technology of extremely small size that is implemented at nanoscale (1nm-100nm) and has application in real world. Unique physical and chemical properties of nanomaterials can be exploited for applications that benefits society. Nanoparticles have been integrated into health, food, space, chemical and cosmetic industry prepared via green synthesis methods. Physical method requires high energy, space and are expensive. Chemical method of synthesis produces toxic chemicals which are hazardous to environment. Synthesis of nanoparticles via green synthesis method using biological components is under exploitation. Green synthesis is a revolutionary technique for development of eco-friendly approach to synthesize nanoparticles. These biological components contain some phytochemicals that would act as reducing, capping and stabilizing agents. Plant metabolite contains hydroxyl, carbonyl and amine functional group that react with metal ion and reduce its size to nanoscale. Plant based nanoparticles are safe, cost effective, biodiversity controlled and are easy for industrial scale preparation. Hence use of plant synthesis in biological method offers stark advantages over other biomolecules. Metal and Metal oxide nanoparticles (NPs) have received substantial research attention due to their exceptional electrical, optical, magnetic and catalytic properties.

ZnO NPs have become one of the most popular metal oxide nanoparticles in biological applications due to their excellent bio-compatibility, economic and low toxicity. ZnO NPs have emerged a promising potential in biomedicines, especially in the fields of anticancer and antibacterial fields, which are involved with their potent ability to trigger excess reactive oxygen species (ROS) production, release zinc ions, and induce cell apoptosis. In addition, zinc is well known to keep structure integrity of insulin, so these nanoparticles also have been effectively developed for antidiabetic treatment [1].

Zinc oxide nanoparticles (ZnO NPs) is considered to be one of the most important metal oxide nanoparticles and are employed in various fields due to their peculiar physical and chemical properties. As the main component of various enzymes, zinc takes part in body's metabolism and play crucial roles in proteins and nucleic acid synthesis, neurogenesis etc. Nano-ZnO with small particles size, makes zinc more easily to be absorbed by the body. ZnO is graded as ''GRAS'' (Generally Recognized As Safe) substance by US food and Drug Administration (FDA), hence used in food industry [2].

As reported by WHO, over 200 diseases ranging from cancer to diarrhoea are caused by hazardous food that contain chemical substance and microorganisms, such as bacteria, viruses and parasites. Due to such food-prone pathogenic microorganism, the scientific community has focused research on materials for packaging, which are upcoming technologies specially designed to prevent the growth of microbes in foods and preserve their safety, aroma, quality and freshness, hence ZnO NPs show good application in food industry [3].

Human skin plays an important role in protecting the body from mechanical damage and microbial infection. Hence it becomes important to prepare wound dressing to promote wound healing properties faster. The ideal wound healing should follow the following characteristics; it should be non-toxic and non-irritating, biodegradable, excellent antibacterial properties, good moisture, air permeability and sufficient mechanical strength. Naturally occurring biopolymer like chitosan, cellulose and protein like gelatine, keratin shows excellent properties to wound healing due to their biological properties. Previous studies have shown that biopolymer dressing can accelerate collagen deposition and angiogenesis and also inhibit inflammatory responses. Moreover, when incorporated in hydrogels based wound dressing, the overall contact time is increased. Biopolymer is biocompatible polymeric network that can absorb significant liquids, while also ensuring moist wound environment [4].

2. **Literature review**:

(a) **Food packaging:**

The rising consumer concerns about food quality and health benefits which are impelling the researchers to find way that can enhance food quality without disturbing the nutritional value of the product. The demand of nanoparticles-based material has been increased in the food industry as many of them contain essential elements and also found to be non-toxic. They have been found to be stable at high temperature and pressure. Nanotechnology offers complete food solution from food manufacturing, processing to packaging. Nanomaterials bring about a great difference not only in the food quality and safety but also in health benefits that delivers food. Many organizations, researchers, and industries are coming up with novel techniques, methods and products that have a direct application of nanotechnology in food science. Nanotechnology combined with other areas of research such as life science, medicine, engineering, and information technology has gained significant importance in recent years. It has also proven its importance in packaging technology. This has brought large benefits to food and nutrition sector. The world's leading food industry like ''Nestle'', ''Unilever'' and ''Kraft's'' are exploring nanotechnology in food processing and packaging sector. Food is the edible substance made up of plant or animal origin, because it contains necessary nutrients like carbohydrates, proteins, vitamins, fats, and minerals to sustain life, provide energy and promote growth. Contamination of food can take place at any stage of food chain from production to consumption. The presence of infectious microbes leads to food poisoning, which can be life threatening especially for children, elderly person, pregnant women, and immunocompromised person. Hence it becomes immense important that the food should be properly protected at every stage by using good quality of protecting materials, which are non-toxic, effective, and safe. Food packaging serves as the largest category of applications of nanotechnology in food sector. Use of biosensors for detection of bacteria, smart packaging, active and intelligent packaging, and monitoring the food quality are some of the applications in food industry. Food production produces more than 20% of the plastic into the environment. But this leads to plastic pollution leading to non-sustainability and non-biodegradability. Maintaining of gases and moisture of food also serves as important properties in food packaging. Biopolymers are environmental eco- friendly and shows their properties to improve food protection while maintaining their texture, quality, freshness and safety. Addition of nanoparticles into films has made it fire resistant, light weight, stronger in thermal and mechanical properties and less permeable to moisture and gases. When these films are incorporated into plastic films, they are capable of having oxygen content inside the packaged food. They also act as a barrier to keep food fresh and increase their shelf life for an extended period of time [5]-[8].

ZnO NPs based bio-composites are of great interest in research area of food packaging material due to their improved multifunctional characteristics like mechanical, barrier and antimicrobial properties. Also, a maximum decline in oxygen, carbon dioxide, and water vapor permeability would be studied while tensile strength and young's modulus would be observed to increase for different (bio)polymer/ZnO NPs. These innovative bio-polymer nanocomposite films can be potentially applied as food packaging material with improved properties. Based on comprehensive investigation, a well-defined feature of this nanocomposite is increased in its interfacial area as compared to traditional nanocomposites. Upon surface modification of these nanoparticles, the desired properties of matrix can be improved further even at low wt % of nanoparticles [9]-[12].

(b) Wound healing:

Wound healing is a complex and dynamic process that involves the body's ability to repair and regenerate damaged tissues. This process is important to maintain the integrity of the skin and underlying tissues after an injury. Wound healing occurs in various phases: haemostasis, inflammation, proliferation and remodelling. Each phase is marked by specific cellular activities and signalling pathways that work together to restore the structure and function of the affected area. In recent years, advances in medical science have led to the development of innovative wound healing treatment including bio-engineered materials, growth factor, and nanotechnology, which aim to accelerate healing, reduce scarring, and prevent infection [13]-[15]. Effective wound management is essential to improve patient outcomes, particularly in chronic and complex wounds, where healing can be delayed or impaired. Nanotechnology has emerged as a transformative approach in the field of wound healing, offering innovative solutions to enhance the body's natural repair mechanism. By utilizing materials at the nanoscale, researchers and medical professional can design treatments that are more effective in promoting tissues regeneration, reducing inflammation, and preventing infections. Nanotechnology based wound healing therapies often involve the use of nanoparticles, nanofibers, and nanocomposites. These materials can be engineered to deliver drug, growth factors or antimicrobial agents directly into the wound site with high precision. Nanoparticles can be designed to release healing agents in response to specific conditions within the wound, such as changes in pH or temperature, ensuring that treatment in both timely and targeted.

This review will focus on using a naturally occurring biopolymer to accelerate collagen deposition. Combination of ZnO NPs with a biopolymer shows effective and long-lasting antibacterial properties. Metal nanoparticles are mostly used in wound dressing due to their unique physio-chemical and repairing properties. By incorporating a biopolymer with zinc oxide leads to ideal nanocomposites which can enhance wound healing properties. ZnO nanocomposites received considerable interest due to presence of metal oxide nanoparticles enhancing the physical and antibacterial properties of the natural biopolymer. Cytotoxicity of metal nanomaterial is reduced when wrapped in natural biopolymer. Currently, there are many metal oxides available, out of which ZnO NPs proves to be excellent for wound healing, and therefore focused on preparation of zinc oxide biopolymer-based nanocomposites which will be beneficial for infection control and healing properties [16]-[18]

3. Methodology:

- **Step No.01: Synthesis of metal nanoparticles using plant extract:**

  Plant extract is used as a reducing agent for conversion of metal to metal oxide nanoparticles.

  Characterization of the above synthesized nanoparticles will be done based on physical and chemical properties using various analytical techniques.

- **Step No.02: Application in food packaging:**

  Synthesized nanoparticles are then combined with ZnO NPs to produce a Nano composite. These Nano composites films prepared are then tested for its antimicrobial properties with different food sample or with different bacterial culture medium.

- **Step No.03: Application in wound healing:**

  ZnO NPs are combined with biopolymer to form Nano composites. Its activity can be tested on different bacterial culture medium. Also, its properties at various concentration of metal oxide beneficial for infection control and healing properties will be studied [19].

4. Results and Discussion:

1. Green nanoparticles synthesis are safer and environmentally friendly than physical and chemical methods. The green source acts as a stabilizing and reducing agent for the synthesis of nanoparticles of controlled size and shape.
2. Various versatile nanoparticles are synthesized in a range of size, shape and chemical composition, offering extensive applications in various fields.
3. Among various parameters an efficient composition are chosen and tested on different samples.
4. The structural and optical properties of nanoparticles is investigated by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), X-RAY diffraction (XRD), Dynamic light scattering (DLS), Differential scanning calorimetry (DSC), Scanning electron microscope (SEM), and Ultraviolet-visible spectroscopy (UV-Vis).
5. The uniform size and shape of nanoparticles suggest a consistent and controlled synthesis process. The positive zeta potential indicates that the nanoparticles are

likely to remain stable in colloidal solutions, which is important for their application in wound healing. The crystalline structure further confirms the successful synthesis of ZnO NPs with the desired properties.

6. Antibacterial activity confirms that ZnO NPs nanoparticles exhibited strong antibacterial activity against both gram-positive (eg. *Staphylococcus aureus*) and gram-negative (eg. *Escherichia coli*) bacteria. The minimum inhibitory concentration (MIC) was determined [20].
7. The results indicate that ZnO NPS effectively inhibit the growth of harmful bacteria, suggesting that these materials could significantly enhance food safety by reducing the risk of contaminations. The increased barrier properties provided by ZnO NPS are significant for preserving the freshness and nutritional quality of food.
8. The maintained organoleptic properties suggested that ZnO NPs do not negatively impact the sensory qualities of the food, which is essential for consumer satisfaction.
9. In the field of food packaging, nanoparticles is used to protect food from microbes, UV light and to increase its shelf life.
10. Addition of metal oxide nanoparticles into polymer are allow production of nanocomposites with increased mechanical strength, water and oxygen barrier properties and can also confer other benefits including antimicrobial activity and light blocking properties.
11. Migration studies have demonstrated that negligible number of nanoparticles migrate from packaging into food simulants or food, suggesting that consumer exposure to their nanomaterials and its associated health risk would be low.
12. Metal nanoparticles are combined with a naturally occurring bio- polymer as it would perform better than individual components in wound healing.
13. In general, the two materials work together to yield nanocomposites with biocompatibility, excellent antibacterial properties, and appropriate physical properties to accelerate wound healing [21],[22].

Challenges and limitations:

1. Toxicity of nanoparticles: The safety of nanoparticles used in food packaging is a major concern. If nanoparticles migrate from the packaging into the food, they could potentially pose health risk. The long-term effect of ingestion nanoparticles is not fully understood, and more research is needed to assess their safety.

2. There is a lack of standardized regulations and testing methods for assessing the safety of nanomaterials in food packaging. This uncertain can hinder the approval and adoption of nanotechnology-based packaging solutions.
3. The disposal and recycling of nanotechnology- based food packaging materials can be challenging. Nanoparticles may persist in the environment and potentially cause ecological harm if not properly managed.
4. The development and production of nanotechnology-based packaging materials are often expensive. This higher cost may limit their use to high- value products or niche markets, making it difficult to achieve widespread adoption in the food industry.
5. Consumer may be aware of products packaging using nanotechnology due to concern about safety and environmental impact. Gaining consumer trust and acceptance is critical for the success of these technologies [23]-[25].
6. Producing nanotechnology-based packaging materials on a large scale while maintaining quality and consistency is challenging. The manufacturing processes for nanoparticles can be complex and require significant investment.
7. Incorporating nanotechnology into existing packaging processes and supply chains may require modifications or new equipment's, which can be costly and time-consuming.
8. There is often a lack of public understanding about nanotechnology, which can lead to skepticism or fear. Consumer may be hesitant to purchase food products packed with nanotechnology due to perceived risk.
9. As nanotechnology is relatively new in food industry, regulations are continuously evolving, this can result in delays in the approval process for new materials and technologies, slowing down innovation and commercialization.
10. Nanoparticle can interact with biological tissues in ways that are not yet fully understood, potentially leading to cytotoxicity, inflammation, or other adverse effects. Ensuring that these materials are safe for use in the human body is critical.
11. These bandages are versatile and can be used for different types of wounds, including abrasions, cuts and surgical incisions.
12. Research is going on to develop ''smart'' wound dressing that incorporate ZnO NPs along with sensors that can monitor wound conditions, such as pH or infection markers. These dressings could provide real-time feedback on the wound status and release therapeutic agents as needed.

13. As the field of nanotechnology advances, there is potential for creating personalized wound care solutions. ZnO NPs bandages could be tailored to the specific needs of the individuals' patients, based on factors such as wound type, location and patient health status.
14. Bandages can be modified to various wound types, and ongoing research continues to explore their potential in smart and personalized wound care solutions. However, safety remains a priority, and further studies remain a priority, and further studies are needed to fully understand the long-term effects of ZnO NPs in wound healing.
15. For Characterization and synthesis purpose certain instruments are available in our research lab but for better facility we may prefer IIT, TIFR, ICT-Mumbai institutions.

Conclusion:

Nanoparticles produced through green technology are notably superior to those manufactured using physical and chemical methods across various metrics. The primary objective of green chemistry is to replace highly corrosive, hazardous, and polluting acid catalysts with eco-friendly and renewable alternatives.

Zinc oxide nanoparticles (ZnO NPs) are considered safe, with a low associated health risk from exposure to nanomaterials. These nanoparticles demonstrate enhanced antimicrobial properties, making them useful for extending the shelf life of food products. Studies on the antibacterial effects of ZnO NPs against *E. coli* and *S. aureus* confirm their efficacy, particularly when used in varying concentrations. Moreover, bioplastics developed with ZnO NPs are biodegradable, which significantly reduces greenhouse gas emissions, decreases reliance on fossil fuels, and offers potential for biodegradability or compostability, thereby contributing to the reduction of plastic pollution.

Zinc oxide nanoparticles hold significant promise for future applications in both food packaging and wound healing due to their unique properties. The future of ZnO NPs is vast and full of potential. As research continues to advance, we can anticipate more innovative and multifunctional packaging solutions that leverage these unique properties to improve food safety, extend shelf life, and contribute to environmental sustainability. However, ongoing attention to regulatory and safety concerns will be crucial for their successful implementation. With advancements in research and technology, the following developments and trends could shape the future use of ZnO NPs:

1. **Enhanced Antimicrobial Packaging**: ZnO NPs have shown effectiveness against a broad spectrum of microorganisms, including bacteria, fungi, and viruses. Their

integration into food packaging could create more potent antimicrobial surfaces, reducing the need for preservatives and extending shelf life. Combining ZnO NPs with other antimicrobial agents or nanoparticles (e.g., silver or titanium dioxide) could result in synergistic effects, further enhancing the antimicrobial efficacy of packaging materials.

2. **Improved Barrier Properties**: Incorporating ZnO NPs into polymers could enhance the barrier properties of food packaging materials against oxygen, moisture, and UV light, thereby better preserving the quality and freshness of perishable foods. Future developments may focus on improving the oxygen-scavenging properties of ZnO NPs, leading to more effective packaging solutions for oxygen-sensitive foods.
3. **Smart Packaging Applications**: ZnO NPs could be integrated into smart packaging to act as sensors, detecting changes such as the presence of gases released by spoiling food or variations in temperature and humidity.
4. **Sustainable Packaging Solutions**: Research could focus on developing ZnO NPs-based materials that are easier to recycle or degrade, aligning with global trends toward reducing plastic waste and promoting circular economies.
5. **Bio-Nanocomposites for Food Safety**: Bio-nanocomposites incorporating ZnO NPs help improve food safety, extend shelf life, and address regulatory and safety concerns, which are crucial for their successful implementation.
6. **Wound Healing Enhancements**: ZnO NPs possess unique properties that enhance the wound healing process, making them a promising option for treating various types of wounds. These nanoparticles exhibit strong antimicrobial properties against a wide range of bacteria, including both Gram-negative and Gram-positive bacteria, as well as fungi. This helps prevent infections, accelerates wound healing, and reduces the risk of complications, particularly in chronic wounds.
7. **Anti-Inflammatory Benefits**: ZnO NPs provide anti-inflammatory properties, reducing inflammation at the wound site. This can alleviate pain and swelling, contributing to a more comfortable healing process. Additionally, ZnO NPs stimulate the formation of new blood vessels, improving blood supply to the wound area and providing essential nutrients and oxygen needed for tissue regeneration.
8. **Hydrogel Bandages**: Hydrogels containing ZnO NPs create a moist environment conducive to wound healing. They are effective against burns, ulcers, and surgical wounds, offering a cooling effect that soothes pain and discomfort.

9. **Nanofiber Bandages**: These bandages can be designed to provide a controlled release of ZnO NPs, ensuring a sustained antimicrobial effect over time.
10. **Composite Dressings**: ZnO NPs can be combined with other materials like chitosan, alginate, or collagen to create composite dressings. These dressings offer multiple benefits, including antimicrobial action, moisture retention, and enhanced tissue regeneration.
11. **Sprayable Formulations and Coatings**: ZnO NPs can be incorporated into sprayable formulations or used as coatings on conventional bandages, allowing even distribution across the wound surface.

In conclusion, the application of ZnO NPs in food packaging and wound healing presents a promising future. Continued research and development in this field, alongside careful consideration of regulatory and safety concerns, will be essential for realizing the full potential of ZnO NPs in these critical areas.

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A REVIEW ON SELECTION OF VARIOUS FEEDSTOCKS FOR HYDROCHAR PRODUCTION THROUGH HYDROTHERMAL CARBONIZATION

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Abstract:

Hydrothermal carbonization (HTC) as an effective and sustainable approach for converting wet biomass feedstocks, such as agricultural residues, municipal solid waste, and industrial by-products like sewage sludge, into valuable hydrochar. HTC stands out among thermochemical methods due to its ability to process high-moisture materials without the need for energy-intensive drying. The review emphasizes the critical role of feedstock selection, detailing how properties such as cellulose, hemicellulose, lignin content, and moisture levels influence the yield and quality of the hydrochar produced. Additionally, the study explores the chemical reactions and mechanisms involved in HTC, highlighting how different feedstocks affect the composition and characteristics of hydrochar. By optimizing feedstock selection and process conditions, HTC can significantly enhance waste management practices and contribute to renewable energy production, making it a promising technology for sustainable development.

Keywords: Hydrothermal Carbonization, Hydrochar, Agricultural Feedstocks, Municipal Solid Feedstocks, Industrial Feedstocks.

1. Introduction

Waste generation in emerging nations is rapidly increasing due to urbanization, with wet biodegradable waste (containing 70-80% moisture) making up around half of all municipal solid waste (MSW). By 2050, global MSW production is expected to rise by 70%, reaching 3.4 billion metric tonnes (BMT). Inefficient shipping and harvesting practices lead to the loss of about 3 billion tonnes of food annually, with 1.3 BMT ending up as waste in retail and consumer settings (Kaza *et al.,* 2018). To manage this, various technologies can convert biomass sources like lignocellulose, MSW, and sewage sludge (SS) into usable forms of solid, liquid, and gas through biochemical, physicochemical, and thermochemical processes (Menon and Rao, 2012). Among these, thermochemical processes such as pyrolysis, gasification, and incineration are widely used to treat organic waste by converting wet feedstock into solid carbonaceous products (Sharma *et al.,* 2019). However, biomass has drawbacks as a sustainable resource, including low energy content, high moisture, low density, heterogeneity, and the presence of contaminants.

Selecting an appropriate conversion method depends heavily on biomass properties, pretreatment techniques, and logistics (Frombo *et al.,* 2009). For example, toxic substances in biomass can inhibit microorganisms in biotechnological processes, and long residence times in these methods can drive up manufacturing costs and volumes (Karthikeyan and Visvanathan, 2013). Conversely, thermochemical methods, which do not require microorganisms, are quicker, often completed within minutes to hours (Yeoh *et al.,* 2018), making them suitable for treating heterogeneous, low-purity materials like sewage sludge. Slow pyrolysis, a thermochemical process, yields solid biochar as well as bio-oil and syngas, which can be upgraded into biofuels. These products have diverse applications, including energy storage, water and gas treatment, and soil amendment (Karakas *et al.,* 2017). However, high moisture content (>60%) in raw biomass can make slow pyrolysis economically challenging, requiring larger storage volumes and controlled drying, which is a limitation for certain industrial organic wastes (Elkhalifa *et al.,* 2019).

Hydrothermal carbonization (HTC) is a promising wet waste conversion technology that has gained attention for its ability to utilize high-moisture feedstocks, converting them into a carbon-rich material known as hydrochar. HTC, conducted at 180-260°C in a closed vessel with excess water (>70% by weight), transforms waste into hydrochar and process wastewater (Basso *et al.,* 2016). The process is adaptable to a variety of wet waste types, including MSW and specific lignocellulosic and non-lignocellulosic materials (Zhai *et al.,* 2016; Chen *et al.,* 2017). HTC also produces hydrochar that is more grindable, energy-dense, and hydrophobic, leveraging moisture as an organic solvent and catalyst, which enhances the aromaticity of the solid products (Funke and Ziegler, 2010). This review paper aims to explore the feedstock used for hydrochar production through HTC.

2. Feedstock used for hydrochar production

Hydrothermal carbonization, also known as wet pyrolysis, is an effective method for converting biomass into a dense energy-rich product called hydrochar. Hydrothermal processes offer notable advantages among thermochemical methods, primarily because they enable the processing of wet biomass feedstock without the need for energy-intensive biomass drying (Akarsu *et al.,* 2019). The rapid urbanization and population growth inevitably lead to the generation of substantial quantities of wet biomass, comprising MSW, sewage sludge, aquaculture and algal residues, and paunch waste. A wide range of waste materials can be employed for hydrochar production, including agricultural and forestry waste, municipal waste, green waste, and food waste (Lu *et al.,* 2013). There is limited understanding regarding the specific role of feedstock properties in shaping the characteristics of carbonization products. The characteristics of the hydrochar obtained through hydrothermal carbonization are influenced by the properties of the initial feedstock. Different feedstocks lead to hydrochars with distinct chemical properties. The majority of existing studies have primarily focused on carbonizing complex feedstocks such as wood, plant material and food wastes. Cellulose and glucose are the most commonly carbonized pure compounds, often used as representative models for biomass. Feedstock properties encompass proximate analysis (fixed carbon (FC), ash, volatile matter (VM)), ultimate analysis (hydrogen, carbon, oxygen), and chemical composition (hemicellulose, cellulose, lignin content) (Nzediegwu *et al.,* 2021).

The choice of feedstock is crucial for ensuring both sustainability and profitability in energy production. It is vital to consider the availability and cost of feedstock in the local area. Using substrates that are by-products of nearby agricultural and industrial activities reduces supply and transportation costs, benefiting the economic balance of the process. This choice also improves sustainability by reducing emissions from long-distance biomass transportation. (Basso *et al.,* 2015). If the company responsible for the by-product also handles its disposal, utilizing it as a feedstock for energy production becomes an attractive and advantageous alternative.

Feedstock properties exert a greater influence on energy and carbon content of hydrochar, while process conditions have a stronger impact on hydrochar yield. The carbon densification achieved through the carbonization process is higher in pure feedstocks, except for lignin, compared to complex feedstocks like paper, wood and corn (Li *et al.,* 2015). Differences in yield resulting from the carbonization of pure compounds can be attributed to both structural properties and feedstock chemical. The carbon content of the feedstock has a direct relationship with the generation of solid products, suggesting its influence on yield. Changes in feedstock structure and properties also contribute to variations in yield. Summary of the composition of different feedstocks shown in table 1.

2.1 Agriculture Feedstock

Agricultural waste is a highly promising feedstock due to its abundant cellulose and hemicellulose content, as well as its higher fixed carbon content compared to other feedstocks. The composition of agricultural biomasses typically consists of hemicellulose (20-40% by weight), cellulose (40-60% by weight) and lignin (10-25% by weight), along with other lipid extracts. (Bardhan *et al.,* 2021). These biomass materials have heterogeneous surfaces with low surface areas and porous structures. They are distinguished by a significant presence of hydroxyl, carboxylic, and phenolic functional groups, along with a relatively lower initial carbon content (Nzediegwu *et al.,* 2021). These properties contribute to the low percentage of FC and high VM content observed in agricultural biomass-hydrochar. Both grassy biomass and agricultural residues share a common characteristic of having higher inorganic (ash) content compared to woody biomass (Reza *et al.,* 2014).

Table 1: Summary of the various kinds of feedstocks composition

Feedstocks	Cellulose (%)	Hemicellulose (%)	Lignin (%)	References
Coconut Husk	30.55	56.45	38.82	Minowa *et al.,* 1998
Wheat straw	28.8	39.4	18.6	Demirbas, 2004
Sewage sludge	2.4	3.3	22.5	Moon *et al.,* 2015
Barley straw	31-45	27-38	14-19	Saini *et al.,* 2015
Sweet sorghum bagasse	34-45	18-27	14-21	Saini *et al.,* 2015
Sugarcane bagasse	45–55	20–25%	18–24%	Du F-L *et al.,* 2018
Pine sawdust	43.8	25.2	26.4	Heidari *et al.,* 2019
Rice hulls	39.8	14.9	11.3	Heidari *et al.,* 2019
Coconut coir	44.20	22.10	32.80	Olatunji *et al.,* 2021
Rice Straw	38.14	31.12	26.35	Olatunji *et al.,* 2021

Cellulose, the predominant component of lignocellulosic material, comprises D-glucose subunits connected by β−1,4 glycosidic bonds. Lignocellulosic cellulose is composed of both crystalline fibers and regions with an amorphous arrangement. The cellulose chains predominantly form separate fibers that are weakly interconnected through hydrogen bonding. Cellulose, on the other hand, undergoes hydrolysis, dehydration, isomerization and fragmentation reactions, followed by polymerization and condensation reactions (Sharma *et al.,* 2019). Cellulose, characterized by an unbranched crystalline structure with a crystallinity degree of 67-83% and a degree of polymerization of 1000-2000, typically yields higher results. On the other hand, starch, with a lower degree of polymerization and reduced crystallinity compared to cellulose, exhibits relatively lower yields. This difference can be explained by the gelatinization process that occurs when starch is heated. The heating causes the starch granules to melt, swell, and eventually collapse, leading to the destruction of its crystalline structure. Consequently, the glucosyl units associated with starch become distorted and adopt a less stable conformation (Lu *et al.,* 2013).

Hemicellulose, which is found in lignocellulosic materials, is a complex polymer composed of pentose sugars like hexose and xylose sugars (Wang *et al.,* 2018; Zabed *et al.,* 2016). It has a lower degree of polymerization compared to cellulose. In the plant cell wall structure, hemicellulose plays a vital role by associating with cellulose through hydrogen bonds and forming covalent bonds with lignin, thereby enhancing the rigidity of cell walls. Hemicellulose can be relatively easily separated from the main components of biomass at specific temperatures, often breaking down into monomers. It consists of various sugars, primarily xylan and glucomannan, with short lateral chains, along with acetic acid, hexuronic acids (β-D-glucuronic acid, α-D-4-O-methylglucuronic acid, α-D-galacturonic acid), pentoses (β-D-glucose, β-D-mannose, α-D-galactose), and deoxyhexoses (α-L-rhamnose, α-L-fructose) (Kumar, 2013). These structural characteristics make hemicellulose less resistant to chemical degradation processes. During the hydrothermal carbonization of agricultural feedstocks, hemicellulose undergoes a series of reactions, including decarboxylation and dehydration. These reactions result in the release of water molecules and the decomposition of long-chain polymers into a wide range of organic compounds, such as alcohols (e.g., methanol, phenols), organic acids (e.g., acetic, oleic, lactic, phenolic), and saturated hydrocarbons and aromatic compounds (e.g., decane, methyl tetrahydrofuran).

Lignin is a heteropolymer comprising three methoxy substituted phenyl propane units (p-coumaryl, sinapyl alcohol and coniferyl (Cao *et al.,* 2018). It forms a robust framework within plant cell walls due to extensive cross-linking. Lignin is primarily bonded to hemicelluloses through covalent bonds, resulting in a strong association that hinders mechanical degradation and microbial degradation. Lignin degradation can be simplified as a rapid degradation into soluble fragments, followed by slow repolymerization. Lignin's presence and its covalent bonds with hemicelluloses contribute to the stability and resistance of plant cell walls.

Lignocellulosic biomass, derived from plants on land, is an abundant and renewable resource that consists mainly of cellulose, hemicellulose, and lignin polymers. It also contains smaller molecules such as inorganics and extractives. This non-food resource holds great potential for sustainable applications (Wang *et al.,* 2018). Lignocellulosic biomass, such as agro-waste (straws, husks, stalks) and woody residues (roots, wood chips leftover residue,), is particularly suitable for hydrothermal carbonization. These biomass sources offer a continuous supply, low cost, and renewability. Research studies have shown that the composition of the feedstock, particularly the lignin content, plays a crucial role in determining the composition of carbonization products. In order to examine the influence of lignin on carbonization, scientists conducted experiments using mixed feedstocks, such as straw, cauliflower, grass, and beechwood. The results indicate that lignin can impact the release of carbonization intermediates and potentially impede the carbonization process by creating a protective barrier around the feedstock (Dinjus *et al.,* 2011).

2.2 Municipal feedstock

Municipal solid waste (MSW) refers to the waste collected from suburban and urban areas, including households, localities and commercial establishments. MSW is a complex mixture comprising various materials such as recyclables (paper, clothes, glass, metals), biodegradable waste (food and plant leftovers), chemical hazardous waste (paints, solvents), petrochemical materials (plastic, rubber), electronic waste, biomedical waste, toxic waste (pesticides, herbicides), and inert compounds like rocks and soil (Marzbali *et al.,* 2021). The presence of mineral and organic elements at different concentrations complicates the degradation of organic compounds. MSW has a wide range of particle sizes, requiring additional processing steps such as sorting, shredding, and sieving to obtain uniform carbonaceous materials. The composition of MSW varies depending on collection sources, consumption habits, and socio-economic factors. It typically contains medium to low fixed carbon content and high percentage of volatile matter. The presence of a significant amount of volatile matter in the feedstock initially can have a negative effect on the development of micro and meso-porosity due to potential recombination with the aromatic structure (Azzaz *et al.,* 2020). The ash content in the feedstock can vary significantly depending on the mineral composition of the waste. MSW management involves various methods including physical, chemical, biological, and thermal conversion techniques such as pyrolysis and HTC. HTC, in particular, enables low-temperature carbonization of MSW, affecting the gaseous composition, carbonization yield, and physico-chemical properties of the resulting by-product with reduced CO2 emissions.

Food waste is generated in households through the process of combining various ingredients, including grain products, fresh or processed food, fats and oils, sweeteners, nuts, poultry, and meat (Pecchi *et al.,* 2022). Fruit waste, known for its higher moisture and glucose content, shows promise as a feedstock for hydrothermal carbonization. The elevated sugar content in fruit waste biomass can contribute to energy savings during the process (Sevilla and Fuertes, 2009).

2.3 Industrial feedstock

The accumulation of organic waste from industrial activities is a growing global concern, particularly in developed regions. Nevertheless, this organic waste holds potential for energy reuse through the process of hydrothermal carbonization (Dos Santosh *et al.,* 2022). The feedstock from industrial waste such as sugarcane bagasse, sewage sludge etc are used as feedstock for hydrochar production.

Sewage sludge (SS) encompasses various types of sludge, including primary sludge, digested sludge and secondary sludge depending on the source of wastewater and treatment processes. The production of sewage sludge continues to increase, raising concerns about its management. One of the main challenges is its unfavourable dewatering properties due to biological activity and high organic content. Even after mechanical dewatering, the moisture content of the sludge remains above 65%, limiting effective disposal options (Paiboonudomkarn *et al.,* 2023). Thus, moisture removal poses a significant obstacle to the treatment and disposal of SS.

Sewage sludge as a feedstock is complicated due to its challenging characteristics, such as high moisture content, the presence of pathogens, heavy metals, and a high ash content. However, sewage sludge contains substantial amounts of organic matter, primarily proteins, lipid, polysaccharides, nucleic acids and humic substances (Xu *et al.,* 2022). The relative proportions of these organic components vary depending on the source of sewage and the treatment processes employed. During hydrothermal carbonization, the organic ingredients, including extracellular polymeric substances and microorganisms, undergo depolymerization into their constituent monomers. These monomers then undergo decomposition through hydrolysis, decarboxylation, dehydration, and deamination. The resulting reactive fragments can recombine through condensation polymerization.

In the context of hydrothermal carbonization of sewage sludge, proteins, the primary components linked by peptide bonds, contribute the largest proportion of organic materials. The breakdown of proteins during this process is closely associated with the reduction of volatile solids, indicating devolatilization. Protein hydrolysis under hydrothermal conditions initiates with proton attachment to the peptide bond, leading to its splitting and the formation of carbocation and amino groups. Subsequently, hydroxide ions attach to the carbocation, forming carboxy groups. During the conversion of proteins, they are broken down into smaller peptides with decreasing dominant size fractions as temperatures increase (Wang *et al.,* 2019). The decomposition of amino acids derived from proteins mainly involves deamination and decarboxylation reactions, resulting in the formation of volatile fatty acids, aldehydes, hydrocarbons, amines, and ammonia. The hydrolysis rate of proteins is relatively lower compared to that of polysaccharides due to the higher stability of peptide bonds.

Polysaccharides, including cellulose, hemicellulose, and starch, undergo solubilization and hydrolysis during hydrothermal carbonization (Xu *et al.,* 2022). Cellulose can be rapidly hydrolyzed, yielding oligomers and glucose monomers. Glucose is the main hydrolysis product of cellulose and further decomposes into fructose, furan derivatives, and aldehydes. Hemicellulose, with its random and amorphous structure, hydrolyzes more quickly than cellulose, resulting in the production of xylose, furfural, and other intermediates. The hydrolysis of starch is comparatively easier and faster than that of cellulose, resulting in the production of glucose (Villamil *et al.,* 2020). In hydrothermal carbonization, the reaction pathways for polysaccharides involve the conversion of polysaccharides into pentose and hexose species. Subsequently, dehydration reactions occur, leading to the formation of furfural intermediates. Intermolecular dehydration then produces hydrochar from furans (Tesca *et al.,* 2019). The resulting hydrochar exhibits polyaromatic networks and a polyfuranic structure, primarily formed through the cyclization and condensation of intermediates from polysaccharide degradation.

Conclusion:

Hydrothermal carbonization (HTC) offers a promising method for converting various wet biomass feedstocks, including agricultural residues, municipal solid waste, and industrial by-products like sewage sludge, into hydrochar. The choice of feedstock significantly influences the yield and characteristics of the resulting hydrochar, with factors such as carbon content, moisture, and structural composition playing crucial roles. HTC's ability to process high-moisture materials without extensive drying requirements makes it an attractive option for waste management and sustainable energy production. Continued research into feedstock properties and optimization of HTC conditions will further enhance its potential for environmental and industrial applications.

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DEEP LEARNING FOR TEXT AND SEQUENCES

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1. Introduction:

The characteristics of learning as a machine learning task are similar whether we are dealing with an image or a long-form text document. Unless you believe that computers reason and form representations of the world in a fundamentally different way from humans, a reasonable deep learning architecture should be able to learn any knowledge representation from data, from music and speech to novel writing and video. However, heuristic strong AI could accelerate the power of practical AI.

1.1. Definition of Deep Learning

Deep learning is a set of algorithms that in many cases falls under the umbrella of what people refer to as machine learning, which itself sits within artificial intelligence. As a set of algorithms, deep learning can be well defined and readily implemented, but in practice deep learning is about the feature weighting and architecture of those algorithms.

1.2. Importance of Deep Learning in Text and Sequences

The significance of deep learning in handling text and sequences is steadily growing. Recent progress has led to major advancements in areas such as automatic language translation, improved speech recognition, automated document classification, and recommendation systems. Now, the math aspect of this progress is important, but its true importance lies in the vast amount of information that is involved and the depth with which it can be analyzed. In today's world, big data in the form of customer emails, support tickets, product reviews, social media feeds, and meeting transcripts is being generated at an unprecedented rate. However, enterprises are struggling to fully utilize the potential of this data. Fortunately, deep learning methods serve as a powerful tool to unlock the value hidden within this data.

1.3. Overview of the Work

This monograph is a broad investigation into deep learning for text and sequences. Each chapter is accessible to a general computer science or engineering audience, while the material is deep enough to be of use to graduate students, academia researchers and industry professionals.

2. Deep Learning Models for Text

Deep learning models for text have become increasingly important since the rise of online social networks and media, as well as the increasing ability of consumers to produce digital content. The chapter begins with the natural language basics and the bag-of-words model, along with theories about semantic representations and distributional semantics that it draws from. It then moves on to neural architecture and different models that have been used in the literature, such as feedforward neural nets, recurrent neural networks, convolutional neural networks and recursive neural networks. The chapter finally discusses the key concepts that authors need to know while building supervised and unsupervised models for text analytics and the various feature learning methodologies that exist in the literature.

2.1. Recurrent Neural Networks (RNN)

An important distinction between MLPs and RNNs is the presence of connections between nodes on the same layer. While MLPs consist of single feedforward layers with no connections between nodes of the same layer, in RNNs, the connections between nodes can form directed cycles. This means that the network is not just a directed graph, but also a graph with a topology that changes with time. RNNs can be seen as a network that applies the same set of weights recursively over a sequence of inputs, of which one input (at a time) is given to the network at each point in time. It is this differentiation that defines RNNs and makes them particularly apt for sequential data, in which the relationships between inputs are just as important as the content of the individual inputs themselves. However, as mentioned earlier, the gradients of the loss function with respect to the weights in a network can become either very large or very small, which results in the proliferation or decimation of gradients, respectively.

2.2. Long Short-Term Memory (LSTM)

LSTMs are explicitly designed to carry information across long stretches of time. They have a chain-like structure and the repeating module in a standard RNN is replaced by a special structure. The key to this strategy is the cell state, the horizontal line running through the top of the diagram. It runs straight down the entire chain, with only some minor linear interactions. It is very easy for information to just flow along it unchanged. Information in the cell state can be added or removed carefully by gates.

2.3. Gated Recurrent Units (GRU)

One type of RNN that we mentioned in Section 2.1 is called a gated recurrent unit (GRU). This is an LSTM variant that was proposed around 2014 and in my experience, it's been effective for many sequence tasks. It's also a small and simple model that can still capture long-range dependencies. The following is a simplified version of the computations for the GRU given an input sequence x = (x1, x2, ... , xT). Set ht = 0. Two gates update and reset are introduced to help manage how information is passed around the network in between time steps. The update gate decides how much of the current state is kept and how much of it is passed forward to the next time step.

2.4. Attention Mechanisms

Attention mechanisms are a part of most of the models that incorporate deep learning with the natural processing of languages. The attention mechanism, through focusing on the words, creates weighting of those words, so that at different steps of the model the network receives only specific elements. This decreases the workload of the model as the workers and gets rid of noise in the process. Even though in most applications, the attention mechanism is used as one between two elements of the network that involves the natural processing of languages, it is an exceptional option to most all of the deep learning trainings.

3. Deep Learning Models for Sequences

Sequence models based on deep neural networks are commonly used for processing time-series data and text. An example of such a model is the feedforward neural network that takes fixed length vectors and processes them. In the context of this chapter, the most relevant class of sequence models is the set of architectures that accept variable length inputs, generate a single, fixed length output and are trained to do so. Such models are very important for multiple applications, e.g., sentiment classification, named entity recognition, question answering, and natural language inference. This chapter introduces three types of models that can be used for learning from sequences: Convolutional Neural Networks (CNNs), Transformer models, and recurrent architectures.

3.1. Convolutional Neural Networks (CNN) for Analyzing Sequential Data

There are a number of key reasons we might want to use CNNs for sequential data. One reason is efficiency. A classic problem with RNNs is that they can be slow to train and are limited in their ability to take advantage of parallel computation because of their sequential nature. CNNs can effectively perform many of the same sequence processing functions as RNNs but at a fraction of the computational cost. CNNs can find all instances of a feature within range of its receptive field at once. This is different to an RNN which needs to step through each element in the sequence, updating its hidden state at each step.

3.2. Transformer Models for Processing Sequences

First, we formally introduce the transformers and then discuss in detail how they function. Finally, we will present and compare the higher-level applications that transformers can be used for such as machine translations which could not have been possible using RNNs in the conventional way.

3.3. Sequence-to-Sequence Models for Sequential Data Processing

The sequence-to-sequence (seq2seq) model is probably one of the most well-known sequence-based models. It has been popularized by its ability to translate sequences from one domain to another. The model utilizes two recurrent neural networks, an encoder and a decoder. The encoder reads the input sequence and processes the information. Then, the final hidden state of the last time step is transformed to the initial hidden state of the decoder. Finally, the decoder uses this state to decode the output sequence. One of the disadvantages of the original seq2seq model is that the quality of the translated sequences starts to decrease as the length of the sequences increases. To solve this problem, the attention mechanism was introduced which enabled the model to focus on the most critical parts of the input text when predicting the subsequent output.

3.4. Bidirectional Encoder Representations from Transformers (BERT) for Understanding Sequences

Bidirectional Encoder Representations from Transformers (BERT) for Understanding Sequences Recently, Google revealed the Bidirectional Encoder Representations from Transformers (BERT), which is designed to understand the purpose of the words in their surrounding context. The name with the transformer design demonstrates that the model thinks about the complete sentence, rather than simply processing single words training. The bidirectional components of the product are composed of a left-to-right lesson and a right-to-left model. A list of transformer attention heads works to concentrate on closely related words in the process, supplying BERT with context for those words. The training data is created by leaving 15 percent of the words in each sentence removed with the relevant context otherwise left intact, enabling BERT to predict the missing words, so as to effect improve learning on how to understand the context of words.

4. Applications of Deep Learning in Text and Sequences

Sentiments can be analyzed in a piece of text such as a tweet or product review using a variety of techniques, from simple probabilistic models to advanced deep learning architectures. These deep learning models belong to a category of algorithms called sequence models or sequence-to-sequence models. We will describe sequence-to-sequence models and how they can be applied to text and other sorts of sequences.

4.1. Analyzing Sentiments in Text

This info helps to understand analyzing sentiments in a text. Sentiment analysis is a popular application to which deep learning techniques have been applied, as it is particularly amenable to modeling using neural nets. Automatic sentiment analysis requires human supervision at the early phases of systems development when models are being trained. At this stage, humans need to annotate a large dataset of text with some measure of sentiment, for example, whether the author is expressing a negative opinion, a positive one, or is reporting facts only and therefore opinion neutral. Annotations are typically acquired via crowdsourcing platforms where people log in to deliver their judgements, usually for small monetary rewards.

4.2. Identifying Named Entities in Text

Named entities are sequences of words that are used to refer to specific types of individuals. These words have special meaning and the proper identification of named entities is essential in several natural language processing tasks such as information retrieval, question-answering, and text summarization. The sequences of words in the examples highlighted in Table 4.1) are named entities, but not all named entities fit this template. It is interesting to observe that sometimes information about named entities spans more than two tokens. In the first example, the term iPhone is a named entity, but its information is given more than once.

4.3. Enhancing Machine Translation with Deep Learning

One of the main drawbacks of traditional machine translation techniques is that they are designed specifically for a certain pair of source-target languages. It is not straightforward to extend these techniques to support translation in multiple languages. On the other hand, the neural network-based approaches to machine translation can support translation in multiple languages provided the language-specific data is available for model training.

4.4. Generating Text Summaries using Deep Learning

By leveraging the Recurrent Neural Networks (RNN), we can generate individual words in a sentence by predicting the next word from a context window. After many words are generated, the sentences and paragraphs can then be generated, effectively creating a summary of the original text. A more advanced approach is to use attention mechanisms, which tend to work significantly better than standard RNNs in grammatically correct sequencing. The use of attention mechanisms means that the order of the sentences is nonlinear and must return to previously generated words frequently, making it an ideal use case for generating summaries.

5. Training and Evaluating Deep Learning Models

Start Training on a Single Layer Start by training a single layer network to get a sense of how horse racing beer can be across the big food and Phenred. This will give you an easy to debug baseline. More documentation on checking progress can be found at How to debug.

5.1. Preparing Text and Sequences for Training and Evaluation

The training data and validation will be on the format of Python generator object via tf.data. Data set. from_generator_words. This again allows the avoidable memory error. For the tokenize dataset, the output will be padded up to the length of list of token sequences within the dataset. The validation and training split ratio will be 0.1, which is 10% of the training set. There will be a vocabulary of 14,000 words. Tokenizer, texts_to_matrix and pad_sequence Keras modules are used extensively throughout the book for text manipulation. These topics are introduced wherever needed.

5.2. Optimal Architecture Selection for Deep Learning Models

This section is about how to choose the best architecture for your deep learning model. The architecture actually comprises two decisions: the number of layers and the number of memory cells in each layer. As will be shown, there are some general rules about how to choose the number of cells in each layer; on the other hand, however, the number of layers is something you must decide by trial and error. This section focuses on taking the best decision for both of these issues.

5.3. Hyperparameter Optimization for Deep Learning Models

A key factor in achieving the optimal performance of deep learning models lies in the careful choice of hyperparameters, for instance the initial learning rate or the dropout rate. Hyperparameter optimization is computationally expensive due to the sheer number of models that at the very least must be trained and evaluated. A common technique employed to tackle this issue is Bayesian optimization. This technique builds a probabilistic model to capture the behavior and response of the system for different hyperparameters.

5.4. Performance Assessment of Deep Learning Models

When exploring accuracy, we can introduce metrics like the confusion matrix or F1 score to understand how effectively our model performs. Recall and precision are also used to calculate these metrics and are summarized by equations. These metrics must be analyzed when changing hyperparameters, as increasing accuracy without reason demonstrates overfitting. This information, combined with the trained data set, is what persuades us to increase datasets sizes, in particular when using a neural network model. It is easy to fall into trap of overfitted data and people look for ways to combat this problem. Regularization can be used to achieve a manageable complexity and provide more improved testing results. Using accuracy and our confusion metrics together, we can help explain how their balance is needed to mitigate the possibility of overfitting.

6. Future Directions and Challenges

Developments in attention mechanisms and vision-enhanced sequence models have paved the way for more sophisticated techniques in the deep learning community. Recently, a transformer-based text-to-text neural network called T5 (Text-to-Text Transfer Transformer) trained on a multitude of NLP tasks has shown great potential in understanding and generating long text sequences. It also offers a unified architecture for different NLP tasks. Researchers are exploring the possibilities of employing these models for long-sequence tasks, and then learning to improve computational efficiency in these models through architecture optimization methods. Also, there have been a few attempts at using knowledge distillation to make these models computationally light. In addition, untapped potential in multi-modal representation learning and generation presents itself as an exciting avenue of research.

6.1. Innovations in Deep Learning for Text and Sequences

In the realm of deep learning, conventional architectures rely on convolutions and recurrent connections to process sizable text data. Nonetheless, as novel challenges arise, such as quoting, open-ended complex document answering, and conversational agents, it becomes necessary to explore new approaches to enhance performance. This chapter delves into the latest innovations employed to tackle the difficulties encountered when working with text, not just on a single sentence basis, but at the page or document level.

6.2. Addressing Ethical Concerns and Bias in Deep Learning

One crucial aim in improving the ethical discernment concerning text and sequence models is set a curriculum for the progress of intuition in deep learning models. The drive to go about and get close to this stands on the rationale that deep learning models are not infallible and there's still the necessity to test, verify, and audit them. Ethical risks instilled in the use of incoherent language can get in the way of relationships between systems and humans, sometimes leading to unintended negative results. It is paramount to commence this ethical curiosity with certain phrases used to reveal bias in the system.

6.3. Surmounting Data Limitations in Deep Learning

One potential solution to the scarcity of data is utilizing techniques like domain adaptation, which aims to make deep learning systems applicable for new subsets of a data source. This involves transforming models trained on a source domain, where data is abundant, to work with a target domain which is scarce. This is achieved by aligning data distributions between the source and target domains. Another method to supplement data shortfalls is to use techniques for synthetic data generation. This enables the automatic augmentation of training data to simulate instances for which limited data is available. The third advancement that we foresee in the area of surmounting data limitations using deep learning is learning with less data. In this fast-evolving universe of deep learning, we anticipate models which would require less quantity of examples to learn accurately. This includes reinforced learning models, transfer learning, self-taught learning models, etc.

6.4. Deciphering the Interpretability of Deep Learning Models

Firstly, despite the numerous methods that seek to interpret the models, there is still not a universally agreed upon way for interpreting deep learning models. The most straightforward way to interpret an ML model is to distinguish how the model makes its predictions. This often involves establishing which features of the input data the model has deemed important, and understanding how these features were processed to arrive at those decisions. Nevertheless, a direct interpretation of deep learning models like this is not entirely possible, mainly because the features of the input data are not readily interpretable to humans.

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MAGNETIC PROPERTIES OF MATERIALS

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Abstract:

Magnetic properties of materials describe their response to external magnetic fields, driven by the alignment of magnetic moments within the material. These properties include diamagnetism, where materials create an opposing magnetic field, resulting in a weak repulsion; paramagnetism, where unpaired electrons align with an external field, causing weak attraction; and ferromagnetism, characterized by spontaneous alignment of magnetic domains leading to strong, persistent magnetization. Antiferromagnetism and ferrimagnetism involve opposing magnetic moments within the material, with antiferromagnetism showing no net macroscopic magnetization and ferrimagnetism exhibiting partial net magnetization. Superparamagnetism occurs in nanoscale materials, where magnetization is induced in the presence of a field but disappears once it is removed. These diverse magnetic behaviors are crucial in applications ranging from data storage and medical imaging to advanced electronic devices and magnetic levitation technologies.

Keywords: Magnetic Properties, Paramagnetism, Diamagnetism, Ferromagnetism, Antiferromagnetism

1. Introduction:

Magnetic properties of materials are fundamental characteristics that describe how substances interact with magnetic fields. These properties arise from the movement and alignment of electrons within atoms and the resulting magnetic moments. Understanding these properties is crucial for various technological applications and scientific investigations.

Magnetism is the ability of a material to attract or repel other materials. Magnetic force is mostly derived from the movement of charged particles. The magnetic behavior of a substance can be attributed to its atomic structure. Electrons in atoms move in a planetary motion around the nucleus. Materials' magnetic behavior is influenced by their orbital motion and spin, which produce distinct magnetic moments. Any material can respond to a magnetic field. A material's atomic structure influences its response and determines whether it is strongly or weakly magnetic.

2. Magnetic Materials – Terms:

- **Magnetic Moment:** The magnetic moment of an atom or particle is a measure of its magnetic strength and direction, stemming from the spin and orbital motion of electrons.
- **Magnetic Field:** An external influence that affects magnetic materials, causing them to align their magnetic moments in certain ways.
- **Magnetic Susceptibility:** Ratio of the intensity of magnetization produced in the sample to the magnetic field intensity which produces magnetization. It has no units.

$$\chi = \frac{M}{H}$$

- **Magnetization:** Converting a nonmagnetic material to a magnetic material.
- **Intensity of magnetization:** It is magnetic moment per unit volume.
- **Relative permeability:** The ratio of flux density produced in a material to the flux density produced in a vacuum by the same magnetizing force.
- **Magnetic flux (Φ):** The total no: of magnetic lines of force in a magnetic field (unit-Weber)
- **Magnetic flux density (B):** Magnetic flux per unit area at right angles to the flux direction. (Wb/m^2)
- **Magnetic field intensity (H):** Magneto motive force per unit length of the magnetic circuit. It is also called magnetic field strength or magnetizing force. (A-turns/m)
- **Permeability (μ):** The ability of a material to conduct magnetic flux through it. (H/m)
- **Magnetic dipoles:** Magnetic dipoles exist in magnetic materials, similar to electric dipoles. Magnetic dipoles are tiny magnets with north and south poles instead of positive and negative charges. The force of a magnetic field causes dipoles to align with it. Electrically charged particles move and generate magnetic forces. These forces supplement any existing electrostatic forces. Magnetic forces can be understood as distributed fields represented by imaginary lines. These lines also represent the force's direction.

3. Origin of Permanent Magnetic Dipoles:

Permanent magnetic dipoles are formed by the intrinsic magnetic moments of elementary particles, usually electrons, due to their spin and orbital angular momentum. Here's a brief overview:

  - **Electron Spin:**
    - **Definition:** Spin is a fundamental property of electrons that generates a magnetic moment. Each electron acts like a tiny bar magnet with its magnetic field.
    - **Contribution:** In materials where electron spins align in a uniform direction, they create a net magnetic field, leading to permanent magnetism.
  - **Orbital Angular Momentum**
    - **Definition:** As electrons orbit the nucleus, their movement generates a magnetic moment.
    - **Contribution:** In atoms with unpaired electrons, the combined effect of orbital motion and spin creates a magnetic dipole moment.
- **Magnetic Domains**
  - **Definition**: In ferromagnetic materials, atoms group into regions called magnetic domains, where the magnetic moments are aligned.
  - **Contribution**: When most domains align in the same direction, the material exhibits strong permanent magnetism.
- **Exchange Interaction**
  - **Definition**: A quantum mechanical effect that causes the alignment of neighboring electron spins to minimize the system's energy.
  - **Contribution**: This interaction reinforces the alignment of magnetic moments in certain materials, making their magnetization stable and permanent.
- **Material Structure**
  - **Definition**: The crystalline structure and atomic arrangement in a material affect the alignment of magnetic dipoles.
  - **Contribution**: Materials like iron, cobalt, and nickel have favorable structures that support long-range magnetic ordering and permanent magnetism.

4. Classification of Magnetic Materials:

Magnetic materials are classified based on their response to external magnetic fields. The classification is primarily based on how these materials interact with magnetic fields and their intrinsic magnetic properties. Here's a comprehensive overview of the different types of magnetic materials (1-3).

Diamagnetic Materials

- **Definition**: Materials that create an induced magnetic field in the opposite direction of an applied magnetic field, leading to a weak repulsive force.

- **Magnetic Behavior**: Exhibits a negative magnetic susceptibility, meaning the induced magnetization is very weak and only occurs in the presence of an external magnetic field.
- **Examples**: Bismuth, copper, graphite

Paramagnetic Materials

- **Definition**: Materials that have unpaired electrons, which align with an external magnetic field, resulting in a weak attraction.
- **Magnetic Behavior**: Exhibits a positive but weak magnetic susceptibility, meaning the material becomes magnetized in the direction of the external magnetic field but does not retain magnetization once the field is removed.
- **Examples**: Aluminum, platinum, and certain metal ions.

Ferromagnetic Materials

- **Definition**: Materials with strong and permanent magnetization due to the alignment of magnetic domains in the same direction.
- **Magnetic Behavior**: Exhibits a high positive magnetic susceptibility and retains magnetization even after the external magnetic field is removed. These materials have a well-defined hysteresis loop.
- **Examples**: Iron, cobalt, nickel.

Antiferromagnetic Materials

- **Definition**: Materials in which adjacent magnetic moments align in opposite directions, effectively canceling out the overall magnetization.
- **Magnetic Behavior**: Exhibits zero net magnetization in the absence of an external field due to the opposite alignment of magnetic moments, but exhibits a strong response when exposed to a magnetic field.
- **Examples**: Manganese oxide (MnO), iron oxide (FeO).

Ferrimagnetic Materials

- **Definition**: Similar to antiferromagnetic materials, but with unequal opposing magnetic moments, resulting in a net magnetization.
- **Magnetic Behavior**: Exhibits a net magnetic moment due to the unequal opposing alignment of magnetic moments in different sublattices or ionic sites.
- **Examples**: Magnetite (Fe_3O_4), certain types of mixed metal oxides.

Superparamagnetic Materials

- **Definition**: Nanoscale magnetic particles that exhibit magnetization in the presence of an external magnetic field but lose it once the field is removed.

- **Magnetic Behavior**: Exhibits strong magnetization when exposed to a magnetic field, but the magnetization fluctuates rapidly due to thermal energy when the field is absent.
- **Examples**: Iron oxide nanoparticles.

Ferrites

- **Definition**: A type of ceramic compound consisting of iron oxides mixed with other metals, often exhibiting ferrimagnetic behavior.
- **Magnetic Behavior**: These materials are typically magnetic at room temperature and are used in various applications due to their high magnetic permeability and low electrical conductivity.
- **Examples**: Nickel-zinc ferrite, manganese-zinc ferrite.

Soft Magnetic Materials

- **Definition**: Materials that can be magnetized and demagnetized easily.
- **Magnetic Behavior**: Exhibits low coercivity, meaning they require only a small magnetic field to become magnetized and can be demagnetized easily. They are useful in applications requiring frequent magnetization changes.
- **Examples**: Soft iron, silicon steel.

Hard Magnetic Materials

- **Definition**: Materials that retain their magnetization after the external magnetic field is removed.
- **Magnetic Behavior**: Exhibits high coercivity, meaning they require a strong magnetic field to demagnetize. They are used in permanent magnets.
- **Examples**: Neodymium magnets, samarium-cobalt magnets.

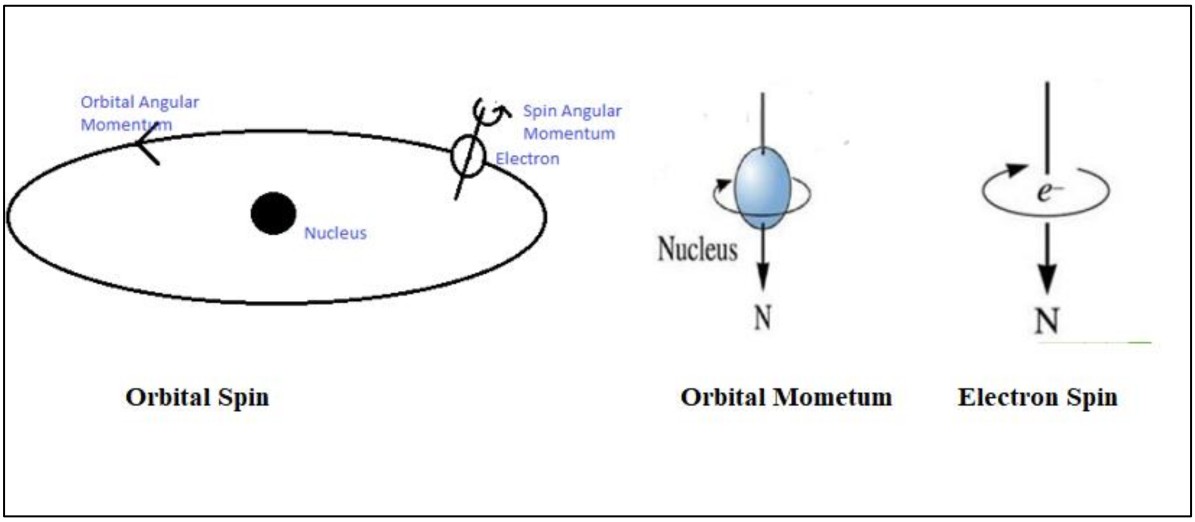


Fig. 1: Origin of Magnetic Dipoles

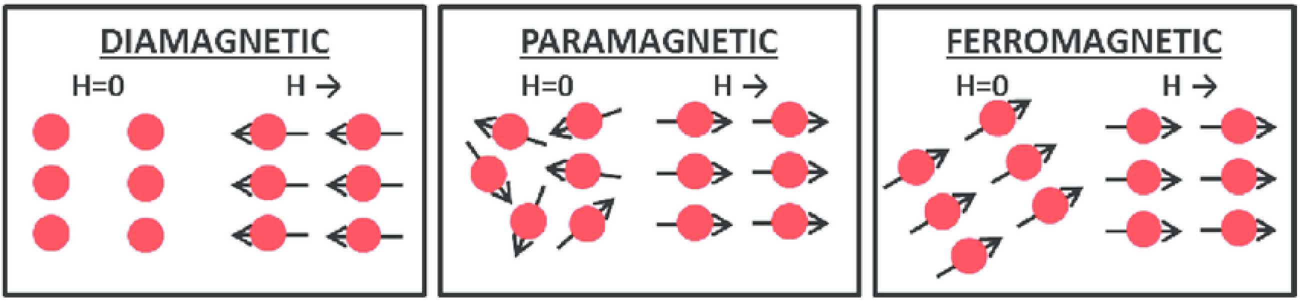
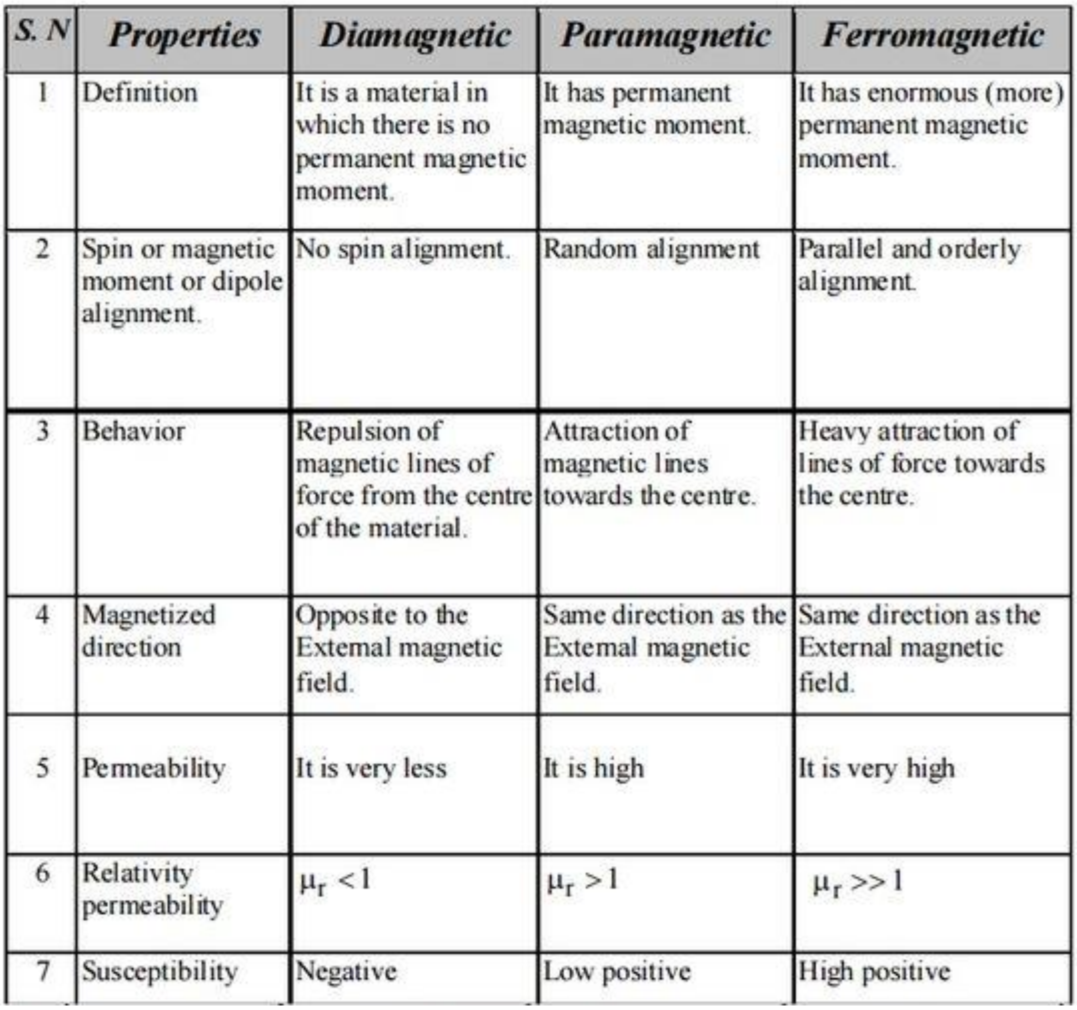


Fig. 2: Schematic representation of diamagnetic, paramagnetic, and ferromagnetic materials microscopic structures at rest and in the presence of a magnetic field H

5. Comparison of Magnetic Materials:



S. N	Properties	Diamagnetic	Paramagnetic	Ferromagnetic
1	Definition	It is a material in which there is no permanent magnetic moment.	It has permanent magnetic moment.	It has enormous (more) permanent magnetic moment.
2	Spin or magnetic moment or dipole alignment.	No spin alignment.	Random alignment	Parallel and orderly alignment.
3	Behavior	Repulsion of magnetic lines of force from the centre of the material.	Attraction of magnetic lines towards the centre.	Heavy attraction of lines of force towards the centre.
4	Magnetized direction	Opposite to the External magnetic field.	Same direction as the External magnetic field.	Same direction as the External magnetic field.
5	Permeability	It is very less	It is high	It is very high
6	Relativity permeability	$\mu_r < 1$	$\mu_r > 1$	$\mu_r >> 1$
7	Susceptibility	Negative	Low positive	High positive

Conclusion:

In summary, permanent magnetic dipoles arise from the quantum mechanical properties of electrons and their interactions within materials, leading to the alignment and stabilization of magnetic moments. The classification of magnetic materials provides insight into their different responses to magnetic fields, which is crucial for selecting the right material for specific applications. From diamagnetic and paramagnetic materials with weak interactions to ferromagnetic and ferrimagnetic materials with strong and permanent magnetization, understanding these classifications helps in designing and utilizing materials for various technological and industrial uses. From diamagnetic and paramagnetic materials, which exhibit weak responses to external magnetic fields, to ferromagnetic, antiferromagnetic, and ferrimagnetic materials, which demonstrate significant and often permanent magnetization, each type plays a unique role. Superparamagnetic materials offer intriguing properties at the nanoscale, while soft and hard magnetic materials serve specific functions in applications ranging from electronics and data storage to medical imaging and energy systems. Understanding these magnetic properties allows for the tailored design and utilization of materials, driving advancements in technology and addressing various industrial needs.

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