

Development of Functional Carbon Materials from Marine Biomass Resources toward Industrial Applications

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産業利用を目指したマリンバイオマス資源からの
機能性炭素材料の開発

**Development of Functional Carbon Materials from
Marine Biomass Resources toward Industrial
Applications**

2024 年 3 月

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Abstract

Carbon materials are essential in numerous industries, yet their production primarily relies on fossil carbon sources, outperforming biomass-derived carbon in crucial properties. This study explores the functionalization of marine biomass carbon materials (MBC) to substitute traditional fossil sources, reducing carbon emissions in the industry. Leveraging marine biomass's high yield, efficient carbon sequestration, and minimal environmental impact, this research investigates the potential of MBC as an environmentally friendly carbon materials for industrial applications.

Chapter 1 outlines industry's need for greener carbon materials, highlighting challenges in replacing fossil sources with biomass. Marine biomass advantages over terrestrial counterparts are underscored, addressing ongoing research in the field. The focus on fulfilling industrial demands for functionalized MBC is established, emphasizing existing carbon material characteristics. A direction for MBC functionalization is proposed, aligned with industrial carbon material requirements.

In Chapter 2, pyrolysis and elemental analysis of marine biomass unveil high concentrations of alkali and alkaline earth metals (AAEM), increasing with pyrolysis temperature. However, high temperatures prompt AAEM gasification, and their also removal through liquid-phase cleaning. The chapter introduces novel low-cost washing methods—acetic acid and CO₂

aeration washing—for AAEM removal. Comparative experiments with water washing reveal their efficacy in purifying MBC, achieving higher carbon content and lower ash content than commercial raw coal or coke.

Chapter 3 delves into surface pore structure of MBC, an essential aspect for functionalization. Unique non-activated pyrolysis generates a porous structure on MBC, suitable for industrial activated carbon. Experiments varying pyrolysis temperatures reveal increased specific surface area (SSA) with gasification of alkali metals. Enhanced washing methods demonstrate substantial SSA increase, implying AAEM's blocking effect on the pore structure. Superior SSA is achieved without activation process, peaking at $1198 \text{ m}^2\cdot\text{g}^{-1}$, indicating significant progress towards activated carbon-like properties.

Chapter 4 concentrates on the comprehensive enhancement of MBC to produce activated coke suitable for industrial pollutant purification. A crucial aspect in this enhancement is the splitting tension strength, a property that holds significant importance in the practical application of activated coke in industrial settings – a characteristic typically absent in general biomass activated carbon. Surprisingly, MBC demonstrates noteworthy splitting tension strength under specific conditions. By adjusting pyrolysis and coking temperatures, along with employing various washing methods, a balance was achieved among the carbon content, pore structure, and strength of MBC. The findings suggest potential for MBC to

replace activated coke derived from traditional sources. The chapter concludes by outlining future research plans.

Chapter 5 provides a comprehensive summary of the thesis.

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Chapter 1.

General introduction

1.1. Carbon materials in industrial application

1.1.1. Types and application fields of industrial carbon materials

Carbon materials, predominantly composed of carbon element, have found extensive application prospects across diverse industries owing to their rich versatile structures, abundant sources, and unique properties. As shown in Figure 1.1, Notable industrial carbon materials include high-conductivity graphite utilized in battery electrodes [1], diamond with exceptional hardness employed as abrasives in geological drills and cutting tools [2], carbon fiber with high tensile strength used in aircraft manufacturing [3], semiconductor silicon carbide materials used in chip manufacturing [4], and carbon-based iron reducing agents employed in mineral smelting [5]. Advanced activated carbon (AC) materials offer diverse applications in chemical energy storage [6], as chemical fillers [7], and for soil remediation [8]. Owing to their versatile forms and adaptable modification strategies, carbon materials continue to witness extensive usage across various advanced industries, such as in lithium batteries [9] and stealth materials [10].

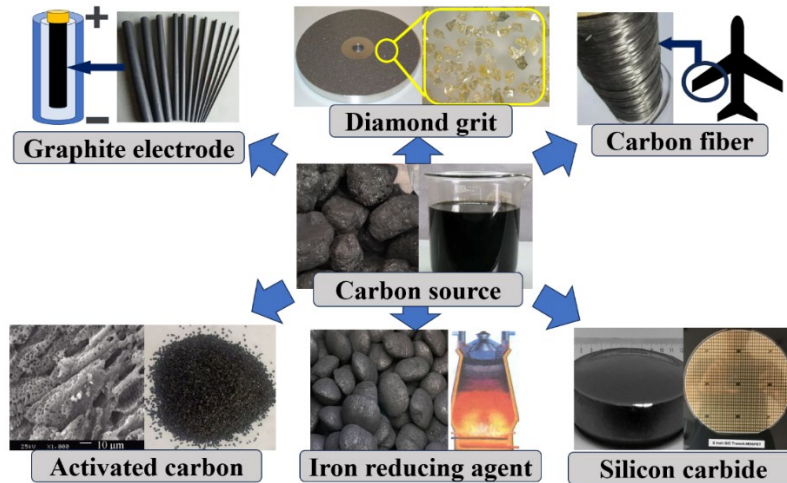


Figure 1.1. The application fields of carbon materials in industry.

1.1.2. The challenges faced by current industrial carbon materials

Currently, industrial carbon materials primarily originate from traditional fossil fuel-based carbon sources such as coal and oil [11]. The derivatives of these fossil fuels such as methane, ethylene, asphalt, and polyacrylonitrile are unsustainable materials. Therefore, the escalating concerns regarding climate change attributed to the utilization of these conventional sources and their derivatives have become a bottleneck, eventually impeding sustainable development in economies, societies, and ecological environments at the global scale. Consequently, addressing this crisis by reducing reliance on traditional carbon sources and achieving carbon neutrality have emerged as critical global imperatives for governments and scientists across the world. Therefore, the quest for raw materials for widely-used carbon materials in industries aligning with sustainable development, has gained significant prominence [12]. Scholars

across nations have turned their focus to various sustainable carbon sources in research and application. For instance, organic waste has been repurposed as a carbon source to create new carbon materials [13] and biomass has been utilized as a raw material for the synthesis of the carbon materials [14]. Among these, biomass, a renewable carbon source, boasts diverse types, abundant reserves, and is considered to be a potent, cost-effective, easily accessible, and sustainable alternative to conventional fossil fuel-based carbon sources [15].

1.2. Biomass-based carbon materials

1.2.1. Biomass as a potential alternative to traditional fossil fuel-based carbon sources

Biomass refers to various organic compounds, metabolites, and their derivatives that can be easily obtained in nature from agriculture industry, forestry, stock farming, and also from urban waste. As a significant source of organic matter, biomass offers environmental benefits and advantages including diverse species and ample reserves [16]. Figure 1.2. depicts that biomass operates within the carbon cycle of the biosphere without contributing additional carbon dioxide (CO₂) to the atmosphere. By substituting traditional fossil fuel-based carbon sources with biomass, industry can stand to substantially curtail carbon emissions [17]. Nonetheless, the current utilization of biomass remains limited, with the

majority being discarded and underutilized [18]. Conventional disposal methods such as incineration, landfilling, and composting lead to considerable environmental pollution and heightened greenhouse gas emissions, significantly affecting the ecosystem. In response, the exploration and application of biomass-derived carbon materials have garnered significant research attention worldwide. This initiative aims to address the reliance of industrial carbon materials on conventional fossil sources and effectively repurpose the discarded and neglected biomass into high-value functional carbon materials.

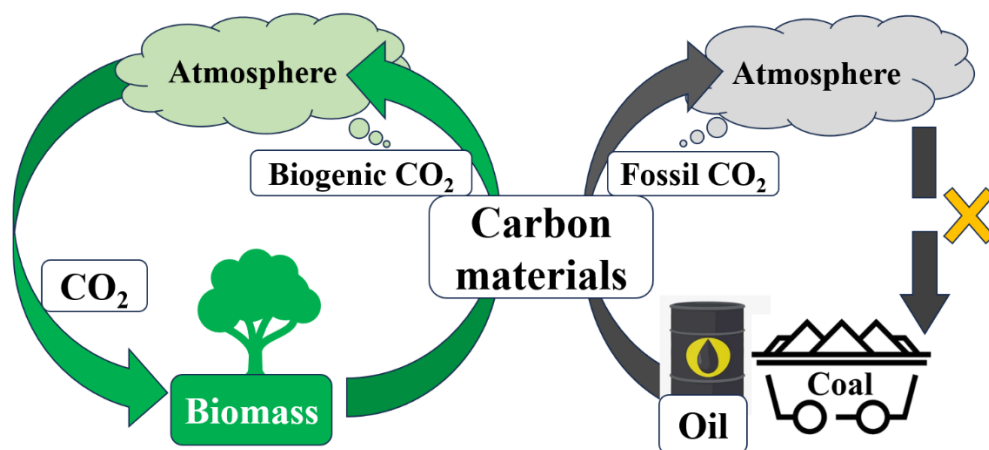


Figure 1.2. Carbon reduction of biomass

1.2.2. Basic characteristics and advantages of biomass-based carbon materials

As a raw material rich in carbon, biomass materials have always been a high-quality source for the fabrication of carbon materials with outstanding characteristics. In oxygen-deprived or low-oxygen

environments, carbon-rich biomass materials undergo high-temperature pyrolysis, producing a highly aromatized solid substance known as biomass carbon (BC) material [19]. These materials boast a large specific surface area (SSA), well-developed pore structures, and high ion exchange capacity [20, 21]. Comprising elements such as C (exceeding 60%), H, O, N, S, and trace amounts of other elements [22], the chemical composition of BC materials primarily includes aliphatic and aromatic compounds, along with key functional groups such as aryl, phenolic, benzene rings, carbon groups, and aliphatic double bonds [23]. Throughout the pyrolysis process, BC generally retains the structural features of the original biomass, showcasing developed pore structures and expanded SSAs [24].

BC materials, as a renewable resource with promising development prospects, offer several advantages in industrial applications, as follows:

- 1). Cost-effectiveness and eco-friendliness [25]: Unlike traditional fossil fuel-based carbon sources, biomass is abundant and renewable, facilitating easy accessibility. Moreover, the preparation process for BC is relatively less polluting with lower energy consumption.
- 2) Diverse sourcing and variability: Biomass is available in various types and structures, impacting the microstructures and elemental compositions of resulting carbon materials. By selecting different types of biomass raw material, tailored carbon materials with specific advantages or functions can be obtained.
- 3). Versatile structure and adaptability: BC materials contain diverse chemical

structures and functional groups, enabling *in-situ* heteroatom doping and facile synthesis of composite materials with other substances. With simple preparation and modification processes, they can find applications across different industries. Many studies have validated the feasibility of partially replacing raw coal with carbon materials made from biomass. For example, application of charcoal in the metallurgical industry has been proven to be safe and effective in reducing carbon emissions through engineering practice and theoretical calculations [26].

Biomass raw materials typically fall into two categories, namely, terrestrial biomass (TB, such as straw [27] and fruit shells [28]) and marine biomass (MB, including crustaceans [29] and algae [30]). These biomasses can be used as raw materials in diverse applications. For instance, linen fabric derived from flax serves as a raw material, activated by ammonia-driven one-step carbonization at high temperatures, which introduces nitrogen-containing functional groups while creating numerous pore structures. The resulting flax-based BC has successfully been incorporated into a flexible electrochemical energy storage device [31].

1.3. Marine biomass-based carbon materials (MBC)

1.3.1. Comparison between marine biomass and traditional terrestrial biomass

The oceans cover about two-thirds of the earth's surface, and produce billions of tons of MB annually, constituting the largest untapped resource pool of biomass globally. As shown in Figure 1.3, this MB offers notable advantages in rapid renewable energy compared to TB [32]. Traditional TB, such as trees and grass, typically yields around 400 to 500 $\text{g}\cdot\text{cm}^{-2}\cdot\text{yr}^{-1}$ [33], and in some regions, even lower [34]. In contrast, specific marine algal biomass, such as *Sargassum horneri* [35] and *Ecklonia cava* [36], can achieve yields of 1000-1500 $\text{g}\cdot\text{cm}^{-2}\cdot\text{yr}^{-1}$, respectively. As MB is primarily extracted offshore, its extraction costs are notably lower compared to those of TB, without the need for land occupation or causing soil damage. Moreover, MB lacks the cellulose and hemicellulose content found in TB, making its texture finer and softer. Noteworthy, this distinction simplifies and renders preprocessing after harvesting more manageable and energy-efficient. These characteristics bring advantages in industrial applications, including simple mining processes, low manufacturing costs, relatively low carbon emissions, and excellent physical and chemical properties [37]. Therefore, significant research efforts to use MB as a raw material for the new generation of BC and achieve their functionalization will greatly benefit the carbon material industry.

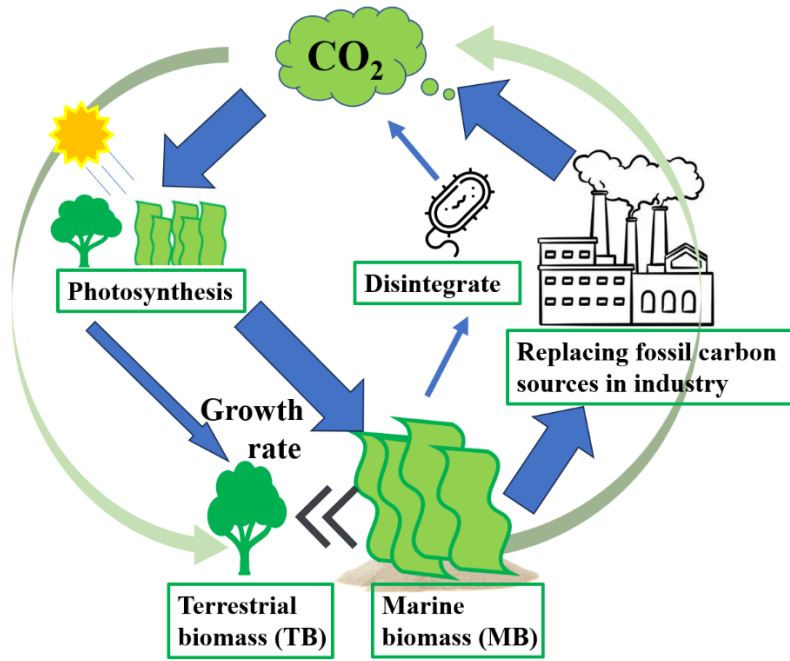


Figure 1.3. Marine biomass has a higher carbon reduction efficiency than terrestrial biomass

Algae, comprising proteins, polysaccharides, dietary fibers, and inorganic salts [38, 39], represent the dominant constituent of MB. The carbonized components derived from algae are relatively simple and highly applicable in various domains. This has led to extensive development efforts, primarily focused on marine biomass-based carbon (MBC) materials derived from MB, with researchers working on its application in eco-friendly industries to curtail greenhouse gas emissions [40]. Moreover, compared with other carbon materials, MBC boasts advantages such as low cost, high yield, and excellent physical and chemical properties [41]. However, the global technological utilization of MBC remains underdeveloped, leading to substantial wastage of these resources.

Therefore, the rational and efficient utilization of MBC has become an urgent concern that requires immediate attention.

1.3.2. Research progress in MBC

Currently, MBC development focuses on photochemical catalysis, electrochemical energy storage, environmental adsorption, among other areas. For instance, Zhou et al. [42] discovered that modified kelp BC loaded with bismuth molybdate and consisting of amorphous carbon demonstrated notable photocatalytic activity and strong electrical conductivity. The surface of the kelp BC harbored diverse transition metals such as manganese, iron, nickel, and copper, fostering efficient electron transfer and achieving synergistic effects among multiple catalytic centers, thereby enhancing its photocatalytic prowess.

Pinero et al. [43] employed light black giant seaweed as raw material for direct pyrolysis under the temperature range of 600–900 °C. Abundant in oxygen-rich hydrocolloids and nitrogen-rich proteins, seaweed offers plentiful oxygen-containing and nitrogen-containing functional groups during pyrolysis. With the increase in temperature, the surface oxygen content of the material decreased, and while the carbonization temperature partially closed the pore structure, it led to a decrease in pore volume. When the mesoporous characteristics were being maintained, the micropore quantity gradually increased, yielding nanoscale porous carbon

with an SSA reaching up to $1,307 \text{ m}^2\cdot\text{g}^{-1}$. Under a current density of $200 \text{ mA}\cdot\text{g}^{-1}$ in an aqueous solution of H_2SO_4 electrolyte (1 M), its specific capacitance reached $264 \text{ F}\cdot\text{g}^{-1}$, and it retained 89% capacitance (1 A) even after 10,000 charge–discharge cycles. In an organic (TEABF_4) electrolyte, LN900t exhibited a specific capacitance of $94 \text{ F}\cdot\text{g}^{-1}$. In a 10-second discharge response test, LN900t demonstrated energy and power density values 1.5 to 2 times higher than those of commercial AC.

Wang et al. [44] produced honeycomb porous carbon with a well-developed microporous structure and nitrogen/oxygen-rich chemical groups using kelp as the raw material through ethanol extraction and chemical modification (KOH , 900°C , 1 h) techniques. The honeycomb morphology and synergistic effect of high oxygen and nitrogen functional groups led to the increase in the SSA of the material ($2,000 \text{ m}^2\cdot\text{g}^{-1}$), shortening electrolyte ion diffusion paths and improving wettability. This enabled the super container electrode to exhibit remarkable specific capacitance ($248 \text{ F}\cdot\text{g}^{-1}$, $1 \text{ A}\cdot\text{g}^{-1}$), good rate capability, and cycling stability ($2 \text{ A}\cdot\text{g}^{-1}$, 10,000 cycles, 91%) in a 6 M aqueous electrolyte.

Eun et al. [45] modified magnetic kelp BC with chitosan, which increased the SSA from 0.97 to $6.17 \text{ m}^2\cdot\text{g}^{-1}$. The modified magnetic kelp BC surface introduced $-\text{NH}$ and $-\text{CN}$ functional groups, reducing the competitive effect of other metal ions and effectively removing Cu^{2+} from wastewater.

The innovative applications of MBC have highlighted the potential of this industry. However, the industrialization of MBC faces limitations in the following three key areas:

Lack of clarity in understanding the pyrolysis process of MB necessitates further systematic investigation. Present research focuses on the end product, overlooking the intricate changes during pyrolysis. This knowledge gap leads to an unpredictable production process, hindering product consistency and impeding the industrial scalability of MBC.

The current preparation process is complex, undeniably demanding a simpler and more efficient strategy. The preparation of MBC typically involves carbonization and activation stages. Issues in the carbonization stage include high energy consumption and low yield. Moreover, the activation phase presents challenges of increased pollution and corrosion. These hurdles lead to significant increase in industrialization costs, disincentivizing production enterprises from adapting their existing production lines.

Performance requirements of carbon materials should align with actual industrial demands. The majority of functionalization research on MBC remains in small-scale experimental phases. Although, the expansion of theoretical research on functionalization is essential, industrial implementation must align more closely with current industry requirements. Adopting MBC for cutting-edge applications, such as

advanced energy storage materials, is premature. Initiation of low-level applications capable of partially replacing traditional fossil fuel-based carbon materials seems more feasible.

Addressing these aspects requires in-depth research and enhancements in the pyrolysis process, preparation strategies, and other critical indicators to achieve functionalization of MBC aligned with industrial needs.

1.4. Key characteristics for achieving current functionalization of MBC

1.4.1. Types and contents of elements

There exists a multitude of raw materials and methods for crafting carbon materials, and the choice of raw materials or agents significantly impacts the elemental composition and concentrations within the final carbon product. This holds immense importance because the types and quantities of elements present in the carbon materials directly influence their application potential. For instance, biomass AC containing iron has shown promise in treating arsenic-contaminated soil due to its extensive SSA and dispersed iron elements capable of interacting and precipitating with surface arsenic elements [46]. However, in the journey toward advanced applications of carbon materials, tracing back to the evolution of fossil carbon sources, the primary goal has been to elevate carbon purity, thereby broadening their industrial utility.

Generally speaking, from TB in inland areas, to coastal biomass, and then to MB in the ocean, a noticeable escalation occurs in non-carbonaceous elements, often termed as impurities. The carbon content of TB, coastal biomass, and MB exhibits a gradual decrease. Consequently, the present challenge for MBC centers around devising simple and cost-effective methods to eliminate these impure elements.

Importantly, the production of BC necessitates both carbonization and activation processes, urging a detailed characterization of biomass impurities during these stages. Thermogravimetric analysis (TGA) stands out as a real-time method that tracks weight changes in sample with the variation in temperature under controlled heating in a specific environment [47]. TGA offers quantitative insights into material decomposition, intermediate products, and thermal stability. Subsequent characterization methods include X-ray fluorescence (XRF) to discern element types and their mass percentages on the carbon material surface. X-ray diffraction (XRD) analysis is used to evaluate crystalline substance types and relative concentrations present on the surface of the carbon material. Elemental analysis gauges carbon content and ash mass percentages in the combustible fraction. Finally, scanning electron microscopy with energy-dispersive spectroscopy (SEM-EDS) measures both carbon content and atomic percentages of impurities within the scanning range.

1.4.2. Surface pore structure

The surface pore structure stands as a pivotal element in the functionalization of MB. Specifically, it refers to the presence of open nanoscale pores on the carbon material surface, acquiring shapes such as wedge-shaped or ink bottle-shaped structures. As shown in Figure 1.4, these pores as micropores below 1 nm, mesopores with the range between 2–50 nm, and macropores with size above 50 nm. Matching appropriate pore structures is essential for diverse application scenarios. For instance, in general AC-based adsorption catalysis, a richer pore structure with a larger SSA harbors more active sites, boosting activity and enhancing overall performance of the carbon material. However, this complexity in pore formation increases costs. Therefore, not all ACs require an overly rich pore structure, contingent upon specific industrial application contexts. Moreover, certain application areas demand specific pore size distributions; for instance, carbon materials for negative electrodes of battery necessitate a higher mesoporous ratio to enhance ion transfer efficiency. Thus, although the surface pore structure remains crucial for carbon materials, it is equally vital to align it with actual industrial needs.

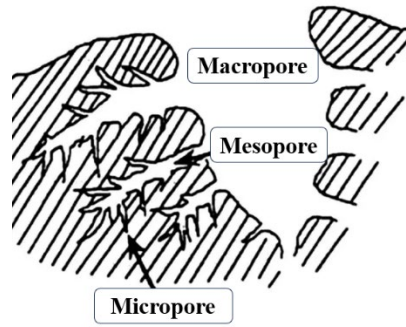


Figure 1.4. Surface pore structure size of carbon materials

The primary method to characterize pore structure is the N₂ adsorption–desorption test. The method is performed by introducing nitrogen into the sample under specific degassing temperature conditions, which is followed by the determination of the adsorption partial pressure, and identification of the corresponding adsorption point [48]. By utilizing the density functional theory method to analyze the N₂ adsorption–desorption curve, SSA and pore size distribution of the sample can be calculated.

1.4.3. Splitting tensile strength

Splitting tensile strength signifies represents the maximum tensile stress borne by brittle materials when splitting cracks occur under uniaxial tension. In various applications, outstanding splitting tensile strength is an important requisite for carbon materials. For instance, in blast furnace smelting, carbon materials are used as reducing agents [49]. In this context, the carbon ore coupling blocks stack up before entering the high-temperature reaction zone. Inadequate strength might cause these blocks to

break prematurely, leading to uncontrolled reactions. Furthermore, as pollutant adsorbent or chemical catalysts [50], carbon materials need to uphold a stable stacked state in the absorption tower or fluidized bed. This requires the preparation of high-strength carbon materials into large particles, which can resist compression and collision between particles while maintaining good fluid permeability. Typically, splitting tensile strength data are garnered through compression tests.

1.5. The key process of functionalization of carbon materials

1.5.1. Pyrolysis process

In general, the currently used production process for carbon materials involves two primary stages, namely, raw material pyrolysis and BC activation. The pyrolysis phase consists of various methods such as slow pyrolysis, rapid pyrolysis, gasification, and hydrothermal carbonization, each characterized by distinct heating rates, retention times, and heating media [51].

1) Slow pyrolysis, often referred to as the traditional carbonization method, involves the slow heating of biomass at a relatively low rate for an extended period (ranging from several hours to several days). Importantly, this method operates under modest reaction equipment and conditions, often using temperature-controlled devices in standard muffle furnaces, an approach widely employed in industrial settings.

2) Rapid pyrolysis denotes the swift heating of biomass in an anaerobic setting to higher temperatures (with heating rates up to $1,000\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$). This process converts original biomass macromolecules into small gas products, volatiles, tar, and other substances. To minimize bio-oil yield, the product usually requires quenching. Compared to slow pyrolysis, rapid pyrolysis typically yields more bio-oil but less BC. The resulting BC often possesses higher density, slight acidity (pH 2.8–3.8), increased water content (15–30%), and reduced heat generation. It is commonly executed in infrared microwave ovens or fluidized bed reactors [52].

3) Gasification pyrolysis is the conversion of biomass into gas mixtures (comprising gas products including CO , H_2 , CO_2 , CH_4 , and limited carbohydrates) at higher temperatures (above $700\text{ }^{\circ}\text{C}$) by manipulating oxidant levels. Owing to the elevated pyrolysis temperature, the BC yield obtained from this method is notably lower than that obtained under slow pyrolysis, with the primary product being gas [53].

4) Hydrothermal carbonization involves placing biomass in a hydrothermal reactor under specific temperature and pressure conditions, using saturated water as the reaction medium. In this process, catalyzed by an appropriate catalyst, the biomass undergoes hydrolysis, dehydration, deoxidation, condensation, and aromatization reactions, ultimately resulting in the formation of BC. This approach is more expensive in industry. The reaction vessel requires materials and processes resistant to

high temperature and pressure, imposing higher equipment standards. Moreover, the resulting wastewater contains numerous broken carbon molecules, demanding further investment in subsequent water treatment processes.

1.5.2. Activation process

Another pivotal stage is the activation process, crucial in optimizing the characteristics of BC to enhance its practical applications. Owing to varying sources of BC raw materials, simple preparatory processes, and limited surface functional group properties, some BC may exhibit lower SSA and singular pore structures, affecting its subsequent applications. To date, several activation methods have been proposed to optimize the properties of BC, categorizing them into traditional approaches such as physical and chemical activation, along with advanced techniques such as self-activation and *in-situ* activation, based on activation mechanisms and application domains.

1) Physical activation regulates BC through water vapor or CO₂ and stands as the primary method used in industry. Although the method is environmentally friendly with straightforward preparation steps, it suffers from drawbacks such as low pore-forming efficiency, high activation temperatures, and high energy consumption. Therefore, identification of suitable physical activation gases and temperatures can efficiently induce

pore formation, which can enhance the performance of the carbon material.

2) Chemical activation primarily employs acids or bases (e.g., HPO_4 , KOH , NaOH) as pore-forming agents [56, 57], activating BC through surface etching. For instance, Xie et al. [58] successfully used willow catkins as highly accessible raw materials, and etched their surface to prepare porous carbon via carbonization and KOH activation, thereby enhancing electrochemical performance. In another method, alkali metal salts or alkaline earth metal salts (AAEMs) were used as pore-forming agents (referred to as the molten salt activation method) [59], necessitating further exploration of its pore-forming mechanism. Although chemical activation significantly increases SSAs and improves pore structures, it requires substantial chemical usage, causing equipment and environmental damage. More importantly, it results in a notable reduction in AC material yield, issues requiring subsequent research attention.

3). In the self-activation method, the pores are activated without additional activators, utilizing gases released during material pyrolysis, such as CO_2 and water, to etch surfaces at high temperatures, fostering pore formation. Xia and Shi [60] employed hemp core fibers as raw materials for BC, utilizing the self-activation method to create porous BC materials. By heating hemp core fibers under vacuum conditions, gases were generated from biomass pyrolysis, which underwent activation and formed pores on the surface at high temperatures, achieving an SSA of $2432 \text{ m}^2\cdot\text{g}^{-1}$.

Through mathematical modeling, researchers determined 1090 °C as the optimal self-activation temperature for hemp stem core fibers.

4). The *in-situ* activation method efficiently forms pores by removing a substance from biomass and creating pores in the space vacated, facilitating pore formation activation. Liang et al. [61] utilized polytetrafluoroethylene (PTFE) as a pore-forming agent, mixed it with milled rice husks, and then carbonized and activated the mixture under inert gas and high temperature conditions in a single step. This method employed PTFE to generate HF gas at high temperatures, etching natural silica inside rice husks. *In-situ* activation proved to be superior to simply using HF or NaOH, achieving SSA of 2051 m²·g⁻¹ for rice husk porous carbon material. Liang et al. [62] further applied this method to plant leaves, obtaining a high SSA of 1609 m²·g⁻¹ with a favorable pore structure. This technique entails simple steps, bypasses pre-carbonization, and eliminates the use of harmful corrosive agents such as NaOH or KOH. However, maintaining controlled pore formation effects within the same raw material via *in-situ* activation proves challenging due to consistent internal Si content across the same biomass.

1.5.3. Washing process

Different carbonization and activation processes necessitate distinct washing methods to eliminate residual chemicals or impurities. For

instance, physical activation and self-activation primarily utilize gaseous agents for pore formation, which simplifies the washing process. However, the washing process for chemical activation is comparatively intricate. The high-temperature etching by the activator on the carbon surface during chemical activation may leave residual chemical agents within the deep pore structure, making their removal a challenging task. Consequently, standard water washing might struggle to eliminate such residues, requiring additional measures such as acid washing or other high-energy washing processes to effectively eradicate pesticide residues.

In case of *in-situ* activation, the primary mechanism involves the removal of specific non-carbon elements from the surface of the carbon material, thus facilitating the release of the pore structure. Washing in the context of *in-situ* activation demands specialized methods or agents to eliminate elements from their original sites, for instance employing potent acids such as hydrofluoric acid [63].

Currently, for MBC, a washing process that fulfills material performance requirements and simultaneously it is simple and environmentally friendly, does not exist. Therefore, the development of a suitable, cost-effective, and eco-friendly washing method is pivotal for advancing the functionalization of MBC within the industry.

1.6. The research content of this thesis

The utilization of MBC holds the promise of ushering traditional industries into a greener, carbon-reduced future, given its high yield, renewable nature, and minimal soil impact. However, the current functionalization process for MBC is intricate, demanding high energy and causing severe environmental pollution, still distant from substituting traditional fossil carbon materials. The proposed functionalization of MBC, centered on industrial needs, is outlined in the following three chapters:

- 1). Low-concentration Acetic Acid and CO₂ Aeration Method for AAEM Removal from MBC
- 2). Optimization of MB Pyrolysis Process and Facilitation of Pore Structure Release for MBC Activation
- 3). Fine-tuning of Preparation Processes to Equilibrate Surface Pore Structure and Material Splitting tensile strength

These chapters aim to address the multifaceted enhancement of MBC attributes, starting from the elimination of non-carbon impurities, moving toward refining the pore structure, and ultimately achieving a balance between surface pore design and material splitting tensile strength.

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Chapter 2.

Preliminary functionalization of MBC by AAEM removal from through simple washing methods [1]

2.1. Introduction

As introduced earlier, the fundamental pursuit of functionalizing marine biomass carbon (MBC) materials is to enhance and evaluate their performance parameters, in order to align them with established, industrially applied carbon materials. Among the primary challenges faced in the research on carbon materials, elucidation and optimization of the composition and volume of elemental constituents is a difficult task, which are pivotal across various application fields, be it raw coal, coke, or BC materials. Excessive non-carbon elements can trigger intricate, unmanageable alterations during preparation, severely impacting their subsequent applications.

The publicly accessible data evidently indicate that compared to terrestrial biomass (TB), MB contains higher quantities of alkali metals and alkaline earth metals (AAEMs), including elements such as potassium (K), sodium (Na), calcium (Ca), magnesium (Mg), and chlorine (Cl) [2]. These AAEMs actively engage in the pyrolysis and carbonization of raw material, complicating control at high temperatures and jeopardizing product

uniformity [3]. Their presence, in particular AAEMs and Cl, poses hindrances in traditional industries such as mineral smelting [4]. In mineral carbon coupling materials, MBC materials serve as both a reducing agent and a carbon framework, liberating alkali metals and Cl during blast furnace reactions, which causes severe corrosion [5, 6]. Alkali metals also curtail the reactivity of carbon materials within blast furnaces due to mineral coupling [7]. Despite the presence of impurities in MBC, harnessing its potential for carbon reduction remains a significant advantage. The key challenge lies in effective elimination of these AAEMs and Cl to fully exploit the potential of MBC and functionalize it appropriately.

Existing methods for removal of AAEM in industry fall short of the evolving demands. Although water washing [8] efficiently clears water-soluble AAEMs (e.g., chlorides) from MBC with cost-effective and straightforward equipment, it is limited in the range of compounds it can extract. In contrast, acid washing, a solution for insoluble or deeply embedded impurities [9], incurs high chemical costs, subsequent wastewater discharge causing environmental pollution, and equipment maintenance, contrary to green chemistry principles. Although ultrasonic washing [10] accelerates impurity removal under low pollution conditions, its high equipment expenses and energy consumption pose challenges for industrial prospects. Given these limitations, an urgent need exists for

obtaining an efficient, cost-effective, and eco-friendly method for AAEM removal.

This chapter addresses the AAEM-related drawbacks for specific MBCs used in industrial applications. Herein, preliminary functionalization of MB, simulating industrial preparation steps, is presented. First, adjustment of pyrolysis process of MB and assessment of AAEM conversion and migration during high-temperature reactions are discussed. Subsequently, exploration strategy of two eco-friendly, straightforward washing methods for AAEM removal from MBC is presented, comparing them against the water washing method. Compared with commercially available traditional fossil coke, MBC offers a promising potential for low-carbon industry carbon materials.

2.2. Experimental

2.2.1. Raw material preparation

All raw biomass utilized in this study was supplied by Nippon Steel Company (Tokyo, Japan), encompassing two types of coastal MB harvested from Japan's shores, namely, kelp (Kombu, KB) and Undaria (Wakame, WKM). Further, TB samples, i.e., coconut shell (CS) and sawdust (SD), were utilized for comparative analysis. Alginate (AGA), the primary component of MB, was sourced from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). The dried biomass was crushed to sizes smaller

than 250 microns, and denoted as Raw WKM, Raw KB, Raw CS, Raw SD, and Raw AGA, respectively. Figure 2.1. illustrates the specific preparation process. The MB powder was fed into a tubular furnace and subjected to pyrolysis in a nitrogen atmosphere at temperatures of 600, 800, and 1000 °C, respectively, for 2 h. This resulted in the formation of MBC products, labeled as WKMx, KBx, CSx, SDx, and AGAx, respectively, with x indicating the pyrolysis temperature.

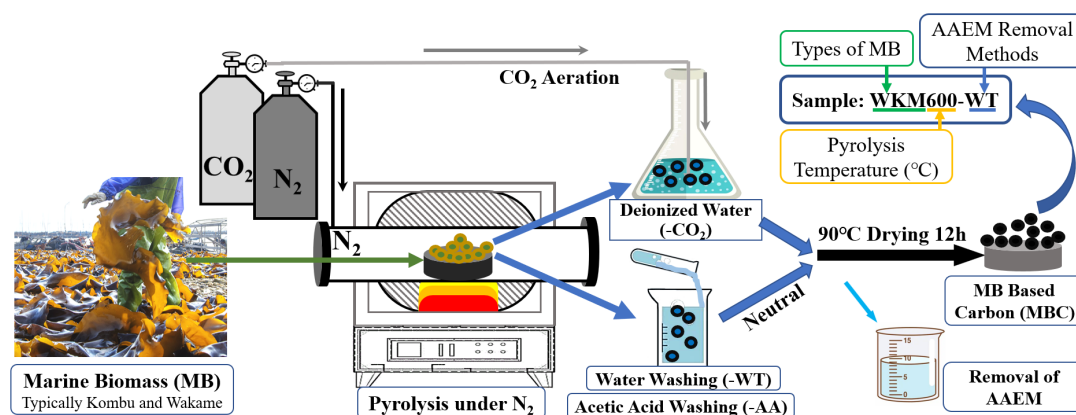


Figure 2.1. MBC preparation and AAEM removal processes. [1]

2.2.2. Removal of AAEM from MBC

Based on comprehensive analysis of pyrolysis process, WKM800 and KB800 were selected for AAEM removal experiments. Three methods, namely, pure water washing (WT), CO₂ aeration washing, and 1% acetic acid (AA) solution washing, were employed at room temperature. The procedure for AAEM removal from WKM800 and KB800 is illustrated in Figure 2.1. Parameters for washing were determined from preliminary experiments (refer to Table A2.1 and Table A2.2 in the supplementary data).

In the pure water washing method, MBC (0.5 g) was dispersed in deionized water (500 mL), stirred for 2 h, and then filtered. These samples are denoted as MBCx WT (e.g., WKM800-WT and KB800-WT). In CO₂ aeration method, CO₂ gas was introduced at the rate of 100 mL·min⁻¹ with stirring, which yielded samples labeled as WKM800-CO₂ and KB800-CO₂. Acetic acid, selected for its low toxicity and minimal environmental impact, was utilized: briefly, MBC (1 g) was dispersed in a 1% acetic acid solution (1000 mL), stirred for 2 h, and rinsed with deionized water to neutral pH. The resulting sample was named as MBCx AA (WKM800-AA and KB800-AA).

2.2.3. Material characterization equipment

Thermogravimetric analysis (TGA) was conducted using a TG analyzer (STA2500 Regulus, Selb, Germany). Elemental analysis was carried out by X-ray fluorescence (XRF; ZSX Primus IV/RX9; Rigaku, Tokyo, Japan) method and by using an elemental analyzer (CHN Coder; MT-5). Oxygen content (O_{diff.}) was derived by subtracting the sum of carbon, hydrogen, and nitrogen contents from 100%. X-ray diffraction (XRD) analysis was carried out using an X-ray diffractometer (Rint Ultima III, Rigaku).

2.3. Results and discussion

2.3.1. *Pyrolysis process of MB*

Notably, TGA serves as an effective tool to illustrate the changes in quality observed during the pyrolysis of carbon materials and to gauge the thermal degradation and stability of carbon materials produced at different temperatures. Figure 2.2A depicts an overall retention of a larger quantity of solid pyrolysis products in MB compared to those in TB throughout the pyrolysis phase. A detailed examination reveals the following three distinct stages within the MB curve: 200–400 °C, 400–800 °C, and 800–1000 °C. The significant decrease in weight within the 200–400 °C range is attributed to the low-temperature pyrolysis of biomass, where small volatile molecules evaporate and get expelled from the system. In the 400–800 °C range, the reduction in weight primarily corresponds to the thermal contraction and recombination of the BC framework, transitioning toward the formation of a six-membered carbon ring. Between 800–1000 °C, the raw material further carbonizes, progressing toward graphitization, with the mass tending to stabilize. Notably, a specific degree of weight loss is observed in the production of WKM and KB at this stage. Conversely, the raw TBs and raw AGA align more closely with the anticipated outcomes of pyrolysis of pure biomass, maintaining a relatively stable quality. This distinction indicates that WKM and KB entail the absence of high-temperature volatile components in other biomass materials.

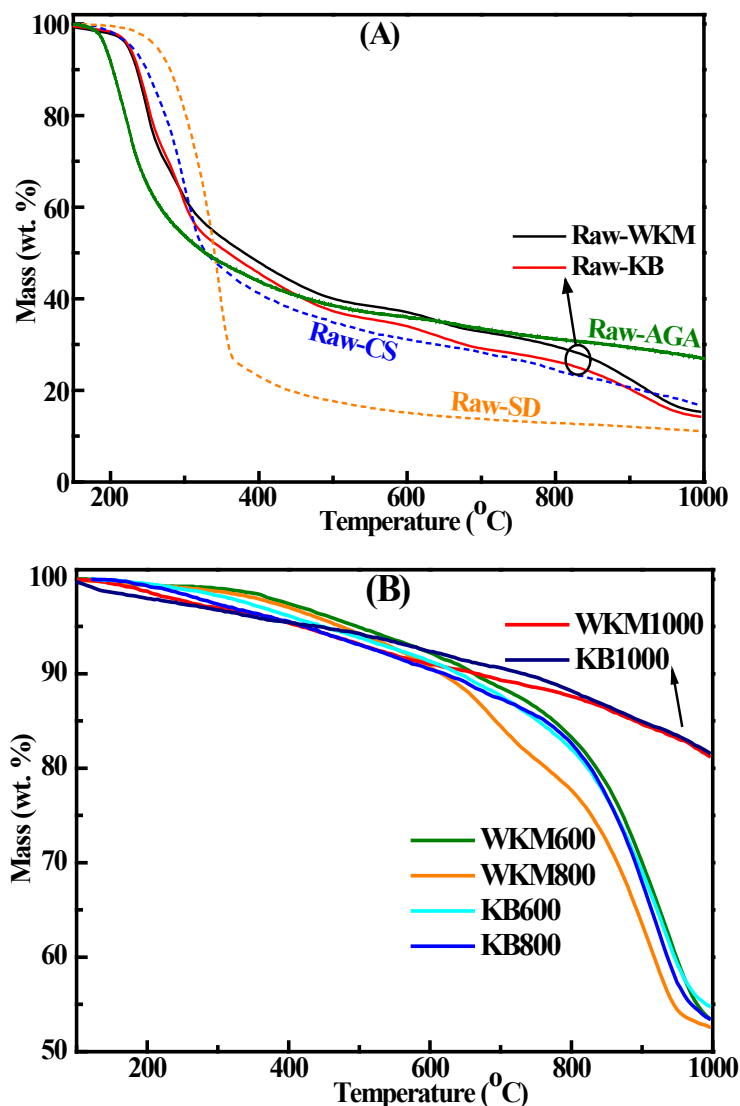


Figure 2.2. TG curves in N_2 of: (A) raw biomass (MB: continuous line, TB: broken line) and (B) MBC pyrolyzed at different temperatures. [1]

Figure 2.2B presents the TG curves of MBC prepared at three different carbonization temperatures ranging from 600 to 1000 $^{\circ}\text{C}$. At 1000 $^{\circ}\text{C}$, both WKM1000 and KB1000 exhibit a gradual, steady decrease in weight. In contrast, samples carbonized at 600 or 800 $^{\circ}\text{C}$ (WKM600, WKM800, KB600, and KB800) display a sharp decline in weight at

temperature above 800 °C, resembling the pattern observed in the original WKM and KB. However, this sharp decrease in weight is absent in the pyrolysis curve of Raw AGA, also part of MB (as shown in Figure 2.2A). This absence indicates that the mass reductions observed at 800–1000 °C for Raw WKM, WKM600, WKM800, Raw KB, KB600, and KB800 cannot be attributed to the volatilization of primary organic matter (C, H, O, etc.) present in MB. To probe the types of volatile substances at temperature above 800 °C, XRD analysis was subsequently performed.

Figure 2.3 depicts the outcomes of XRD characterization. Evidently, both WKM (Figure 2.3A) and KB (Figure 2.3B) exhibit distinct and sharp diffraction peaks, while Raw AGA exhibits extremely weak and almost undetectable diffraction peak signals. It indicates that MB samples contain highly crystalline compounds, which are almost imperceptible in AGA. Comparative analysis and calculation results reveal that the original MBs contain crystalline NaCl, originating from the marine environment where MB grows. After carbonization at 600 °C, KCl crystals reappeared, potentially due to the higher crystallization temperature of KCl. Moreover, WKM800 and KB800 displayed peaks of CaS and MgO with higher crystallization temperatures but lower intensity. Notably, WKM1000 exclusively displayed diffraction peaks of CaS and MgO crystals, without detecting NaCl and KCl crystals. Although XRD pattern of KB1000 indicates the presence of NaCl and KCl crystals, the intensity of these

peaks diminishes notably. Consequently, the weight loss observed by TGA above 800 °C might be linked to the volatilization of NaCl and KCl within the 800–1000 °C range.

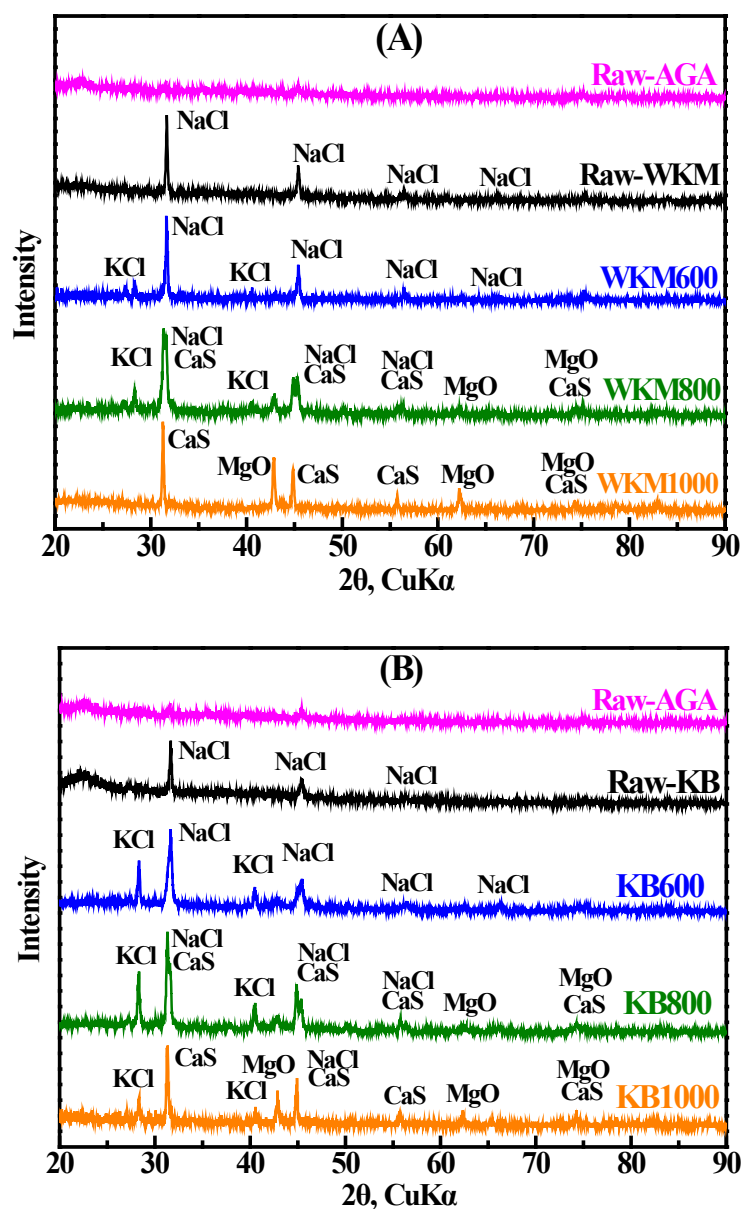


Figure 2.3. XRD patterns of MB and MBC: (A) WKM and (B) KB. [1]

The XRF characterization offers a semi-quantitative analysis of the elemental composition within MB and MBC. Table 2.1 lists the XRF element mass ratios of MB and MBC, alongside TBs as control samples. In MB, Na and Cl were the only elements detected, corroborating and supporting the findings from XRD analysis. Within the carbonized samples, the organic (CHO) elements in WKM800 and KB800 decreased compared to those in WKM600 and KB600. This outcome could be linked to a higher loss in mass of volatile small molecule carbon during the increase in temperature from 600 to 800 °C, as opposed to the gasification amount of AAEMs. However, when the temperature reached 1000 °C, the content of Na, K, and Cl dropped substantially from 16.8 mass% in WKM800 and 18.2 mass% in KB800 to 2.7 mass% in WKM1000 and 2.2 mass% in KB1000, respectively. The XRF data strongly indicate that the mass loss observed in MBC at 800–1000 °C (as depicted in Figure 2.2) and the disappearance or significant weakening of the KCl and NaCl peaks in the XRD mode of MBC1000 (Figure 2.3) are attributed to the high-temperature vaporization of Na, K, and Cl elements.

Table 2.1. XRF elemental compositions of raw and carbonized samples of MB and TB [mass%].[1]

Sample	CHO	AAEMs and other elements						
		Na	Mg	K	Ca	P	S	Cl
Raw-AGA	98.4	1.2	--	--	--	--	--	0.2
AGA600	92.4	5.9	--	0.2	0.1	--	--	0.8
Raw-WKM	84.5	5.4	1.2	1.4	1.5	0.2	0.7	5.0
WKM600	80.9	7.5	1.5	1.8	1.9	0.2	0.8	5.3
WKM800	77.0	8.7	2.1	2.0	2.5	0.3	1.1	6.1
WKM1000	87.5	0.4	3.5	1.3	4.1	0.5	1.5	1.0
Raw-KB	88.3	3.0	1.1	1.6	1.6	0.1	0.9	3.4
KB600	80.8	6.2	1.5	2.6	2.3	0.1	1.2	5.0
KB800	74.5	7.9	2.2	3.4	3.1	0.2	1.6	6.9
KB1000	85.4	0.2	4.0	1.7	5.2	0.3	2.6	0.3
CS600	93.5	1.0	0.3	2.9	0.2	0.1	--	1.8
CS800	96.5	0.4	0.2	2.7	0.1	0.1	--	0.2
CS1000	97.1	0.2	0.1	1.9	0.2	0.1	--	--
SD600	99.5	--	--	0.2	0.1	--	--	--
SD800	99.5	--	--	0.3	0.1	--	--	--
SD1000	98.9	0.5	--	0.4	0.1	--	--	--

--: Undetected.

Numerous studies have demonstrated that alkali metals and Cl present in coal [11, 12] and biomass [13, 14] can undergo complete vaporization above 900 °C. The volatilization mechanism involves high-temperature release of alkali metal salts [15], along with the high-temperature etching reaction of surface carbon, causing small broken carbon molecules to

eliminate certain high-energy alkali metal atoms during the vaporization process. A similar trend can also be observed in CS800 and CS1000, albeit not notably pronounced (Figure 2.2A). This subtle change in CS is attributed to its growth environment nearshore, which contains a minimal amount of alkali metal elements. Notably, the mass ratio of AAEM elements Ca and Mg in MBC increases with increasing carbonization temperature from 600 to 1000 °C. This upsurge is due to the high-temperature stability of alkaline earth metal compounds, although literature reports suggest their involvement in catalytic reactions, impacting formation and gasification of surface carbon molecule [16]. Comparative analysis indicates that although MBC holds several advantages over TB, undeniably, a lot more systematic explorations and further advancement remain necessary.

In summary, a significant portion of Na, K, and Cl in MBC can vaporize during pyrolysis at 800–1000 °C. However, compounds of Mg and Ca exhibit high stability at these elevated temperatures. In the subsequent research, this study will explore the following two washing methods: first is the utilization of CO₂ aeration method, which is a novel approach within carbon material purification; and second is the use of an eco-friendly organic acid aqueous solution washing technique. These methods will be compared with the traditional washing approaches. Among the samples to be washed, WKM800 and KB800 possess the

highest AAEM content, posing challenges for removal and thus selected as representative subjects to evaluate the washing efficacy.

2.3.2. MBC after washing

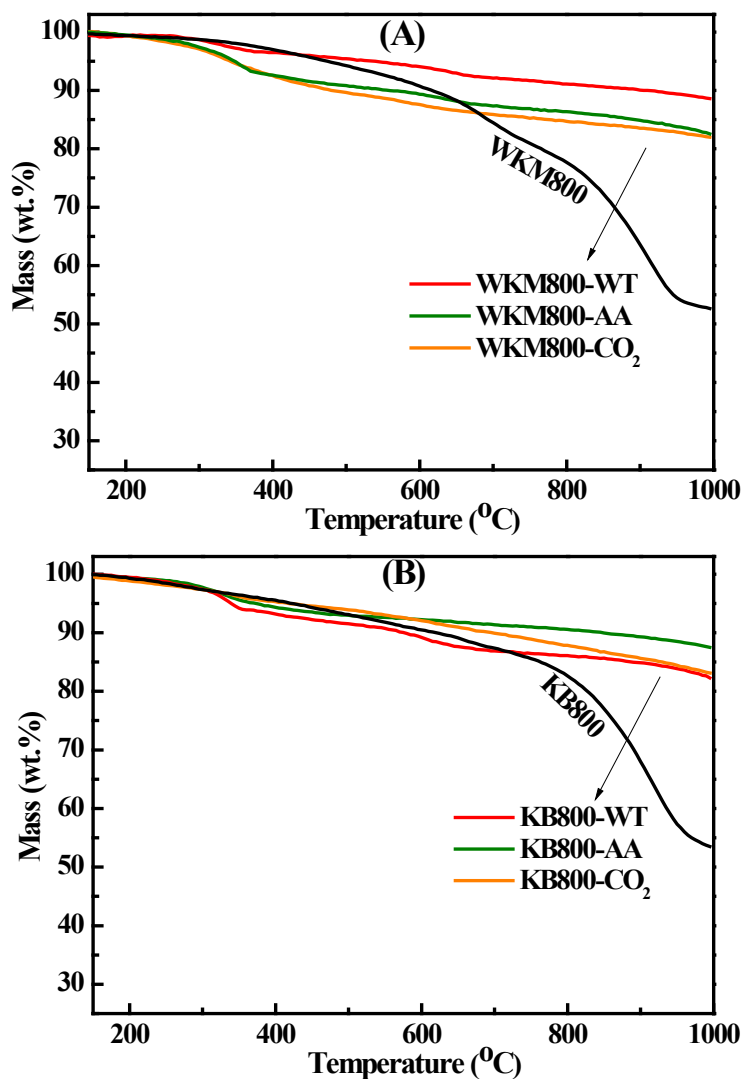


Figure 2.4 TG curves in N₂ of MBC subjected to different washing processes: (A) WKM and (B) KB. [1]

According to the process outlined in section 2.2, three methods including pure water, CO₂ aerated water, and acetic acid aqueous solution methods, were employed for AAEM removal. The TGA results (Figure 2.4)

reveal a significant alteration in the cliff-like decrease of MBC within the 800–1000 °C range after AAEM removal treatment. In contrast to WKM800 and KB800, all samples subjected to washing; i.e., WKM800-WT, WKM-AA, WKM-CO₂, KB800-WT, KB-AA, or KB-CO₂, no longer display cliff-like mass loss, even at temperatures exceeding 800 °C. This result suggests the effective removal of certain high-temperature volatile AAEMs and an enhanced thermal stability of the carbon material itself. Moreover, this phenomenon indirectly underscores the performance of MBC following carbonization at 1000 °C, indicating the efficacy of high-temperature treatment in eliminating volatile AAEMs and enhancing the thermal stability of MBC.

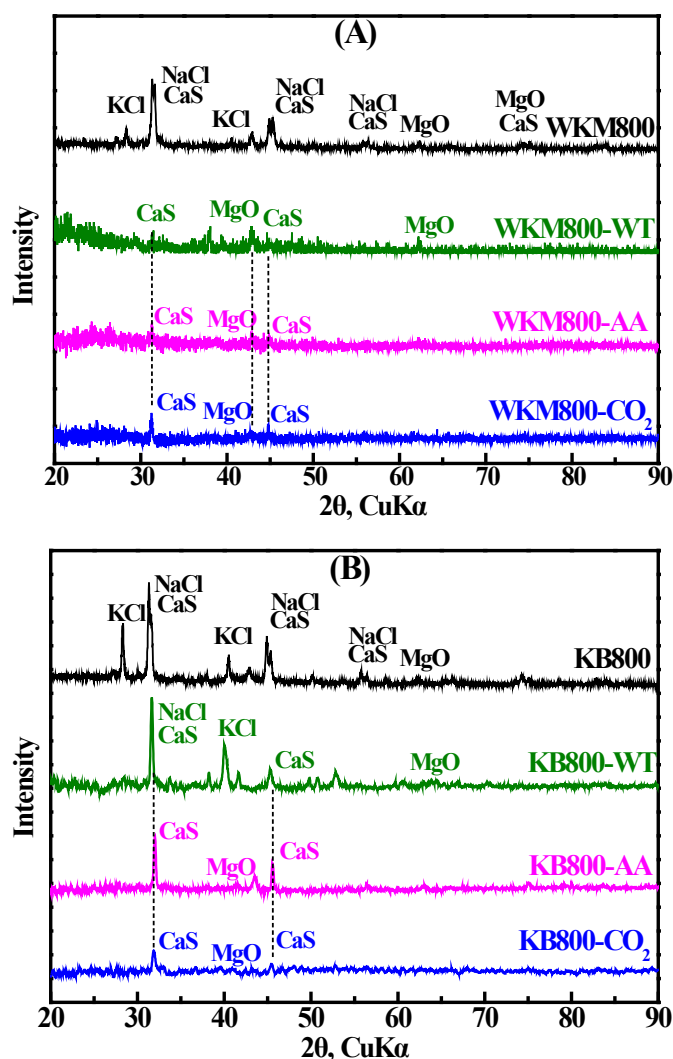


Figure 2.5. XRD curves of MBC subjected to different washing processes: (A) WKM and (B) KB. [1]

Figure 2.5A depicts that the phase analysis of MBC treated with pure water (-WT), CO₂-aerated water (-CO₂), and acetic acid aqueous solution (-AA) is essential. Relative to the carbonized WKM800, the signal corresponding to alkali metal salt crystals in the washed WKM800-WT is nearly imperceptible, with the signal strength predominantly stemming from alkali earth metal salt crystals such as MgO and CaS. In case of WKM800-AA and WKM800-CO₂, the intensity of alkaline earth metal salt

peaks diminishes, and NaCl and KCl crystals become nearly undetectable. Although both are variants of MB, the signal of alkali metal salt crystals in KB800-WT subjected to post-washing is detectable, albeit with decreased intensity. The signal strength primarily arises from the abundant alkaline earth metal salt crystals. Correspondingly, KB800-AA and KB800-CO₂ also exhibit scarce alkali metal salt content and prominent peaks of CaS and MgO. Nonetheless, a comparative analysis between the peak intensities of KB800-AA and KB800-CO₂ indicates that using a low-concentration (1 mass%) acetic acid aqueous solution and CO₂-aerated water yields superior AAEM removal compared to that under pure water. The contrast in results between WKM and KB can be attributed to microstructural variances resulting from the disparities in MB types.

Table 2.2. The XRF elemental compositions of MBC subjected to different washing processes [mass%].[1]

Sample	CHO	AAEMs and other elements						
		Na	Mg	K	Ca	P	S	Cl
WKM800	77.0	8.7	2.1	2.0	2.5	0.3	1.1	6.1
WKM800-WT	90.6	--	4.1	0.1	3.1	0.2	1.3	0.2
WKM800-AA	93.1	--	1.8	0.0	2.0	0.3	2.4	0.1
WKM800-CO ₂	94.5	0.1	2.1	0.0	1.7	0.3	1.1	0.1
KB800	74.5	7.9	2.2	3.4	3.1	0.2	1.6	6.9
KB800-WT	89.7	0.1	3.7	0.1	4.2	0.2	1.5	0.1
KB800-AA	95.4	--	1.7	0.0	1.1	0.2	1.2	0.1
KB800-CO ₂	95.0	--	1.9	0.0	1.4	0.3	1.2	0.1

--: Undetected.

Similarly, Table 2.2 presents the XRF characterization corresponding to the preceding discussion. Both WKM800 and KB800 contain Na, K, Mg, Ca, Cl, and some non-metallic sulfur (S) and phosphorus (P) elements, predominantly existing on the surface of the carbon material in the form of functional groups. As inferred from TGA and XRD analyses, Na, K, and Cl are effectively eliminated after washing. Given the high solubility of alkali metal salts in water, the removal of these elements from MBC via simple water washing is feasible. However, residual amounts of approximately 4 mass% Mg and Ca remain in WKM800-WT and KB800-WT, respectively.

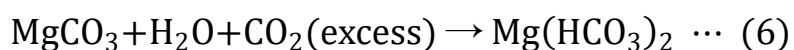
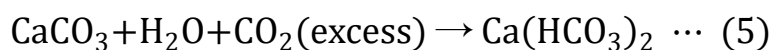
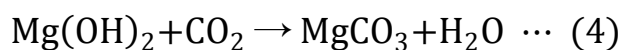
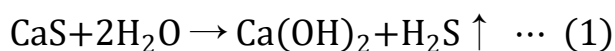
To further diminish the lingering alkaline earth metal elements, acetic acid washing method was employed to target the removal of Mg and Ca. Acetic acid, a liquid organic acid at room temperature, is widely employed in mineral purification for its cost-effectiveness and environmental friendliness. This study utilizes a 1 mass% acetic acid solution, even lower in concentration than typical edible vinegar. The contents of Mg and Ca in sample WKM800-AA post-acetic acid washing decreased to 1.8 and 1.7 mass%, respectively. Similarly, their contents in KB800-AA reduced to 2.0 and 1.1 mass%, respectively.

Subsequently, a novel CO₂ aeration washing technique, was introduced, which is primarily applied in air flotation sewage treatment processes. This study pioneers the application of CO₂ aeration washing to remove AAEMs

from MBC, yielding promising outcomes. Specifically, the Mg and Ca content in WKM800-CO₂ and KB800-CO₂ after CO₂ aeration and water washing declined to 2.1 and 1.9 mass%, respectively, while Ca decreased further to 1.7 and 1.4 mass%, respectively. Importantly, this method minimizes chlorine content to less than 0.1 mass%. This post-treatment method elevates the carbon purity of MBC sans additional acidic agents, proves to be cost-effective, and mitigates equipment corrosion. Furthermore, any residual alkaline earth metals in the discharged washing solution fall within permissible limits for natural water bodies.

The CO₂ aeration washing mechanism primarily involves an increased dissolution of CO₂ in water, altering the ionization equilibrium of carbonate ions toward bicarbonate ions. Bicarbonate salts of alkaline earth metals exhibit greater solubility than their carbonates, resulting in increased dissolution of Ca and Mg in the solid–liquid system within MBC. The process can be detailed as follows: According to the XRD results, Ca and Mg within the MBC sample exist in the crystalline form of CaS and MgO. Initially, these substances react in aqueous solution (chemical formulas (1) and (2)). Their resulting products, Ca(OH)₂ and Mg(OH)₂, further react with CO₂ in water (chemical reactions (3) and (4)), leading to the formation of CaCO₃ and MgCO₃, respectively. Under excessive CO₂, reactions (5) and (6) lead to the conversion of these substances into Ca(HCO₃)₂ and Mg(HCO₃)₂, respectively. The solubility of Ca(HCO₃)₂

and $\text{Mg}(\text{HCO}_3)_2$ in water, at 25 °C and pH = 6.5, is significantly higher, at 0.133 g/100 mL and 0.077 g/100 mL $\times 10^{-6}$ ($K_{\text{sp}} = 1.35$), respectively, compared to CaCO_3 , MgCO_3 , and $\text{Mg}(\text{OH})_2$, which have solubility values of 0.013 g/100 mL [17], 0.011 g/100 mL [18], and 0.0009 g/100 mL [18], respectively. Despite the relatively high solubility of $\text{Ca}(\text{OH})_2$ at 25 °C (0.166 g/100mL), this method remains effective for elements that cannot be entirely dissolved. Leveraging this solubility difference, more Ca and Mg elements in ionic form dissolve in CO_2 -aerated water, facilitating their removal from MBC post-filtration.



In summary, the washing procedures aid in effective elimination of Na, K, and their associated Cl. For the removal of Ca and Mg, both acetic-acid washing and innovative CO_2 aeration washing method proposed in this study demonstrate effectiveness. For achieving higher-purity carbon materials, comprehensive AAEM removal is essential, often necessitating potent acid washing or other high-energy treatment methods. However, the

associated elevated costs and environmental impacts might outweigh the benefits, posing a potential trade-off in industrial applications.

2.3.3. Comparison with commercial coal and coke

The critical step toward the functionalization of MBC involves a comparative assessment with commercially available raw coal and coke, ensuring the potential industrial application of MBC. Deepening functionalization involves meeting standards for industrial carbon material, including, higher carbon content, lower ash content, and elevated grading. Table 2.3 presents an elemental analysis overview obtained on a dry basis (db), encompassing MBC samples alongside raw coal/coke from major global production regions. Dust removal efficiency (DB) serves as the internationally acknowledged evaluation criterion.

Results unveil that WKM800 and KB800 possessed 41.3% and 42.8% carbon content, respectively, with ash content at 30.4% and 29.3%, separately. These findings signify that mere carbonization falls short. However, after being subjected to pure water washing, the carbon content of WKM800-WT surged to 66.7%, while that of KB800-WT increased to 69.0%, and their ash content plummeted to 16.5% and 21.1%, respectively. Post-washing, the quality of MBC rivals that of raw coal extracted from South Africa, Australia, and Russia.

Following acetic acid or CO₂ aeration washing, the carbon content of

WKM800-AA and WKM800-CO₂ elevated to 79.1% and 80.1%, respectively, whereas those of KB800-AA and KB800-CO₂ reached 81.9% and 79.5%, respectively. Furthermore, the ash content of WKM800-AA decreased to 7.5%, that of WKM800-CO₂ decreased to 6.4%, KB800-AA to 9.8%, and KB800-CO₂ to 11.8%. As delineated in Table 2.3, after treatment with acetic acid aqueous solution or CO₂, MBC performance slightly lags behind that of coke produced in Japan but outperforms most coal samples obtained globally.

Table 2.3. Ultimate analysis of MBCs and comparison with commercial coke used in industry (db, dry basis). [1]

Sample	Source	Ultimate analysis [mass%, db]				Ash [mass%, db]	Reference
		C	H	N	O _{diff}		
WKM800	Marine biomass (Japan)	41.3	0.0	1.7	26.6	30.4	This study
WKM800-WT	Marine biomass (Japan)	66.7	1.0	3.4	12.4	16.5	This study
WKM800-AA	Marine biomass (Japan)	79.1	0.4	2.0	11.0	7.5	This study
WKM800-CO ₂	Marine biomass (Japan)	80.1	0.4	2.0	11.1	6.4	This study
KB800	Marine biomass (Japan)	42.8	1.0	1.8	25.1	29.3	This study
KB800-WT	Marine biomass (Japan)	69.0	0.5	0.5	8.9	21.1	This study
KB800-AA	Marine biomass (Japan)	81.9	0.3	0.6	7.4	9.8	This study
KB800-CO ₂	Marine biomass (Japan)	79.5	0.2	0.5	8.0	11.8	This study
Coal (pristine)	Azeiskoe Coal (Russia)	62.4	4.2	1.1	--	--	[19]
Coal (pristine)	Australia	63.8	2.3	1.1	22.8	10.0	[20]
Coke	Australia	67.4	0	0.3	14.6	17.7	[20]
Coal (pristine)	Cordoba Coal (Colombia)	64.8	5.2	2.0	28.1	--	[21]
Coal (pristine)	Loy Yang Coal (Australia)	65.7	4.7	0.6	26.1	3.3	[22]
Coal (Sulphuric Acid Wached)	Loy Yang Coal (Australia)	64.0	4.9	0.7	27.9	2.0	[22]
Coke	Nippon Steel Co. (Japan)	86.2	0.4	1.0	0.0	12.0	[22]
Coal (pristine)	South Africa	66.8	3.7	1.7	7.6	18.0	[23]
Coal (pristine)	Scotland	78.8	4.9	1.7	8.8	4.8	[23]
Coal (pristine)	UK	75.6	4.8	1.7	6.5	9.3	[23]
Coal (pristine, mean)	The United Arab Emirates	72.3	5.0	2.2	--	11.7	[24]

db: Dry basis

Table 2.4 presents the purity of the intrinsic carbon framework in MBC based on dry ash-free (daf) analysis. The data vividly showcase the impact of acetic acid washing and CO₂ aeration washing on carbon derived from WKM, exhibiting an achievable carbon content of up to 85%. Moreover, carbon derived from KB reaches an impressive high carbon content of around 90%. This high-purity MBC material surpasses the coal grades of most mining areas, including countries with well-established steel industries in Europe, China (the largest global iron producer), Indonesia, and Australia (the largest coal exporter). These findings highlight that MBC bears a similar chemical composition to industrial coke, indicating the potential for its further development and application.

Table 2.4. Ultimate analysis of MBCs and comparison with commercial coke used in industry (daf, dry ash-free basis).[1]

Sample	Source	Ultimate analysis [mass%, daf]				Ash [mass%, db]	Reference
		C	H	N	O _{diff}		
WKM800-AA	Marine biomass (Japan)	85.5	0.4	2.2	11.9	7.5	This study
WKM800-CO ₂	Marine biomass (Japan)	85.6	0.4	2.1	11.9	6.4	This study
KB800-AA	Marine biomass (Japan)	90.8	0.3	0.7	8.2	9.8	This study
KB800-CO ₂	Marine biomass (Japan)	90.1	0.2	0.6	9.1	11.8	This study
Coal (pristine)	Australia	83.5	4.8	1.8	8.5	8.1	[25]
Coal (pristine)	Australia	91.4	3.8	1.9	2.2	9.8	[25]
Coal (pristine)	Australia	78.1	4.3	1.1	16.2	21.4	[25]
Coal (pristine)	Roto South Coal (Indonesia)	69.0	4.3	0.3	26.4	2.6	[26]
Coal (extracted)	Roto South Coal (Indonesia)	87.9	4.3	0.0	7.9	0.1	[26]
Coal (pristine)	Pingshuo Coal (China)	79.8	5.6	1.4	12.6	18.5	[27]
Coal (pristine)	Shenfu Coal (China)	79.8	4.7	1.1	13.9	6.3	[27]
Coal (pristine)	Geting Coal (China)	82.0	5.5	1.6	10.5	10.3	[27]
Coal (pristine)	Datong Coal (China)	82.4	4.4	0.9	9.9	16.1	[28]
Coal (pristine)	Upper Silesian Coal (Poland)	88.7	5.4	1.9	4.0	7.2	[28]
Coal (pristine)	Upper Silesian Coal (Poland)	86.2	5.5	2.2	6.1	5.0	[28]
Coal (pristine)	Upper Silesian Coal (Poland)	82.7	6.0	2.5	8.8	7.7	[28]
Coal (pristine, mean)	Kentucky (USA)	82.3	5.4	--	8.0	--	[29]
Coal (pristine)	USA	91.1	4.7	1.2	2.7	5.1	[30]
Coke	USA	96.5	0.6	1.6	1.2	11.0	[30]

daf: Dry ash-free basis

db: Dry basis

2.4. Conclusion

The main objective of this study was to enhance the multifunctionality of MBC by exploring a direct treatment method for pyrolyzing marine biomass (MB) in industrial settings and purifying the derived carbon. The research comprehensively analyzed elemental composition shifts and crystal structure changes observed during conversion from MB to MBC, introducing the innovative use of CO₂ aeration method for efficient MBC purification. Comparison with major coal and coke samples at the global scale provided crucial insights into advancing MBC functionalization. The primary conclusion drawn from these findings is as follows:

MB, as a carbon-rich raw material, boasts advantages such as rapid growth, wide availability, renewability, high yield, and minimal environmental impact during extraction. Thermogravimetric analysis results indicated slightly higher carbon yields post-pyrolysis compared to the results obtained for traditional biomass, yet substantial weight loss was observed at 800–1000 °C. The XRD and XRF analyses confirmed the presence of significant amount of AAEM in MBC, with partial vaporization and evaporation of alkali metal salts at high temperatures (800–1000 °C), impacting MBC quality due to their catalytic effect on the carbon framework.

Utilizing simple, cost-effective, and environmentally friendly methods such as acetic acid washing and CO₂ aeration effectively eliminated

AAEMs from MBC. Comparative analysis showcased that treated MBC exhibited superior carbon and ash content, surpassing most coal (including specific coke types) from major coal-producing regions globally, both on a dry and dry ash-free basis.

In essence, this comprehensive investigation into MBC pyrolysis processes, coupled with straightforward post-treatment methods to remove AAEMs, has substantially elevated attributes of MBC and unveiled immense potential for industrial applications.

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Appendix for Chapter 2

The efficiency of washing processes, including solution concentration, temperature variations, solid-to-liquid ratio, and repeated cycles, significantly impacts the overall effectiveness of the washing method. To identify optimal washing conditions, initial experiments encompassing various parameters were conducted in this study.

Initially, the impact of solution concentration, temperature, and number of repetitions on the removal efficiency of AAEM from MBC were systematically in this study, and the corresponding results are summarized in Table A2.1. The findings reveal that a 1 mass% concentration of acetic acid led to substantial removal of AAEM, indicating its effectiveness at this lower concentration, even compared to vinegar, which typically ranges between 5–8%. Moreover, for further investigation of the CO₂-aerated water washing method, WKM800 was utilized as a representative sample to assess the influence of temperature and repetition cycles. Surprisingly, washing at ambient temperature (25 °C) and a single cycle exhibited results comparable to those at higher temperatures and under multiple washings. Considering the balance between additional expenses and industrial benefits, the experimental conditions employed in this study were employed due to their promising outcomes.

Table A2.1. XRF elemental compositions of MBC after acetic acid aqueous solution washing at different concentrations or CO₂-aerated water washing at different temperatures or repeat counts [mass%].

Sample	CHO	AAEMs and other elements						
		Na	Mg	K	Ca	P	S	Cl
WKM800-AA-0.5%	92.9	0.3	2.9	0.0	2.2	0.4	1.0	0.1
WKM800-AA-1%	93.1	--	1.8	0.0	2.0	0.3	2.4	0.1
WKM800-AA-2%	94.5	0.1	1.9	0.0	1.6	0.3	1.3	0.1
WKM800-AA-3%	93.7	--	1.7	0.1	1.5	0.3	2.3	0.3
WKM800-AA-5%	94.5	--	1.7	0.1	1.3	0.3	1.8	0.3
WKM800-AA-10%	94.5	0.1	1.4	0.1	1.5	0.3	1.8	0.2
KB800-AA-0.5%	92.1	0.3	2.7	0.0	2.3	0.3	2.0	0.1
KB800-AA-1%	95.4	--	1.7	0.0	1.1	0.2	1.2	0.1
KB800-AA-2%	95.2	--	1.6	0.0	1.4	0.3	1.1	0.1
KB800-AA-3%	94.5	--	1.7	0.0	1.3	0.2	1.8	0.2
KB800-AA-5%	95.5	--	1.5	0.0	1.1	0.3	1.2	0.2
KB800-AA-10%	95.3	--	1.6	0.0	1.2	0.2	1.4	0.1
WKM800-CO ₂ -25°C	94.5	0.1	2.1	0.0	1.7	0.3	1.2	--
WKM800-CO ₂ -60°C	94.7	--	1.2	0.0	1.4	0.6	1.9	0.1
WKM800-CO ₂ -80°C	95.1	--	1.7	0.0	1.1	0.3	1.6	0.1
WKM800-CO ₂ -1 st	94.5	0.1	2.1	0.0	1.7	0.3	1.6	--
WKM800-CO ₂ -2 nd	95.0	--	1.2	0.0	1.1	0.5	1.9	0.1
WKM800-CO ₂ -4 th	95.5	--	1.5	0.0	0.8	0.3	1.7	0.1

--: Undetected.

Herein, the solid-to-liquid ratio was established based on the solubility of Mg in excess CO₂. Specifically, the solubility of Mg(HCO₃)₂ in water at 25 °C and pH = 6.5 is 0.077 g/100 mL. The ratio of atomic mass of Mg to the relative molecular mass of Mg(HCO₃)₂ is 0.16, resulting in a concentration of soluble Mg element in the Mg(HCO₃)₂ solution environment being 0.012 g/100 mL. Given the maximum Mg content in

MBC at 4 wt.%, the theoretical solid-to-liquid ratio stands at MBC/solution = 3g/1L. Based on this theoretical calculation, the preliminary experiments outlined in Table A2.2 was designed herein.

In the sample code, the suffix “1:1” refers to “1 gram of carbon per 1 liter of liquid”. The results indicate that maintaining a solid-to-liquid ratio up to 1:1 (WKM800-CO₂-1:1) sustains the removal efficiency of hetero-elements from MBC through CO₂ washing. Although theoretically, 3:1 would be optimal, the complete dissolution of AAEM is hindered by the pore structure and surface functional groups of MBC. Consequently, this study ultimately adopted a solid-to-liquid ratio of 1:1. To ensure a fair comparative analysis among the three methods, the solid-to-liquid ratio, washing time, frequency, and temperature were standardized across all experiments.

Table A2.2. XRF elemental compositions of MBC after CO₂ washing at different solid/liquid ratios [mass%].

Sample	CHO	AAEMs and other elements						
		Na	Mg	K	Ca	P	S	Cl
WKM800-CO ₂ -0.5:1	94.6	--	2.0	0.0	1.6	0.4	1.3	0.1
WKM800-CO ₂ -1:1	94.5	0.1	2.1	0.0	1.7	0.3	1.2	--
WKM800-CO ₂ -2:1	93.9	0.1	2.5	0.0	1.6	0.4	1.4	0.1
WKM800-CO ₂ -3:1	93.5	0.1	2.4	0.0	1.9	0.3	1.7	0.1
WKM800-CO ₂ -5:1	92.6	0.2	2.4	0.1	2.3	0.5	1.9	--

--: Undetected.

Chapter 3.

MBC pore-blocking effects removal to release pore structure for further functionalization [1]

3.1. Introduction

To further advance the functionalization of marine biomass carbon (MBC), exploration of additional potential applications is crucial. Among various functional carbon materials, activated carbon (AC) stands out as a prime porous material. Being a well-established industrial product, AC possesses distinct traits such as highly developed pores, large specific surface area (SSA), robust adsorption capabilities, and stable physicochemical properties. It exhibits the ability to undergo desorption and regeneration after usage failure, making it an excellent candidate for industrial applications, such as an exceptional adsorbent, an effective catalytic carrier, filler, and as other functional materials.

Selecting AC as the next functional direction for MBC stems from its broad theoretical applicability to carbon-rich organic materials, encompassing raw coal, petroleum products, biomass, among others. Industrial sources of AC include anthracite, asphalt, wood, bamboo, coconut shells, olive shells, almond shells, etc. This universal nature of carbon sources indicates a strong feasibility for the development of AC from MBC. Moreover, AC finds extensive use across diverse sectors such

as food, beverages, medicine, water treatment, gas purification and recovery, chemical industry, environmental protection, metallurgy, national defense, agriculture, and so on. The substantial market potential ensures a robust market presence for AC derived from MBC.

Furthermore, although the quantity may not be substantial, prior studies have reported on the application of AC derived from MBC in advanced domains, demonstrating its excellent performance. For instance, Boubakri et al. [2] produced AC from MB via a chemical activation process, and observed a microstructure featuring nanoscale hollow spheres through characterization. Remarkable results were achieved for adsorption of heavy metals from water. In the realm of chemical energy storage, Pourhosseini et al. [3] utilized seaweed as a raw material to create highly ordered microporous/macroporous AC employing slow pyrolysis and robust acid activation technology, which provided outstanding energy storage effects.

However, current research on AC production from MB is constrained by expensive activation methods tailored for specific MB species, thus limiting their widespread industrial applications. As previously outlined, high-energy physical activation or chemical activation stands as the prevailing active method. Yet, the wastewater discharge and equipment corrosion associated with these methods no longer align with the current trend toward carbon neutrality and burgeoning requirements of green

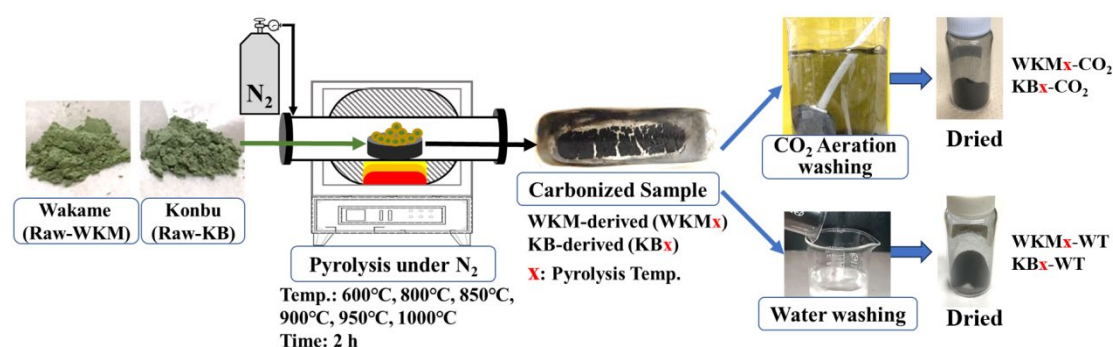
industry. Despite some advanced methods such as the hard template method and soft template method being available for crafting microporous and mesoporous AC [4, 5], their reliance on expensive raw materials and intricate, energy-intensive synthesis steps deviates from industrialization principles and pose significant challenges for large-scale implementation. Therefore, the pivotal challenge for MBC lies in maneuvering the pore structure at a low cost, navigating the activation process, and tailoring it for various green industrial applications [6, 7].

In essence, this chapter primarily delves into exploring the structural alterations on the surface of MBC under diverse pyrolysis temperatures, and endeavors to devise a straightforward, efficient, and eco-friendly activation method to transform MBC into AC. The objective is to confer upon it a substantial SSA and porosity, to advance the functionalization of MBC.

3.2. Experimental

3.2.1. Preparation of marine biogenic carbon and porous MBC

In this study, two prevalent types of seaweed commonly found along the coast of Japan, namely, Luminaria (Kombu, KB) and Undaria (WKM Undaria), were used as the primary raw materials. All the MB samples utilized in this investigation were generously provided by Nippon Steel. The preparation process, outlined in Scheme 1, unfolds across the three key stages:



Scheme 1. Preparation and impurity removal process of MBCs.[1]

1) Drying and Powdering: Raw materials were dried at 90 °C, and then ground to achieve a particle size of 250 μm or less, and denoted as Raw WKM and Raw KB, respectively.

2) Carbonization: The powder obtained from the previous step was subjected to carbonization, a thermal decomposition process, by heating in the N₂ atmosphere. Carbonization temperatures ranged from 600 to 1000 °C, with a processing duration of 2 h. The resulting carbonized

samples are designated as WKMx and KBx, where $x = 600, 800, 850, 900, 950, \text{ or } 1000$ °C, signifying their respective carbonization heat treatment temperatures (in °C).

3) Impurity Removal: Samples from step (2) were subjected to impurity removal through water washing or CO₂ aeration.

Water Washing Method: WKMx or KBx (0.5 g) was dispersed in deionized water (500 mL), stirred for 2 h, filtered, and dried completely at 90 °C. Samples derived via this method are labeled as WKMx WT and KBx WT, respectively.

CO₂ Aeration Method: CO₂ gas was introduced into water at a flow rate of $100 \text{ mL} \cdot \text{min}^{-1}$ during the stirring process, following the steps similar to those used in the water washing method. The resulting samples are designated as WKMx CO₂ and KBx CO₂.

Elemental composition analysis of the Raw-WKM and Raw-KB materials was conducted through CHN analysis using a CHN encoder (MT-5, Yanako, Kyoto, Japan). The composition details are as follows:

Raw WKM: Carbon: 31.6%; Hydrogen: 5.3%; Nitrogen: 1.9%; Ash content: 8.7% (mass fraction wt.%);

Raw KB: Carbon: 31.6%; Hydrogen: 5.4%; Nitrogen: 1.5%; Ash content: 8.7% (mass fraction wt.%).

3.2.2. Characterization of MBC and porous MBC

The microstructure of the sample was observed by scanning electron microscopy (SEM) system (JSM-6700F; JEOL, Japan) equipped with an energy-dispersive X-ray spectroscopy (EDS) system (SmartEDx, Oxford Instruments, UK). The thermal decomposition process of the raw materials during sample preparation was analyzed through thermogravimetric analysis (TGA) using a TG analyzer (German NETZSCH STA2500 Regulus). The composition of the sample was analyzed by X-ray fluorescence (XRF; ZSX Primus IV/RX9, Rigaku, Japan). A nitrogen adsorption/desorption test was conducted on the sample using a nitrogen adsorption analyzer (Nova 2000E Anton Paar Quantachrome Instruments, USA) at 77 K, and the nitrogen adsorption/desorption isotherms of the sample were obtained. By using the isotherm data, the SSA of the sample was calculated by the S-plot method [8, 9]. The pore size distribution (PSD) and pore volume data of the sample were calculated by using non-local solid density functional theory (NLDFT) [10] (assuming that the pores were slit shaped).

3.3. Results and analysis

3.3.1. Initial assessment of intrinsic porosity in MBC using WKM600 and WKM600-WT

To initiate the investigation, we opted for examining low-temperature carbonized MB (WKM600) and its washed counterpart (WKM600-WT) as the primary test samples. Figure 3.1. portrays the nitrogen adsorption and desorption isotherms of WKM600 and WKM600-WT at 77 K.

The results indicate that the adsorption curve of the carbonized sample, WKM600, runs almost parallel, displaying nearly negligible adsorption capacity, signifying the absence of a discernible pore structure. However, post-washing, WKM600-WT reveals notable N₂ adsorption capacity, showcasing the presence of both micropores and mesopores. This accentuates the inherent pore structure characteristic of MBC. Moreover, the mere act of water washing transformed these latent pores into open ones, indicating that water-soluble components in MBC might have obstructed these pores.

Previous studies have indicated that satisfactory pore structure in MB is achievable through high-temperature pyrolysis. Nonetheless, the MB raw material, when washed with water, loses its ability to form pores during subsequent pyrolysis [2]. This observation strongly indicates that water-soluble elements within MB contribute to pore formation. However, the precise mechanism behind pore formation in WKM600 and the newly

discovered pore-blocking effect remains unclear at present.

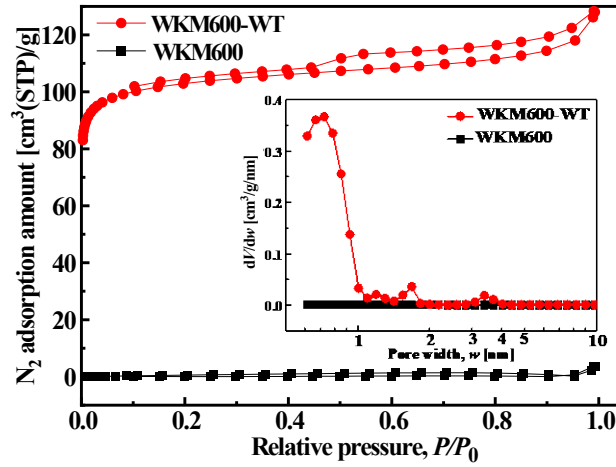


Figure 3.1. N₂ adsorption and desorption isotherms at 77 K for low-temperature (600 °C)-carbonized WKM before and after water washing. Inset: NLDFT PSD. [1]

3.3.2. Analysis of Pore Structure in MBC

The pursuit of a robust porous structure in MBC has led to the systematic exploration via direct pyrolysis, aiming to position MBC as an industrial porous carbon material with a low environmental impact. This study scrutinizes the preliminary inspection outcomes, particularly focusing on pyrolysis temperatures and washing techniques to unravel the inherent porous nature of MBC and explore the mechanisms shaping pore formation and blockage.

Figures 3.2 and 3.3 exhibit N₂ adsorption and desorption isotherms of MBC samples across carbonization temperatures ranging from 800 to 1000 °C and post-washing at 77 K. Among these samples, WKM800 displays limited adsorption capacity, signifying poor porosity. In contrast, other samples exhibit typical Type I isotherms [9], accompanied by H4

hysteresis loops, which are characteristic of microporous materials such as molecular sieves and microporous carbons. These isotherms indicate rapid adsorption at lower relative pressures (P/P_0) and reach an adsorption saturation at a certain P/P_0 . The observed H4 hysteresis loop ($P/P_0 = 0.45–0.90$) indicates the existence of mesopores.

Across varied carbonization temperatures or types of raw biomass, newly carbonized samples consistently exhibited the lowest N_2 saturation adsorption capacity, followed by water-washed samples, and the highest was for the CO_2 -aerated water-washed samples. The SSA calculations via the S-plot method clarify the changes in the pore structure. In Figure 3.2(f), the blue curve demonstrates that SSA of the carbonized MB sample (WKMx) increases with elevated carbonization temperature. This signifies the formation of more pore structures via pyrolysis, partially mitigating pore blockage effects. Post-washing, the overall increase in SSA indicates the removal of water-soluble pore-blocking substances (red curve in Figure 3.2(f)), revealing the presence of intrinsic pores in MBC as observed previously. However, extremely high temperatures might lead to shrinkage or collapse of existing pore structures. After CO_2 aeration and water washing, the SSA of any WKMx CO_2 sample further increased (green curve in Figure 3.2(f)), indicating that water washing reveals intrinsic pores, while CO_2 aeration and water washing liberate deeper pore structures. Similar trends in SSA were noted in carbonized KB samples (Figure 3.3).

Notably, KBx CO₂ showed the highest SSA within the carbonization temperature range of 850–950 °C.

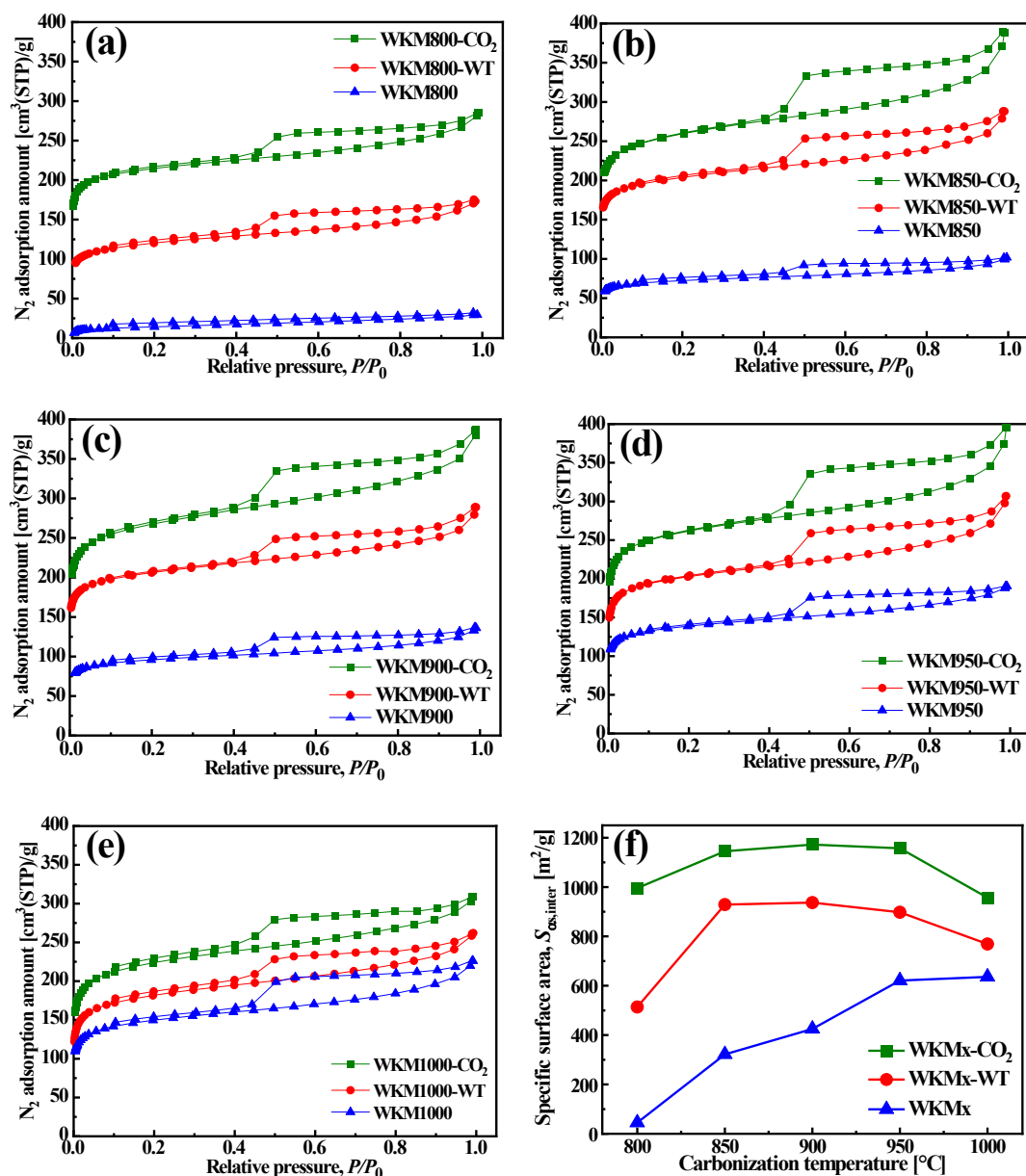


Figure 3.2. N₂ adsorption and desorption isotherms at 77 K for WKMx, WKMx-WT, and WKM-CO₂ prepared at different carbonization temperatures: (a) 800 °C, (b) 850 °C, (c) 900 °C, (d) 950 °C, and (e) 1000 °C. (f) Comparison of internal SSA estimated by the α s-plot method for all WKM-derived samples. [1]

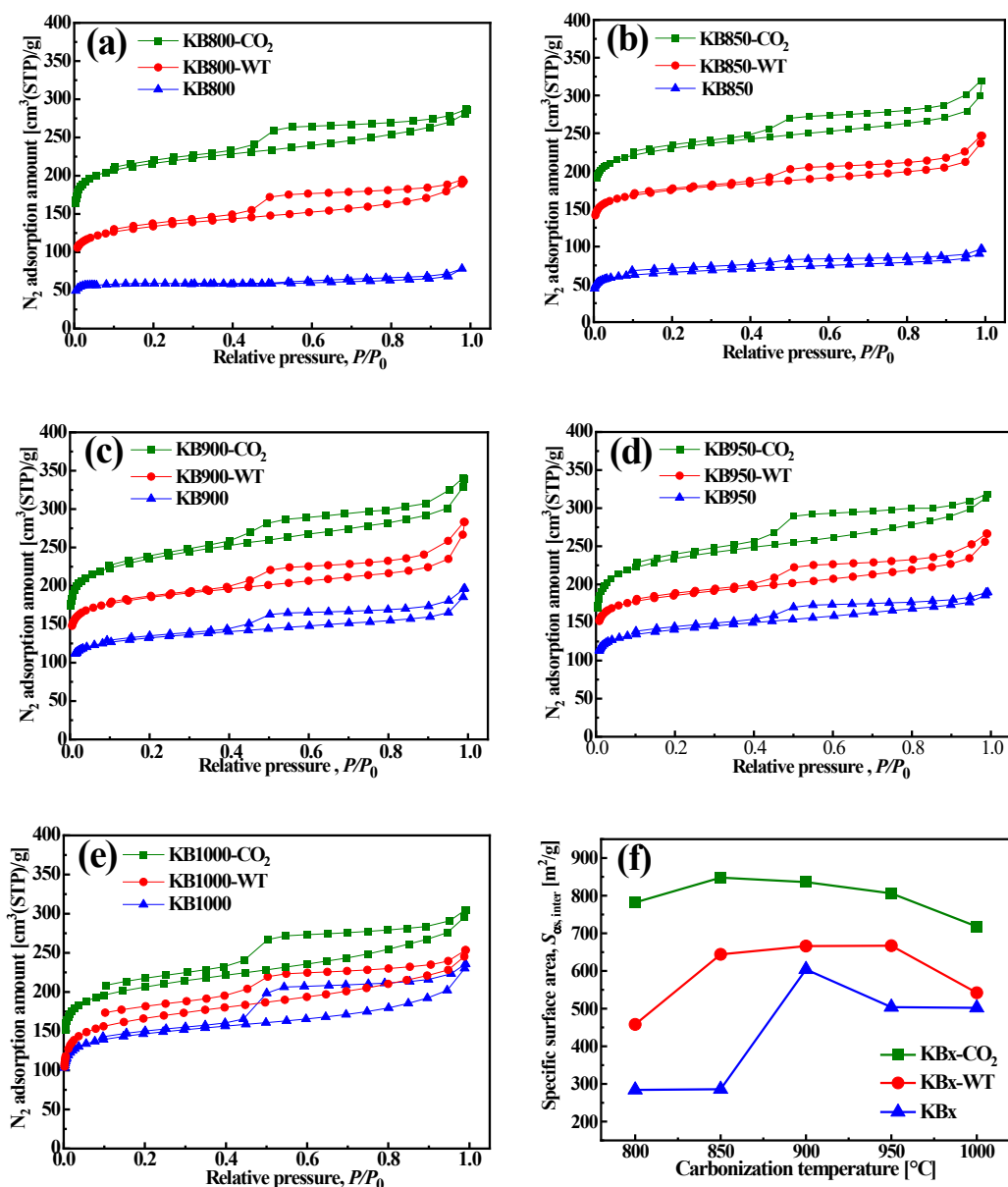


Figure 3.3. N_2 adsorption and desorption isotherms at 77 K for KBx, KBx-WT, and KB-CO₂ prepared at different carbonization temperatures: (a) 800 °C, (b) 850 °C, (c) 900 °C, (d) 950 °C, and (e) 1000 °C. (f) Comparison of internal SSA estimated by the α_s -plot method for all KB-derived samples. [1]

Tables 3.1 and 3.2 present the computed SSA and total pore volume (V_{total}). The V_{total} order aligned consistently with SSA across different carbonization temperatures or original MB types. The carbonized samples exhibited the lowest V_{total} , followed by water-washed samples, and finally, CO₂-aerated water-washed samples. For instance, carbonized WKM samples showcased a total pore volume of up to 0.31 cm³·g⁻¹, whereas water washing yielded a total pore volume of 0.41 cm³·g⁻¹. Following CO₂ aeration washing, the total pore volume further peaked at 0.54 cm³·g⁻¹. Notably, although MBC produced at 1000 °C displayed the highest V_{total} and SSA, samples carbonized between 900–950 °C showed the highest values post water or CO₂ aeration washing. This highlights 900–950 °C as the optimal temperature range for inherent pore creation through pyrolysis. Similar conclusions were drawn for carbonized KB samples (Table 3.2).

Considering the pore volume ratio, MBC predominantly comprises microporous material, primarily with a micropore size of less than 2 nm. The average volume ratio of micropores (V_{micro}/V_{total}) surpasses 60%, with a maximum of 72%, signifying a high concentration of micropores. For instance, WKM900-CO₂ exhibited a V_{micro} of 0.34 cm³·g⁻¹, accompanied by the highest internal SSA (S) of 1172 m²·g⁻¹. KB also falls within the realm of microporous materials. Considering KB850-CO₂ as an example, its V_{micro}/V_{total} reaches 72%, with the highest V_{micro} of 0.31 cm³·g⁻¹ and an SSA of 848 m²·g⁻¹. These subtle disparities in optimal carbonization temperatures between WKM and KB, despite both being algae, may arise due to slight differences in morphology or elemental composition, ultimately impacting the maximization of MBC-derived porosity.

Table 3.1. Pore structural parameters estimated from N₂ adsorption isotherms at 77 K for WKM-derived samples. [1]

Samples	$S_{as,total}$ [m ² /g] ^a	$S_{as,inter}$ [m ² /g] ^b	V_{total} [cm ³ /g] ^c	V_{micro} [cm ³ /g] ^d	V_{micro}/V_{total} [%] ^e
WKM800	48	45	0.04	0.02	50
WKM850	330	322	0.14	0.10	71
WKM900	436	425	0.19	0.13	68
WKM950	633	621	0.26	0.18	69
WKM1000	657	636	0.31	0.19	61
WKM800-WT	536	514	0.24	0.15	62
WKM850-WT	949	929	0.39	0.26	67
WKM900-WT	958	937	0.39	0.27	69
WKM950-WT	922	898	0.41	0.25	61
WKM1000-WT	792	769	0.36	0.23	64
WKM800-CO ₂	1014	996	0.39	0.28	72
WKM850-CO ₂	1177	1145	0.53	0.32	60
WKM900-CO ₂	1198	1172	0.53	0.34	64
WKM950-CO ₂	1189	1157	0.54	0.32	59
WKM1000-CO ₂	980	957	0.42	0.29	69

^a $S_{as,total}$: Total SSA obtained by the α_s -plot method.

^b $S_{as,inter}$: Internal SSA calculated from the following equation, $S_{as,inter} = S_{as,total} - S_{as,exter}$, where external SSA ($S_{as,exter}$) was calculated by the α_s -plot method.

^c V_{total} : Total pore volume obtained by the NLDFT method.

^d V_{micro} : Micropore volume obtained by the NLDFT method.

^e V_{micro}/V_{total} : Micropore volume ratio.

Table 3.2. Pore structural parameters estimated from N₂ adsorption isotherms at 77 K for KB-derived samples. [1]

Samples	$S_{as,total}$ [m ² /g] ^a	$S_{as,inter}$ [m ² /g] ^b	V_{total} [cm ³ /g] ^c	V_{micro} [cm ³ /g] ^d	V_{micro}/V_{total} [%] ^e
KB800	290	284	0.10	0.08	80
KB850	294	286	0.13	0.09	69
KB900	616	604	0.26	0.17	65
KB950	511	504	0.26	0.19	73
KB1000	522	502	0.32	0.18	56
KB800-WT	477	458	0.27	0.17	63
KB850-WT	657	644	0.33	0.23	70
KB900-WT	683	666	0.38	0.24	63
KB950WT	682	667	0.36	0.24	67
KB1000-WT	556	542	0.34	0.23	68
KB800-CO ₂	795	782	0.40	0.29	72
KB850-CO ₂	860	848	0.43	0.31	72
KB900-CO ₂	853	836	0.46	0.30	61
KB950-CO ₂	827	806	0.44	0.30	68
KB1000-CO ₂	735	718	0.42	0.28	67

^a $S_{as,total}$: Total SSA obtained by the α S-plot method.

^b $S_{as,inter}$: Internal SSA calculated from the following equation, $S_{as,inter} = S_{as,total} - S_{as,exter}$, where external SSA ($S_{as,exter}$) was calculated by the α S-plot method.

^c V_{total} : Total pore volume obtained by the NLDFT method.

^d V_{micro} : Micropore volume obtained by the NLDFT method.

^e V_{micro}/V_{total} : Micropore volume ratio.

Figures 3.4 and 3.5 display the PSD curves of carbonized WKM and KB samples. The distinct peak at around 1.1–1.4 nm and the relatively subtle peak at 1.9–2.0 nm indicates the existence of micropores, while the prominent peak at 3.8–3.9 nm signifies the presence of mesopores. The layered porous structure of MBC positions it as a promising material for diverse industrial applications. For instance, micropores serve as active sites for catalysis, electrochemical energy storage, and various reactions, while mesopores facilitate multiphase flux and electron transfer processes.

An important observation is the enhanced prominence of micropores and mesopores in MBC following water washing and CO₂ aeration washing. It indicates that although both micropores and mesopores are inherently formed during MB carbonization, the channels for N₂ molecules to access these pores are obstructed by water-soluble impediments.

Drawing from substantial pore structure data, it is plausible to infer that surface etching reactions crucial for pore formation occur during MB carbonization, with the intensity contingent on the carbonization temperature. Simultaneously, unidentified water-soluble substances introduce pore-blocking effects, which can be mitigated through washing methods to unveil intrinsic porous structure of MBC. The next phase involves further exploration of the mechanisms and relevant factors influencing pore formation, employing characterization techniques such as XRF, TGA, and SEM-EDS.

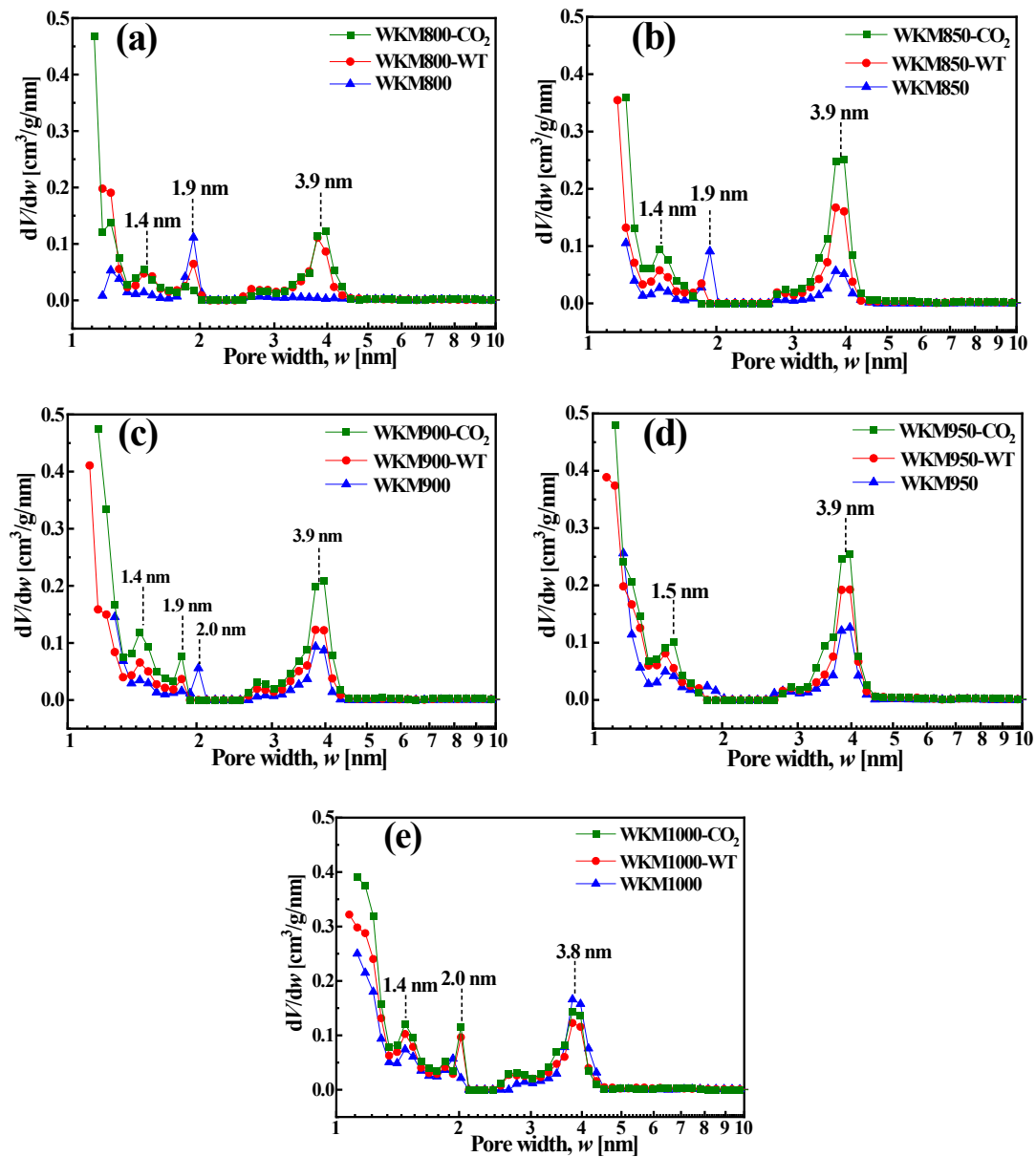


Figure 3.4. Pore size distribution of WKMx, WKMx-WT, and WKM-CO₂ prepared at different carbonization temperatures: (a) 800 °C, (b) 850 °C, (c) 900 °C, (d) 950 °C, and (e) 1000 °C. [1]

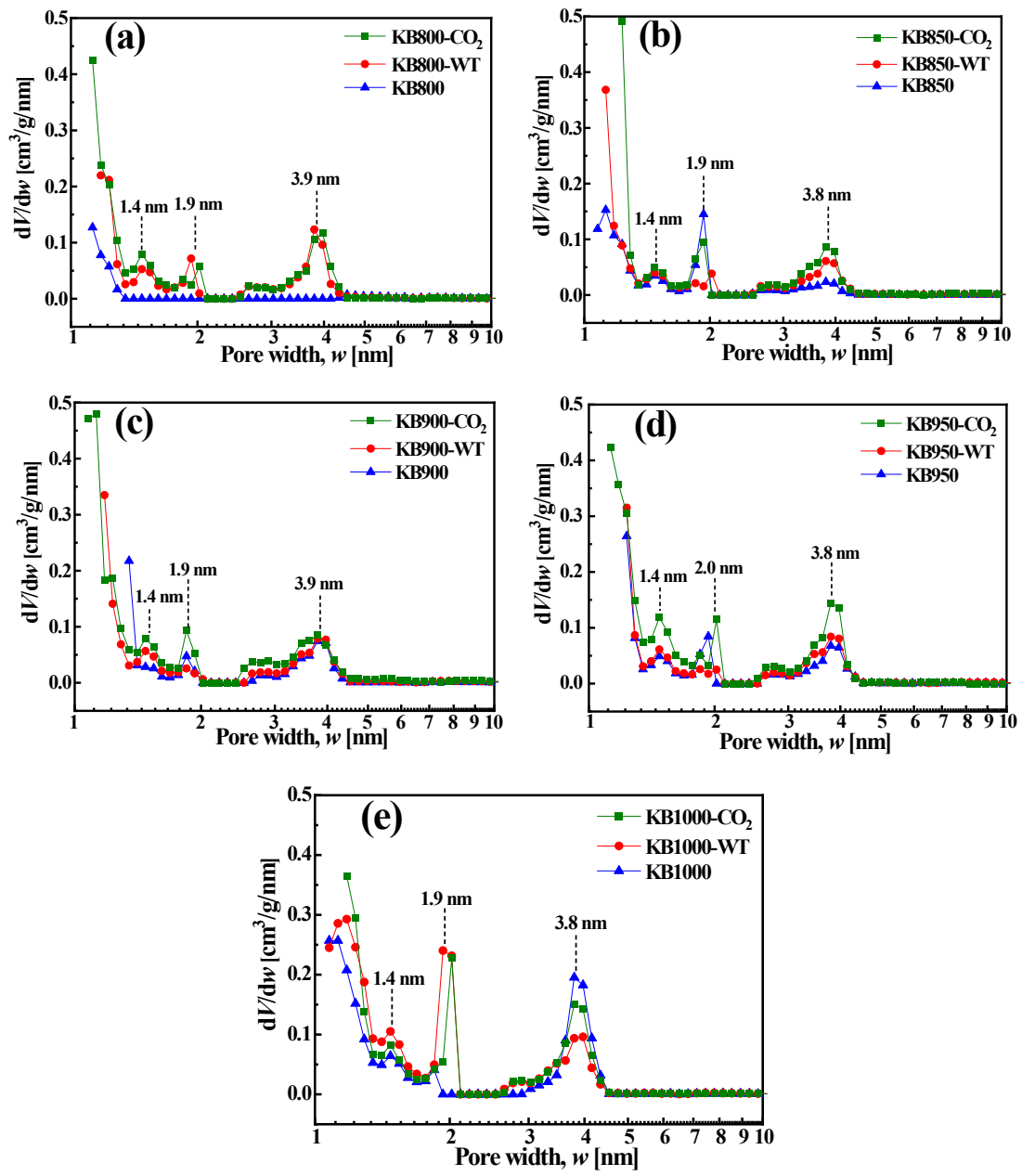


Figure 3.5. Pore size distributions of KBx, KBx-WT, and KB-CO₂ prepared at different carbonization temperatures; (a) 800 °C, (b) 850 °C, (c) 900 °C, (d) 950 °C, and (e) 1000 °C. [1]

3.3.3. Exploring the genesis and unveiling mechanisms of intrinsic pores in MBC

TGA offers valuable insights into the thermal degradation traits of raw materials and pyrolysis products at diverse temperatures. Within the 400 °C range, Raw WKM and Raw KB display notable mass reduction due to the thermal breakdown of organic components, such as alginate (Figure 3.6). However, no discernible mass loss is observed in MBC within this temperature range. At elevated temperatures, in particular, at temperature exceeding 800 °C, substantial mass loss occurs in all samples except in WKM1000, KB950, and KB1000. With increasing carbonization temperatures, the mass loss at higher temperatures diminishes, culminating in nearly no mass reduction for WKM1000, KB950, and KB1000 samples. It indicates complete evaporation of impurities in WKM between 950 and 1000 °C, while impurities in KB evaporate between 900 and 950 °C.

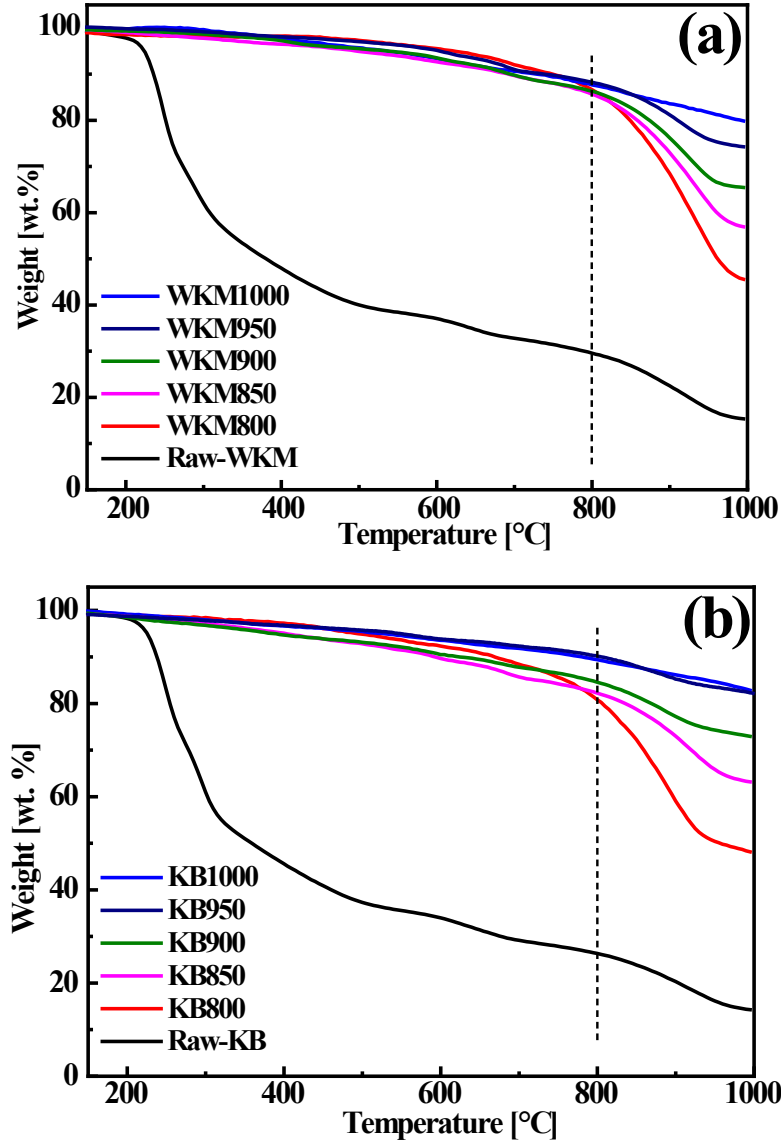


Figure 3.6. TG curves in N_2 of (a) Raw-WKM and carbonized WKM samples, and (b) Raw-KB and carbonized KB samples. [1]

To gain a comprehensive insight into the impurities expelled during the carbonization process, XRF elemental analysis has been proven to be pivotal. This analysis offers quantitative insights into the shifting of the material composition concerning carbonization temperatures. Table 3.3 illustrates that carbonized WKM samples feature a rich impurity profile, primarily comprising sodium (Na), magnesium (Mg), potassium (K),

calcium (Ca) (alkali and alkali earth metals; AAEMs), and chlorine (Cl). These diverse elements are inherent in the original WKM (Table 3.3). With the escalation of the carbonization temperature, the Na and Cl content in MBC derived from WKM gradually diminishes. When the temperature hits 1000 °C (WKM1000), the Na and Cl content declines substantially from 8.7 and 6.1 mass% of WKM800 to 0.4 and 1.0 mass%, respectively. The K element content remains almost steady at 950 °C. Moreover, the trends of Mg and Ca content at higher carbonization temperatures reveal an increase, which occurs as a relative change. That is, the decrease in the content of other elements leads to a marked surge in Mg and Ca content. Similar trends surface in the KB-derived samples, as detailed in Table 3.4. The XRF results confirm that the mass loss observed in TGA results above 800 °C stems from the gasification of Na, K, and Cl species.

The shifts in the content of these element align with the evolution of the intrinsic porous structure of MBC. Potassium compounds serve as effective activators for carbon materials [11] and are deemed crucial for micropore formation in the preparation of MBC. Conversely, NaCl and/or CaCl₂ may contribute to mesopore formation [12-15]. The evaporation of these elements at 850–950 °C leads to extensive etching reactions with the carbon surface, resulting in a profusion of pore structures.

These impurities not only foster the inherent porous structure of MBC as self-maintaining activator, but also induce pore-blocking effects. At a

carbonization temperature of 1000 °C, the evaporation of some pore-blocking material is evidenced by the significant decrease in Na, K, and Cl content in WKM1000 and KB1000 (Tables 3.3 and 3.4), partially unveiling potential pores, as observed through the increased pore structure parameters (Tables 3.1 and 3.2).

The findings from MBC washing bolster this hypothesis. A basic pure water washing method was initially employed to eliminate these minerals. Post-washing, the contents of Na, K, and Cl were almost negligible (Table 3.3), coupled with a notable increase in porosity across all WKM samples (WKMx WT) (Table 3.1). Similar outcomes were observed for KB-derived samples as well (Tables 3.2 and 3.4). However, the average content of Mg and Ca in the WKMx WT sample remained virtually unchanged after water washing. Similarly, the residual content of Mg and Ca in the carbon derived from KB (KBx WT) was also found to be substantial post-water washing. It indicates that Na, K, and Cl exist in water-soluble form and can be effectively removed by pure water washing, while Mg and Ca are impervious to this method.

Recent reports indicate that CO₂ aeration washing can effectively eliminate Mg and Ca compounds in MBC [16], offering an alternative to conventional mineral removal methods. Compared to pure water washing, the CO₂ aeration washing method exhibits higher efficiency in removing Mg and Ca compounds, owing to a chemical transformation from low-

solubility salts (such as hydroxides and carbonates) to high-solubility salts (bicarbonate) in the presence of excess CO₂. After CO₂ aeration washing, the Mg and Ca content of carbonized WKM samples reduced to an average of 1.4 and 1.5 mass%, respectively (see Table 3.3, WKMx CO₂), while those of carbonized KB samples decreased to 1.6 and 1.4 mass%, respectively (see Table 3.4, KBx CO₂), marking a substantial improvement. The operational simplicity of this process, devoid of additional chemical emissions, renders it cost-effective, environmentally friendly, and convenient. Furthermore, the thorough washing from CO₂ aerated water further eliminates pore-blocking effects, revealing more internal pores hidden within MBC (see Tables 3.1 and 3.2 for details). Overall, XRF analysis attests to the efficacy of water washing and CO₂ aeration washing methods in expelling pore-blocking minerals from MBC, thus enhancing the quality and purity of the final carbon product derived from MB.

Table 3.3. XRF elemental compositions of Raw-WKM, MBC, and treated MBC samples prepared from WKM [mass%].[1]

Sample	CHNO	Other elements						
		Na	Mg	K	Ca	P	S	Cl
Raw-WKM	84.5	5.4	1.2	1.3	1.5	0.2	0.7	5.0
WKM800	77.2	8.7	2.1	2.0	2.5	0.3	1.1	6.1
WKM850	76.1	8.3	2.4	2.1	2.9	0.3	1.2	6.7
WKM900	80.0	6.6	2.4	1.7	2.8	0.3	1.0	5.2
WKM950	80.2	4.6	3.3	2.0	3.9	0.5	1.5	4.0
WKM1000	87.6	0.4	3.5	1.4	4.1	0.5	1.5	1.0
WKM800-WT	90.6	--	4.1	0.1	3.1	0.6	1.3	0.2
WKM850-WT	90.5	0.1	4.0	0.1	3.7	0.5	1.0	0.1
WKM900-WT	90.3	0.1	3.9	0.1	3.3	0.6	1.3	0.1
WKM950WT	90.2	--	4.3	--	3.7	0.7	1.1	--
WKM1000-WT	91.2	--	4.1	--	3.1	0.4	1.2	--
WKM800-CO ₂	94.7	--	2.0	--	1.7	0.3	1.2	--
WKM850-CO ₂	95.5	--	1.0	--	1.3	0.5	1.7	--
WKM900-CO ₂	94.2	--	1.5	--	1.7	0.6	2.0	--
WKM950-CO ₂	95.5	--	1.1	--	1.3	0.5	1.6	--
WKM1000-CO ₂	95.4	--	1.4	--	1.2	0.2	1.8	--

--: Undetected.

Table 3.4. XRF elemental compositions of raw and carbonized samples of KB [mass%].[1]

Sample	CHNO	Other elements						
		Na	Mg	K	Ca	P	S	Cl
Raw-KB	88.3	3.0	1.1	1.6	1.6	0.1	0.9	3.4
KB800	74.7	7.9	2.2	3.4	3.1	0.2	1.6	6.9
KB850	79.6	5.8	2.2	3.0	3.3	0.2	1.5	4.4
KB900	81.3	2.7	3.3	3.0	4.6	0.3	2.2	2.6
KB950	81.2	1.7	3.9	3.0	5.5	0.3	2.6	1.8
KB1000	85.7	0.2	4.0	1.7	5.2	0.3	2.6	0.3
KB800-WT	89.7	0.1	3.7	0.1	4.2	0.5	1.6	0.1
KB850-WT	90.9	--	3.7	0.1	3.2	0.3	1.7	0.1
KB900-WT	90.5	--	3.8	0.1	3.0	0.3	2.2	0.1
KB950WT	90.0	--	4.5	0.1	2.3	0.4	2.6	0.1
KB1000-WT	91.7	--	3.8	--	2.3	0.5	1.6	0.1
KB800-CO ₂	94.3	--	1.9	--	1.4	0.3	2.0	0.1
KB850-CO ₂	94.2	--	1.8	--	1.3	0.3	2.2	0.1
KB900-CO ₂	94.6	--	1.7	--	1.5	0.3	1.7	0.1
KB950-CO ₂	95.0	--	1.6	--	1.4	0.3	1.5	0.1
KB1000-CO ₂	94.9	--	1.2	--	1.7	0.3	1.7	0.2

--: Undetected.

SEM-EDS analysis was conducted to validate the elimination of pore-blocking substances in MBC pre- and post-washing treatment. Figures 3.7(a) and 3.7(d) depict crystalline-like particles on the MBC surface. Following the washing process, a substantial reduction in these particles was evident, unveiling the porous surface of MBC (Figures 3.7(b) and 3.7(e)). Upon CO₂ aeration washing, minimal mineral particles were observed on the surface, revealing the distinct three-dimensional (3D) honeycomb structure of WKM and the multi-layer structure of KB, which became prominently visible (Figures 3.7(c) and 3.7(f)).

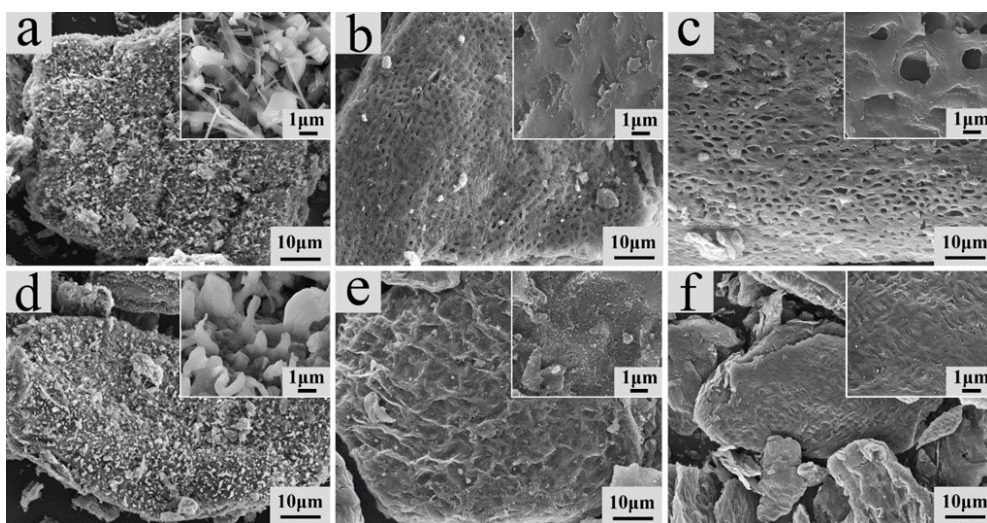


Figure 7. SEM images of: (a) WKM900, (b) WKM900-WT, (c) WKM900-CO₂, (d) KB900, (e) KB900-WT, and (f) KB900-CO₂. Inset: High magnification images. [1]

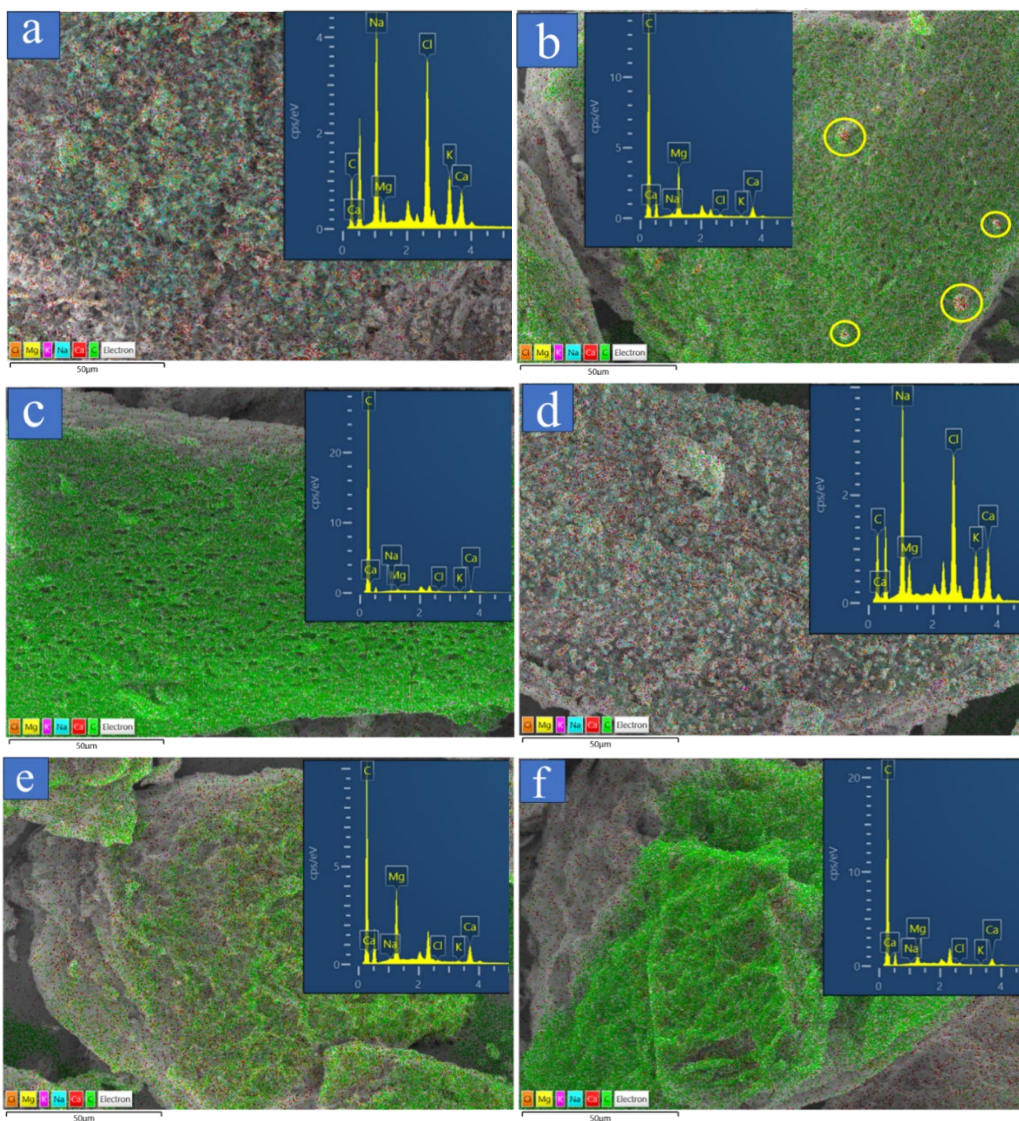


Figure 3.8. SEM images in EDS scanning range of: (a) WKM900, (b) WKM900-WT, (c) WKM900-CO₂, (d) KB900, (e) KB900-WT, and (f) KB900-CO₂. Inset: EDX spectra. [1]

The EDS analysis revealed the elemental composition of surface particles on the unwashed MBC sample, showing the presence of Na, Mg, K, Ca, and Cl elements (refer to Table 3.5 and Figure 3.8 for detailed information). On surfaces scanned for WKM900 and KB900, the mass fractions of carbon elements were 48.2% and 51.2%, respectively. Post water washing treatment, significant reductions in surface Na, K, and Cl

were observed. This exposure unveiled more carbon elements within the EDS scanning range, resulting in a carbon mass fraction of 90.0% for WKM900-WT and 86.7% for KB900-WT. Nevertheless, significant amounts of Mg and Ca persisted on the surface. However, use of the CO₂ aeration washing method effectively removed most of the Mg and Ca from the surface, elevating the carbon content to 98.5% for WKM900-CO₂ and 94.8% for KB900-CO₂. The EDS results aligned closely with the XRF findings, affirming the successful removal of pore-blocking mineral species not only from the outer surface, but also from the interior of MBC particles.

Table 3.5. EDS elemental compositions of MBC samples before and after washing treatments [mass%].[1]

Sample	CHO	Other elements				
		Na	Mg	K	Ca	Cl
WKM900	48.2	16.9	1.8	8.1	6.4	18.4
WKM900-WT	90.0	0.2	5.9	0.2	3.3	0.3
WKM900-CO ₂	98.5	0.0	0.2	0.1	0.9	0.2
KB900	51.2	15.4	2.6	6.8	9.0	14.9
KB900-WT	86.7	0.2	7.7	0.3	4.9	0.2
KB900-CO ₂	94.8	0.1	1.9	0.1	2.7	0.4

The SEM (Figure 3.9) was employed to examine the internal morphology of MBC, focusing on representative samples WKM800-WT and KB800-WT for clear observation post water washing.

The SEM analysis of WKM800-WT showcases an internal structure resembling a 3D honeycomb pattern. A closer examination at high magnification reveals the honeycomb walls to have a thickness ranging from approximately 10 to 50 nm. This 3D honeycomb structure offers robust spatial support for the pores present on the carbon surface, augmenting its adsorption capacity. Moreover, this structure is anticipated to confer high compressive strength to the carbon block, ensuring stability in applications such as adsorbents [17] and electrode materials [18].

Conversely, the SEM image of KB800-WT illustrates multiple layers of carbon flakes, each layer exhibiting a thickness of about 5 to 20 nm. This layered structure provides essential spatial reinforcement for the carbon surface pores. Furthermore, the presence of interlayer channels enables swift flux, indicating the potential of KB-derived porous carbon in multiphase catalysis or ion adsorption. These distinctive morphological attributes offer a wide array of application prospects for porous MBCs. Nevertheless, these distinct characteristics may serve as prerequisites for providing an abundance of pore structures in MBC.

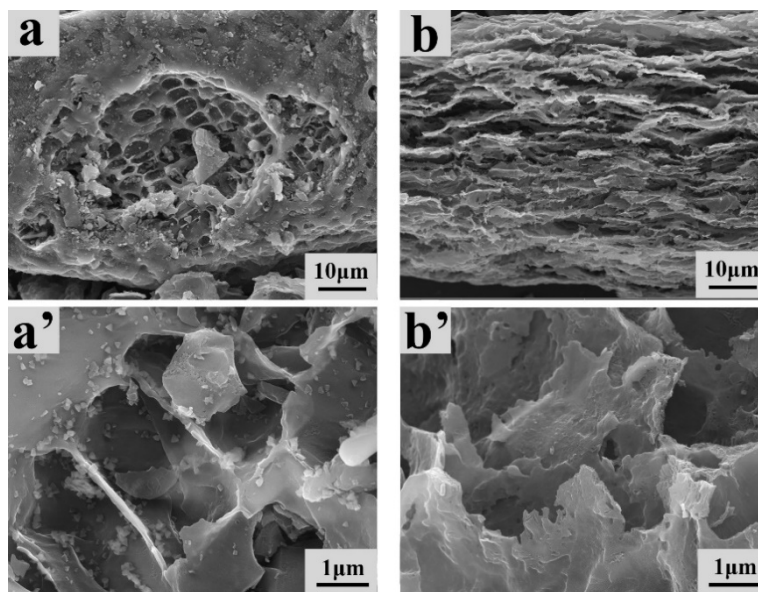


Figure 3.9. Morphological and structural characterization of MBC: SEM images of WKM800-WT at (a) low and (a') high magnifications, and KB800-WT at (b) low and (b') high magnifications. [1]

Figure 3.10 illustrates the plausible mechanism underlying the changes in MBC porosity induced by mineral removal, based on the results obtained from various analytical techniques. Results of SEM and EDS analyses reveal that the carbonized surfaces of WKM and KB samples are enveloped with diverse mineral crystals, resulting in relatively low porosity. However, subsequent washing treatments, validated by XRF, SEM, and EDS results, confirm the substantial removal of minerals from both the outer surface and interior, thereby liberating the initially concealed internal pore structure. This liberation corresponded with significant increments in total pore volume and SSA. Notably, the CO₂ aeration washing method, sans additional activators, effectively eliminated most surface minerals, resulting in a SSA surpassing 1000 m²·g⁻¹.

These observations underscore the close interrelation between elemental composition and pore structure. The genesis of pore structure can be attributed to the catalytic activation reaction of minerals, comprising AAEMs, and chlorine innate to MB during the pyrolysis process. Conversely, the mineral crystals covering the surface impede the pores of the carbonized MB sample, hindering the release of pore structure and contributing to reduced porosity. The employed washing technologies expose potential pore structures while releasing a significant quantity of minerals. Although these mineral elements cause pore blockage, they also undergo effective dispersion, catalyzing the pyrolysis process and thereby fostering the formation of internal pore structures within MBC. This dual effect contributes to the observed positive porosity outcomes in MBC materials. Eventually, a production process for porous carbon materials that is predominantly environmentally friendly has been successfully developed in this study.

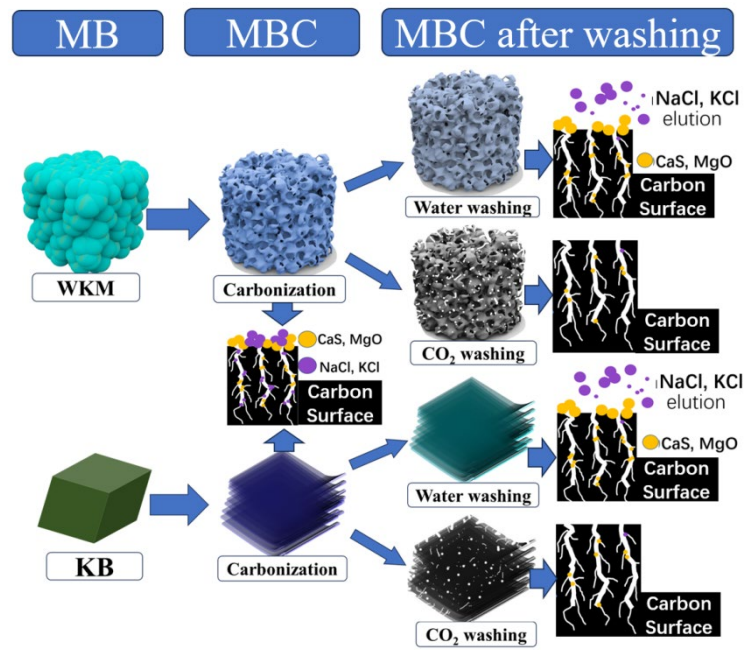


Figure 3.10. Hierarchical pore release mechanism of MBC. [1]

3.4. Conclusion

Marine biomass (MB) demonstrates exceptional efficiency in photosynthetic CO₂ fixation, surpassing other biomaterials. Although carbonized MB-derived carbon (MBC) initially appeared to be devoid of pores, detailed analysis employing XRF, SEM, and EDS unveiled concealed microporous and mesoporous structures through water washing. This comprehensive examination confirmed the near-complete removal of Na, K, and Cl elements via water washing, with CO₂ aeration washing further eliminating Mg and Ca elements. Consequently, the carbon content surged to over 95%, significantly enhancing the quality and purity of the final MBC product. Their removal not only amplified specific surface area and pore volume, but also delineated their role in pore obstruction. Simultaneously, these elements participated in the formation of intrinsic pores within MBC without necessitating external activators. Harnessing the dual effects of natural MB elements could yield highly porous MBC.

Moreover, the emission-free CO₂ aeration washing method presents an avenue to harness industrial CO₂ emissions, paving the way for advancing the carbon capture industry. When combined with CO₂ fixation capabilities of MB during growth, this approach underscores the expansive potential of MBC within the environmentally conscious activated carbon sector.

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Chapter 4.

The balance between strength, carbon content, and pore structure: MBC for potential industrial applications as an activated coke

4.1. Introduction

To delve deeper into the practical applications of marine biomass carbon materials (MBC), it is crucial to explore specific sectors and diverse carbon material benchmarks. Chapter 2 highlights the impressive pore structure and specific surface area exhibited by MBC. While MBC finds applications across various industries, certain conditions currently restrict its broader industrial utilization. Notably, activated coke, crucial for large flue gas absorption towers, demands carbon materials with both high porosity and exceptional splitting tensile strength (referred to as strength hereafter). This chapter focuses on optimizing MBC for the specific domain of activated coke.

Activated coke is widely employed for pollutant removal, leveraging its advantages such as a large specific surface area, well-developed pore structure, and abundant surface functional groups. These attributes contribute to its adsorption and reduction properties. In comparison to activated carbon, activated coke boasts a smaller specific surface area,

enhanced internal pores, well-developed micropores, a unique pore structure, rich surface functional groups, loading and oxidation properties, good chemical stability, high strength (resistance to pressure, wear, and impact), and robust thermal stability. Activated coke efficiently eliminates pollutants like SO_x (SO_2 and SO_3), NO_x , coal dust, Hg, VOCs, dioxins, etc. Its dual nature as an adsorbent and catalyst, along with excellent regeneration performance, presents a distinct advantage [1]. Overall, activated coke inherits the positive traits of activated carbon while overcoming its drawbacks, including high cost, low strength, and susceptibility to crushing.

Currently, fossil-based activated coke are the primary sources in industry, offering technological advantages but contradicting the overarching aim of global carbon neutrality. Biomass, characterized by zero carbon properties, presents a compelling alternative. Biomass-derived carbon materials, produced via high-temperature biomass pyrolysis, exhibit similar compositions and physicochemical traits as fossil-based activated coke used in industries. This likeness positions them as formidable contenders to replace traditional coke. Additionally, ongoing research highlights the gradual integration of biomass to replace conventional coal as a raw material in activated coke [2-3].

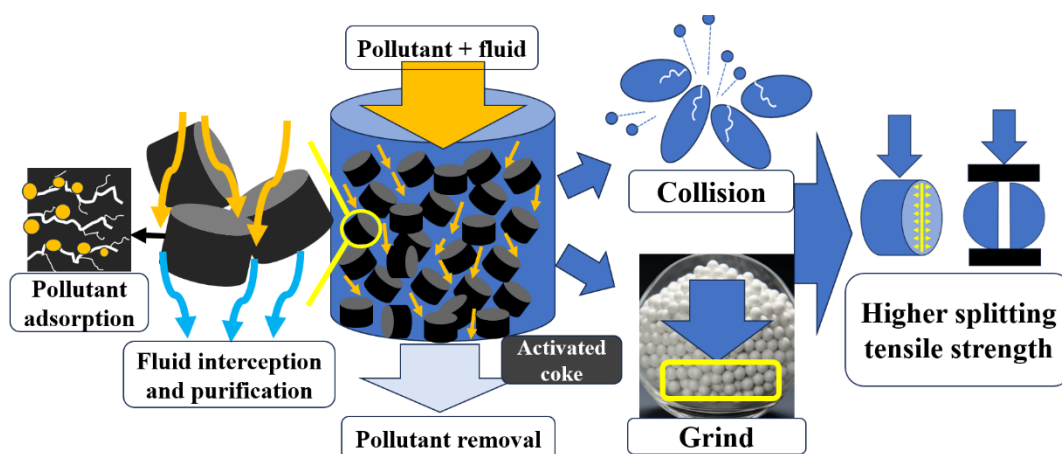


Figure 4.1. The adsorption process of activated coke in the absorption tower and the demand for high strength of activated coke particles

The primary obstacle hindering the advancement of biomass-based activated coke lies predominantly in its strength. The operational mechanism of activated coke within a reactor involves the interception and adsorption of pollutants in the fluid. In a layer of activated coke filter, the fluid intercepted is distributed among the particles, allowing time for pollutant interception. Throughout this period, pollutants are adsorbed into the pore structure within the activated coke, while the unclaimed fluid and pollutants proceed to the next activated coke filter.

From this process (Figure 4.1), it is evident that the particle size of the activated coke directly influences the space it can provide for the fluid. Larger particle sizes result in enhanced filtration capacity, increased pollutant holding capacity, and heightened interception capabilities, all while maintaining a high fluid flux. To further augment space and fluid retention, tower reactors have become an inevitable choice. In a tower

reactor, active coke particles must withstand both the gravitational force from upper-layer particles and the collisions between particles under fluid forces. Therefore, in addition to possessing a well-developed pore structure, active coke must also ensure sufficient strength.

Despite the immense potential of biomass-based activated coke, the direct substitution of coal is challenging due to its extensive history, comprehensive technological base, and multifaceted properties. Therefore, ongoing research primarily employs terrestrial biomass as a carbon source and gradually experiments with substitution at a smaller scale. However, marine biomass (MB), emerging as a novel carbon source, is gaining traction due to its higher yield, simpler extraction, cost-effective development, and eco-friendliness compared to traditional terrestrial biomass. The development of MBC might offer new prospects. Nonetheless, MB often contains high levels of alkali and alkaline earth metals. When subjected to high-temperature fluids during the production of activated coke, certain elements in the material vaporize and cause corrosion to equipment such as absorption towers, consequently reducing the lifespan of the production line. Consequently, the removal of alkali and alkaline earth metals (AAEM) during the preparation of activated coke becomes crucial, as it directly impacts the functionalization potential of MBC.

This chapter is dedicated to examining the potential of activated coke

produced from MBC to serve as a substitute for traditional fossil-based activated coke. The exploration encompasses comprehensive pyrolysis and preparation strategies. Process parameters such as carbonization temperature, coking temperature, and purification steps were adjusted to enhance carbon purity, strength, and pore structure of MBC. These improvements may unlock the potential application of MBC in the activated coke industry.

4.2. Experimental

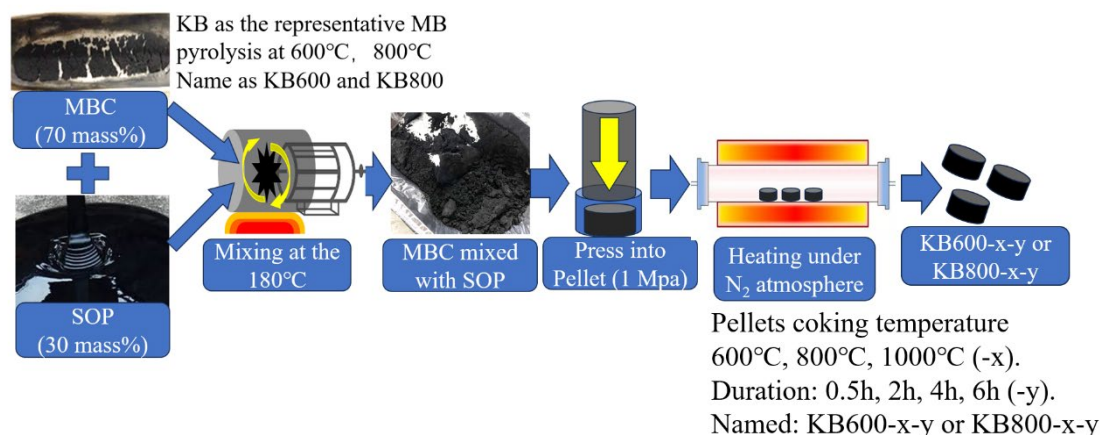


Figure 4.2. Preparation of carbon pellets from marine biomass

As illustrated in Figure 4.2, the sample preparation process is as follows. First, KOMBU (KB) as a representative sample was carbonized at temperatures of 600 and 800 °C, and the resulting carbonized materials were denoted as KB600 and KB800, respectively. Next, these carbonized materials were combined with SOP (Soft pitch) at 180 °C, with a mass ratio of MBC:SOP=7:3. The resulting mixture was compacted into pellets under 1 MPa pressure. Subsequently, the pellets were subjected to coking in a high-temperature furnace at 600-800-1000 (x) °C with a dwell time of 0.5h-2h-4h-6h (y) at 1000 °C, thus generating pellets named KB600-x-y and KB800-x-y.

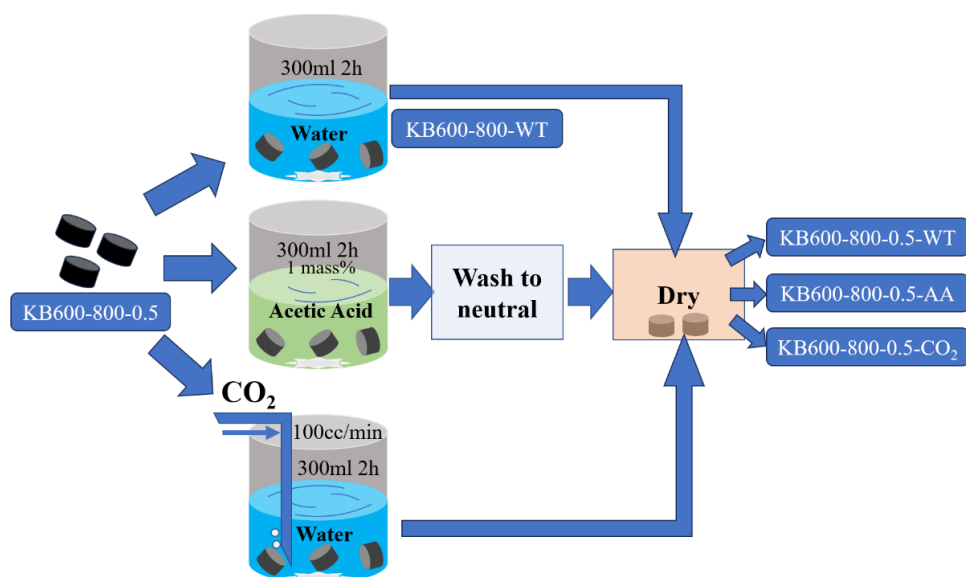


Figure 4.3. Three washing strategies for MBC Pellets

As shown in Figure 4.3, the washing procedure encompassed three stages: water washing, acetic acid washing, and carbon dioxide aeration washing. For representative sampling, KB600-800-0.5 was selected; the detailed explanation for this choice will be provided in the experimental and analytical sections. Initially, water washing was performed by immersing the entire set of pellets in 300 mL of deionized water, stirring for two hours, and subsequently drying to acquire KB600-800-0.5-WT. Next, acetic acid washing was executed by submerging the pellets entirely into a 300 mL solution of 1% mass concentration acetic acid, stirring for two hours, and then drying to produce KB600-800-0.5-AA. Lastly, the CO₂ aeration washing method was applied. The pellets were immersed as a whole in 300 mL of deionized water, with the introduction of CO₂ gas at a rate of 100 mL/min. The mixture was stirred for two hours and dried to yield KB600-800-0.5- CO₂.

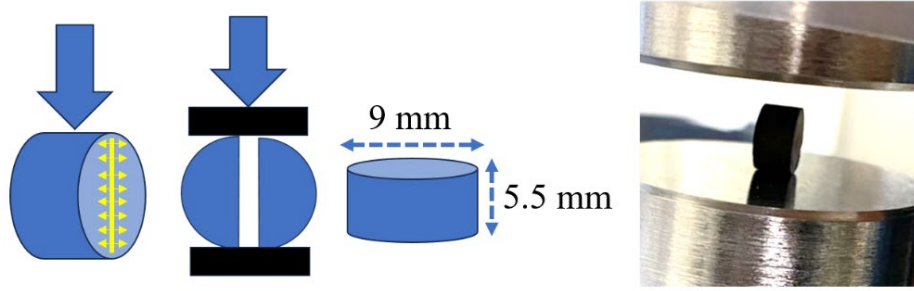


Figure 4.4. Pellets splitting tensile strength testing method and optical photos.

Figure 4.4 illustrates the schematic principle for measuring strength. In this setup, the cylindrical carbon pellet sample was positioned perpendicular to the load vector, aligning its length vector in the same orientation. Vertical pressure was then applied to the sample, inducing horizontal compressive stress and ultimately causing damage to the carbon pellet sample. Consequently, equation (1) [4] was employed using the measurement results to ascertain the maximum loading pressure of carbon pellets.

The equation is expressed as follows:

$$\sigma = 2P / \pi \cdot d \cdot h$$

Where:

σ represents the splitting tensile strength of carbon pellets in Pascals (Pa).

P signifies the load pressure in Newtons (N).

d denotes the diameter of the carbon-containing pellets in millimeters (mm).

h indicates the height of the pellets, also in millimeters (mm).

4.3. Results and Analysis

4.3.1 MBC carbonization temperature analysis:

The initial focus lies in exploring the impact of pyrolysis temperature, as outlined in step one. Table 4.1 delineates the pyrolysis temperature into 600 and 800 °C while maintaining subsequent coking temperatures consistently. Notably, at a pyrolysis temperature of 600 °C, the overall strength of MBC is high. For instance, KB600 exhibits a strength of 12 MPa at coking temperatures ranging from 600 to 800 °C, which decreases to 6.8 MPa at 1000 °C. Simultaneously, a significant decline in content of sodium and chlorine elements is observed, while potassium content shows a slight decrease. This suggests that despite the mixing and compression molding, MBC still undergoes high-temperature gasification of alkali metal salts, potentially contributing to the decline in strength due to damage to the carbon skeleton.

Table 4.1. Comparison of splitting tensile strength and XRF element content at different carbonization and coking temperatures

Sample	Splitting tensile strength (MPa)	Element content (mass%)							
		CHO	Na	Mg	K	Ca	P	S	Cl
KB600-600-0.5	12.0	75.4	7.1	1.6	3.7	2.4	0.1	1.3	8.0
KB600-800-0.5	12.2	77.1	6.7	1.8	3.4	2.3	0.1	1.3	6.9
KB600-1000-0.5	6.8	82.1	2.5	2.9	3.0	3.8	0.2	2.2	2.9
KB800-600-0.5	1.4	77.6	6.2	1.8	3.7	2.1	0.1	1.2	7.0
KB800-800-0.5	1.9	74.5	6.7	2.0	4.0	2.3	0.2	1.4	8.5
KB800-1000-0.5	1.4	82.1	3.2	2.8	2.8	3.2	0.2	1.8	3.5

--: Undetected.

With an increase in the carbonization temperature to 800 °C, the strength of all KB800 samples decreases to below 2 MPa, irrespective of subsequent coking temperatures. This considerable drop in strength can be attributed to the extensive interaction of alkali and alkaline earth metals (AAEM) in KB at 800 °C, which results in the formation of numerous pore structure (As shown in Figure 4.5), causing SOP entered the pore and reduced the binder power. This collapse persists even when combined with SOP and subjected to coking, rendering it ineffective.

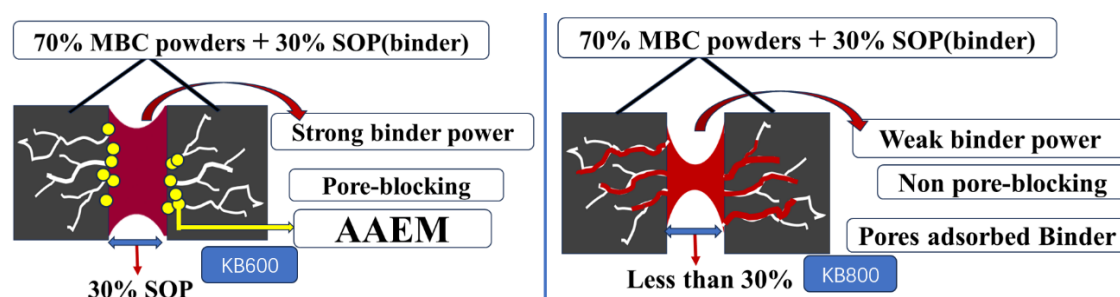


Figure 4.5. The principal speculation that more pore structures will weaken the binder force

Consequently, it can be concluded from this section that the carbonization temperature directly influences the strength of MBC, which maintains high strength below 600 °C. Elevated coking temperatures may induce a decline in strength, albeit within an acceptable range. This decline may stem from alkali metal salt gasification, contributing to increased carbon content. The subsequent investigation aims to identify suitable coking temperatures to further enhance the carbon purity of MBC.

4.3.2 High temperature coking results of the mixture:

Following the uniform SOP mixing and molding process, the impact of different coking temperatures on KB600 pellets, prepared at a pyrolysis temperature of 600°C, was investigated. As depicted in Table 4.2, the coking temperature ranging from 800°C to 1000°C exhibits a significant influence on the strength and elemental constitution of KB600. While the strength does not significantly change with an increase in coking time at 1000°C, the elemental composition shows a drastic change. Specifically, after 6 hours, both Na and Cl almost entirely vanish, the potassium content notably decreases, and the carbon purity dramatically rises to 88.9%. Although the strength declines to 5-6 MPa, it remains within acceptable limits. The subsequent step involves exploring alternative methods to eliminate AAEM while maintaining the current strength level.

Table 4.2. Comparison of splitting tensile strength and XRF element content at different coking temperatures and durations.

Sample	Splitting tensile strength (MPa)	Element content (mass%)							
		CHO	Na	Mg	K	Ca	P	S	Cl
KB600-600-0.5	12.0	75.4	7.1	1.6	3.7	2.4	0.1	1.3	8.0
KB600-800-0.5	12.2	77.1	6.7	1.8	3.4	2.3	0.1	1.3	6.9
KB600-1000-0.5	6.8	82.1	2.5	2.9	3.0	3.8	0.2	2.2	2.9
KB600-1000-2	6.9	87.4	0.9	2.6	2.2	3.6	0.2	1.8	1.0
KB600-1000-4	5.4	88.9	0.2	2.6	1.9	3.7	0.2	1.8	0.3
KB600-1000-6	6.7	88.8	--	2.8	1.8	3.9	0.2	1.9	0.1

--: Undetected.

4.3.3 Washing experiment results

The findings in Chapters 2 and 3 indicate that the elimination of Na, K, and Cl can also be achieved through a water washing process. Considering the challenges posed by the high energy consumption and corrosion associated with the gasification of Na, K, and Cl at 1000 °C, setting the coking temperature to 800 °C is a more feasible industrial option. Subsequently, attempts were made with water washing, organic acid washing, and carbon dioxide aeration washing.

Table 4.3. Comparison of splitting tensile strength and XRF element content of different washing methods.

Sample	Splitting tensile strength (MPa)	Element content (mass%)							
		CHO	Na	Mg	K	Ca	P	S	Cl
KB600-800-0.5	12.2	77.1	6.7	1.8	3.4	2.3	0.1	1.3	6.9
KB600-800-0.5-WT	5.7	84.0	3.4	3.1	1.0	3.7	0.1	1.3	1.3
KB600-800-0.5-AA	6.8	88.8	2.5	1.7	1.3	2.5	0.2	1.0	2.1
KB600-800-0.5-CO2	5.0	89.5	0.8	2.8	0.7	4.0	0.2	0.9	0.6

--: Undetected.

The results presented in Table 4.3 indicate a significant decrease in strength following the three washing methods. Regarding impurity removal, only water washing effectively eliminates a portion of Na, K, and Cl, concurrently raising the carbonaceous element content to 84wt%. Washing with a 1% acetic acid solution further elevates the carbonaceous element content to 88.8%; however, its removal efficiency for Na, K, and

Cl is comparable to water washing. The primary impurities removed here are mainly Mg and Ca. CO₂ aeration washing exhibits better efficacy in removing Na, K, and Cl. Although there is no significant reduction in Mg and Ca, the vast majority of Na, K, and Cl are eradicated, elevating the carbon element content to 89.5%.

4.3.4 Comparison of MBC formed and washed with commercial coke

Table 4.4 presents the comparison between KB600-800-0.5-AA, KB600-800-0.5- CO₂, and various industrial coke products. The carbon contents of KB600-800-0.5-AA and KB600-800-0.5-CO₂ do not exceed 90%, but they still exhibit higher levels than certain may coke products. The specific surface area exceeds that of typical coal-based activated coke products from company. It does indicate adaptability to varying activated coke application through controlled adjustments in pyrolysis and coking temperatures. The strength of MBC surpasses that of terrestrial biomass carbon and remains comparable to coke products, even exceeding ordinary activated coke derived from coal. In summary, the activated coke produced from MBC outperforms traditional fossil-based activated coke in terms of carbon content, specific surface area, and strength, showcasing significant potential for industrial applications. Additionally, MBC exhibits advantages over terrestrial biomass and other coke products, opening up possibilities for its application in a broader range of industries.

Table 4.4. Comparison of various properties between washed MBC samples and commercial raw coal and biomass charcoal

Sample	CHO (mass%)	SSA (m ² /g, αs)	Splitting tensile strength (MPa)	Ref.
KB600-800-0.5-AA	88.8	436	6.8	This work
KB600-800-0.5-CO ₂	89.5	371	5.0	This work
Coal-based activated coke	85.0	350	5.0	Company
Coal CC	89.5	--	3.8	[5]
Coal TC	76.8	--	5.8	[5]
Coke A	88.6	2.1	6.8	[6]
Coke B	89.5	5.9	--	[6]
Charcoal	98.6	51.3	1.2	[6]

--: Undetected.

4.4. Conclusion

Activated coke finds primary use in absorption towers for handling industrial waste gas emissions, with coal being the predominant raw material in its preparation. A crucial objective for reducing carbon in industrial carbon materials is to explore alternatives to coal-based activated coke. This chapter undertakes research on MBC, focusing on pyrolysis temperature, coking temperature, and strength to contribute towards achieving this goal. The specific conclusion is:

1). Utilizing MB as a carbon-rich raw material presents even greater potential for industrial applications compared to the current focus on single-biomass straw-based carbonization and coking research.

2). The complexities of the physical properties required by activated coke surpass those of raw coal. Most types of biomass carbon currently struggle to match the properties of coal-based activated coke, particularly in terms of splitting tensile strength. MBC exhibits outstanding strength, reaching up to 6.8 MPa, far exceeding the strength needed for activated coke in industrial absorption towers. This distinction may stem from the markedly different organic matter types and impurity element content compared to terrestrial biomass carbon.

3). Identified impurities in MBC primarily consist of AAEM. Previous studies have successfully removed these impurities through validated AA and CO₂ washing methods. Upon comparing the activated coke derived

from washed MBC with other products, it is evident that KB600-800-0.5-AA outperforms actual activated coke products. Specifically, it exhibits higher strength, with 6.8 MPa compared to 5.0 MPa, a greater specific surface area of $436 \text{ m}^2\cdot\text{g}^{-1}$ compared to $350 \text{ m}^2\cdot\text{g}^{-1}$, and a higher carbon content of 88.8 wt.% compared to 85.0 wt.%. The research in this chapter highlights that MBC possesses notable strength and a rich pore structure, making it a promising candidate for activated coke.

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4.5. Future work

Future endeavors will delve deeper into the current research scope. Exploring the reactivity and thermal strength of MBC at high temperatures is paramount. This includes understanding its capability for chemical reactions, binding with mineral powders, and resistance against wear and crushing—traits critical in raw coal and coke. The upcoming phase will focus on enhancing these properties in MBC and comparing them directly with traditional raw coal and coke, aiming for potential direct application or partial substitution in blast furnaces.

Additionally, in the realm of activated carbon, there's room to optimize the pore structure of MBC further. Premium activated carbon typically boasts specific surface areas ranging from 2000 to 3000 $\text{m}^2\cdot\text{g}^{-1}$. MBC can undergo specific activation processes to cultivate additional pores, aiming to enter high-value industries like chemical energy storage—a domain aligned with advanced activated carbon applications.

Chapter 5.

General conclusions

Reducing carbon emissions in the industry is crucial for achieving carbon neutrality. This study begins by utilizing high-yield, low-pollution marine biomass (MB) as a carbon-rich raw material, transforming it into marine biomass carbon materials (MBC) through pyrolysis. The investigation focused on elemental composition, pore structure, and splitting tensile strength of MBC, resembling key traits of conventional carbon sources like raw coal and coke. The aim is to pave a functionalization pathway for MBC, aiming to partially substitute traditional fossil carbon materials used in industries.

This thesis thoroughly investigates the pyrolysis process of marine biomass, and elemental composition shifts and structural changes from marine biomass to derived carbon, introducing a CO₂ aeration method for efficient purification. Comparison with coal and coke samples globally offered insights into advancing MBC functionalization. The key findings highlighted advantages of MB as a raw material, emphasizing its rapid growth, wide availability, renewability, high yield, and minimal environmental impact during extraction. Pyrolysis showed slightly higher carbon yields but notable weight loss at 800–1000 °C. Analyses confirmed the presence of alkali and alkaline earth metals (AAEM) in the derived

carbon, impacting its quality due to catalytic effects on the carbon framework. Simple methods like acetic acid washing and CO₂ aeration effectively removed these metals, leading to superior carbon and ash content in the purified carbon compared to major coal types globally, both in dry and dry ash-free conditions.

Initial observations of carbonized MBC lacking pores were revised through detailed analysis using XRF, SEM, and EDS, revealing concealed microporous and mesoporous structures post water washing. This thorough examination confirmed the removal of Na, K, and Cl elements via water washing, while CO₂ aeration further eliminated Mg and Ca elements, elevating carbon content to over 95%. This significantly enhanced the quality and purity of the final MBC product, increasing specific surface area (SSA) and pore volume while revealing their role in pore obstruction and intrinsic pore formation within MBC without external activators. Leveraging natural MB elements could yield highly porous MBC, up to nearly 1200 m²·g⁻¹ of SSA. The emission-free CO₂ aeration washing method opens possibilities to utilize industrial CO₂ emissions, potentially advancing the carbon capture industry. Combining this method with MB's CO₂ fixation abilities during growth highlights the expansive potential of MBC, especially within the environmentally conscious activated carbon sector.

To unlock the extensive application potential of MBC, the focus shifts

towards functionalizing MBC with activated coke as the target. Activated coke is widely utilized in industries, particularly for exhaust pollutant adsorption, owing to its exceptional specific surface area, high strength, and carbon purity. While traditional coal-based activated coke dominates, biomass-based alternatives struggle with low strength, hindering their ability to replace coal for carbon reduction. This chapter employs MBC as a raw material, adjusting pyrolysis temperature, coking temperature, and strength. Notably, sample KB600-800-0.5-AA outperforms actual activated coke products in strength by 6.8 MPa compared to 5.0 MPa, specific surface area by $436 \text{ m}^2\cdot\text{g}^{-1}$ compared to $350 \text{ m}^2\cdot\text{g}^{-1}$, and carbon content by 88.8 wt.% compared to 85.0 wt.%.

Overall, this thesis successfully attains its objectives, progressing through the steps of MB pyrolysis, MBC purification, preliminary MBC functionalization, and deep MBC functionalization. It confirms that MB is an excellent raw material, and MBC is an outstanding carbon material. The critical challenge lies in realizing practical industrial applications, a pursuit that researchers will continue to focus on in the future.

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