Hindawi Journal of Chemistry Volume 2018, Article ID 4319149, 11 pages https://doi.org/10.1155/2018/4319149



# Research Article

# Preparation of Microporous Carbon from Sargassum horneri by Hydrothermal Carbonization and KOH Activation for CO<sub>2</sub> Capture

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Received 4 August 2018; Revised 4 October 2018; Accepted 12 November 2018; Published 13 December 2018

Academic Editor: Ana B. Martin-Diana

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High-performance microporous activated carbon (AHC) for  $CO_2$  capture was prepared from an emerging marine pollutant, *Sargassum horneri*, via hydrothermal carbonization (HTC) and KOH activation. The as-synthesized carbon material was characterized by  $N_2$  sorption-desorption measurement, TGA, SEM, XRD, FTIR, and elemental analysis. Impressively, the activated carbon exhibited high specific surface area (1221  $m^2/g$ ), narrow distributed micropores (~0.50 nm), and a relatively high nitrogen content (3.56 wt.%), which endowed this carbon material high  $CO_2$  uptake of 101.7 mg/g at 30°C and 1 bar. Moreover, the carbon material showed highly stable  $CO_2$  adsorption capacity and easy regeneration over four adsorption-desorption cycles. Two kinetic models were employed in this work and found that the pseudo-first-order kinetic model ( $R^2 = 0.99$ ) provided the best description. In addition, the high  $CO_2$  uptake is mainly attributed to the presence of abundant narrow microporous. The macroporous structure of hydrochar (HC) played an important role in the production of microporous carbon with high adsorption properties. This work provides an efficient strategy for preparing microporous activated carbon from *Sargassum horneri*, and AHC is a promising candidate acting as an efficient  $CO_2$  adsorbent for further industrial application.

#### 1. Introduction

Diverse groups of organisms are found living in the ocean, of which, macroalgae is at least 10,000 different species described to date. Currently, the production of high value-added chemicals from macroalgae has been considered as a promising and long-term methodology to meet the word energy demands, reduce the global warming, alleviate food shortage, etc. [1–3]. Sargassum horneri (S. horneri) is one of the common macroalgae, and it is artificially cultivated for aquatic eutrophication restoration due to its superior absorption capability of nutrients. Meanwhile, S. horneri can compete with microplankton, protozoan, and even bacteria for nutrients, inhibiting the harmful algae blooms [4].

However, ocean-scale build-up of *S. horneri* blooms broke out unprecedentedly, leading to the occurrence of massive golden tides along the West African coast in spring, 2011 [5]. Outbreak of golden tides caused by *S. horneri* was also found in the Yellow Sea of China in December 2016, causing serious economic loss (more than U.S. \$73 million) [6]. Moreover, the so-called *S. horneri* golden tides brought its detrimental side to tourism-based economics, coastal ecosystems, ocean transportation, and water quality [5, 6]. Thus, it is necessary to utilize this emerging abundant waste effectively.

The macroalgae has been widely used to absorb heavy metals and organics or produce bioactive compounds and hydrocolloids [7–10]. *S. horneri* is a prolific renewable

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carbon source, and its cell walls are primarily composed of fibrous cellulose network and alginate mucilage [11–13]. The alginate polymers enable the absorption of metal cations (i.e., Ni<sup>2+</sup>, Fe<sup>3+</sup>, and Mg<sup>2+</sup>) to form metal alginates (Malginates). After carbonization of the Malginates and subsequent acid washing, the metal cations can be removed to produce carbon materials with special porous structure [12]. Therefore, it is promising to utilize *S. horneri* as a precursor for the production of carbon materials.

Pyrolysis is a common method for converting biomass into carbon. However, traditional dry pyrolysis cannot meet the requirement for high carbon yield [14, 15]. Hydrothermal carbonization (HTC) is a thermochemical conversion process where an organic substrate is converted into a solid product enriched in carbon content in the presence of water [16]. It was first described in 1913 by Bergius and was reintroduced to the public in the 21st century by Titirici and Antonietti in Germany [17]. In the recent years, HTC has been discovered to be a very effective and advantageous synthesis method for converting biomass into carbon materials, which are referred as hydrochars. However, hydrochar obtained by the sole HTC process exhibits low porosity, which hinders its potential application for catalysis, electrochemistry, and sorption. From this view of point, further activation treatment is considered as an effective strategy to introduce porosity. In general, activated carbons with welldeveloped porosity, especially narrow microporosity, are prepared by chemical activation using activating agents such as KOH, ZnCl<sub>2</sub>, and H<sub>3</sub>PO<sub>4</sub> [18]. Recently, activated carbons especially microporous carbon prepared by KOH activation have emerged as the most promising adsorbent for CO<sub>2</sub> capture due to their low cost of preparation, high specific surface area, and excellent chemical stability [13, 19].

In terms of the CO<sub>2</sub> capture by activated carbons, it has been reported that the narrow micropores play a decisive role in CO<sub>2</sub> adsorption capacity [20–23]. This is due to the fact that the interaction energy of CO<sub>2</sub> molecules and adsorbent can be greatly enhanced due to the overlapping of the potential fields from the adjacent walls when the adsorption occurs in narrow micropores [21, 24]. This strong adsorption potentials generated by narrow micropores can enhance their filling by the CO<sub>2</sub> molecules. Recently, Sevilla et al. reported that CO<sub>2</sub> uptake capacity was mainly determined by the volume of small micropores (<1 nm) [20, 21]. Further research indicated that the micropores with a diameter smaller than 0.8 nm played a key role in determining CO<sub>2</sub> capture on N-free carbide-derived carbons at 1 bar [22]. Zhang et al. pointed out that the CO<sub>2</sub> capture capacity strongly depended on the small micropores (<0.54 nm) under different adsorption conditions [23]. Therefore, the critical target is to generate narrow micropores for achieving highly efficient CO<sub>2</sub> capture. In addition, it is generally accepted that the introduction of nitrogen-containing functional groups into carbon materials can generate more active sites, strengthening the interactions between carbon surface and CO2 molecules for improving the CO<sub>2</sub> adsorption capacity [25]. The interactions are associated with the formation of the Lewis basic sites and the hydrogen-bonding between carbon surface and CO<sub>2</sub> molecules [26, 27].

Previous research studies focused on the utilization of macroalgae to synthesize carbon materials applied in fields such as catalysts, supercapacitors, and lithium-sulfur batteries [28–34]. However, to the best of our knowledge, the study on preparing microporous carbon from macroalgae for  $\rm CO_2$  uptake was seldom reported. In this work, we reported a facile method to synthesis microporous activated carbon with large quantities of narrow micropores ( $\sim$ 0.50 nm). The synthesis was performed under mild hydrothermal conditions and subsequent KOH activation, and the product was applied for carbon capture and storage (CCS). The  $\rm CO_2$  capture capacity, kinetics, and regeneration of microporous carbon were investigated.

#### 2. Materials and Methods

2.1. Materials. Sargassum horneri was sampled from the Wenzhou coastal area, Zhejiang province, P.R China. S. horneri was washed with deionized water, then crushed by grinder, and sieved into a particle size in the range of  $106-180\,\mu\text{m}$ . Ammonium iron (II) sulfate hexahydrate (Fe (NH<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O, 99.5%, A.R.), potassium hydroxide (KOH, A.R.), and hydrochloric acid (HCl, 38%, A.R.) were purchased from Sinopharm Ltd. (China). N<sub>2</sub> and CO<sub>2</sub> (99.99%) gases were purchased from Hangzhou Special Gas Co., ltd.

2.2. Preparation of Microporous Carbon. The preparation of hydrochar was done according to our previous work [35, 36], i.e., 1.96 g Fe(NH<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O, 10.0 g S. horneri, and 40 mL distilled water were mixed and sealed in 75 mL stainless steel autoclave. Then, the autoclaved mixture was transferred to a preheated oven and hydrothermally treated at 180°C for 2h. After cooling to room temperature, the obtained solid product, denoted as hydrochar (HC), was washed with distilled water until neutral pH and dried at 100°C overnight. Then, the HC was activated with KOH as follows: the equivalent mass of HC and KOH was mixed and then heated in the tube furnace at 600°C for 2h under N<sub>2</sub> atmosphere at a heating rate of 10°C·min<sup>-1</sup>. The resulting solid product was washed with 1 M HCl to remove inorganic salts, washed thoroughly with distilled water until neutral pH, and subsequently dried at 100°C overnight. Activated HC product is denoted as AHC. The AHC was stored in a desiccator for further characterizations.

2.3. Characterization. The surface morphology of the microporous carbon was characterized with a Hitachi S-4700 scanning electron microscope (SEM) at 5.0 kV and 15.0 kV.

Nitrogen adsorption-desorption isotherms were measured at 77 K using an automatic surface area and a pore size analyzer (3H-2000PS1), and the  $\rm CO_2$  adsorption experiment was performed at 273 K. Prior to sorption measurements, the samples were degassed at 200°C for 3 h. BET surface area and pore volume were determined by  $\rm N_2$  adsorption-desorption isotherms. The specific surface area was calculated using the Brunauer–Emmet–Teller (BET) method at relative pressure  $(P/P_0)$  values ranging from 0.04 to 0.32; the total pore volume

 $(V_{\rm t})$  was determined by adsorption amount at the relative pressure of 0.99; the micropore surface area  $(S_{\rm micro})$  and micropore volume  $(V_{\rm micro})$  were calculated by the t-plot analysis; the pore size distributions (PSD) were obtained using the density functional theory (DFT) method.

The infrared spectra of the samples were acquired using a Nicolet 6700 FTIR spectrometer by averaging 24 scans in the  $4000-400\,\mathrm{cm}^{-1}$  spectral range at  $4\,\mathrm{cm}^{-1}$  resolution, and a KBr pellet was used as a reference sample.

The XRD patterns were collected using a PANalytical X'Pert PRO diffractometer with a Cu-K $\alpha$  radiation (40 kV, 40 mA).

Elemental analysis was carried out on an elemental analyzer (Elementar Vario MACRO cube, Germany), and oxygen content was determined by difference.

The thermogravimetric analysis (TGA), derivative thermogravimetry (DTG), and CO<sub>2</sub> adsorption experiments were performed on a thermogravimetric analyzer (NETZSCH TG 209 F3 Tarsus, Germany).

2.4. CO<sub>2</sub> Adsorption Experiments. The CO<sub>2</sub> adsorption performance of the carbon samples were measured by a thermogravimetric analyzer. Initially, 10 mg of the sample was placed in an alumina crucible loaded in a TGA furnace. Prior to each adsorption experiment, the carbon was heated up to 120°C (10°C/min) and kept for 30 min to remove moisture under N<sub>2</sub> flow (40 mL·min<sup>-1</sup>). Then, the carbon sample was cooled to desired adsorption temperature, i.e., 30, 45, and 60°C, respectively, under which the CO<sub>2</sub> adsorption studies were performed for 90 min at a rate of 50 mL·min<sup>-1</sup>. Moreover, the adsorbent regeneration was done by heating to 120°C for 30 min at 10°C·min<sup>-1</sup> under N<sub>2</sub> flow (40 mL·min<sup>-1</sup>). To check the adsorbent stability, the adsorption/desorption procedure was repeated 4 times.

2.5. Experimental Description. HC was prepared from S. horneri by hydrothermal treatment in our previous work [35, 36]. During the hydrothermal carbonization, we investigated the effects of the reaction temperature, the reaction time, and the mass ratio of S. horneri to deionized water on the carbon yield. Fe (NH<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>⋅6H<sub>2</sub>O was used as the catalyst because (i) the presence of iron ions could effectively speed up the hydrothermal carbonization process and significantly reduce the reaction time and the reaction temperature [37, 38], (ii) iron ion had a catalytic effect on the evolution of gases, contributing to produce the carbon materials with higher porosity and surface area in the HTC process [39], and (iii) the introduction of the N-containing surface groups could enhance the CO<sub>2</sub> adsorption capacity. Finally, the carbon recovery and yield could reach up to 65.0% and 51.4%, respectively. The optimized conditions could be described as follows: the reaction temperature at 180°C, the reaction time for 2 h, and the mass ratio of S. horneri to deionized water is 10/40.

## 3. Results and Discussion

3.1. Thermogravimetric Analysis. To investigate the thermal decomposition of S. horneri, hydrochar (HC) and the

mixture of HC and KOH (HC-KOH), the TGA and DTG analysis was conducted under nitrogen atmosphere, as shown in Figure 1. Three stages of weight loss in the TGA-DTG curve of *S. horneri* have been observed in Figure 1(a). The first stage occurred at the temperature range of 30-200°C, with one peak centered at 68°C, due to vaporization of adsorbed water on the surface [40]. In the second stage, a significant weight loss of approximately 38% was achieved between 200 and 400°C, corresponding to the decomposition of biopolymer fractions [41]. In the DTG curve, two extensive peaks were detected between 200 and 350°C. The first peak (between 200 and 280°C) and the second peak below 350°C might be associated with the decomposition of carbohydrates and proteins, respectively. The thermal degradation patterns were similar to that of macroalgae reported by Li et al. [42]. The weight loss of the final stage at a temperature range of 400-800°C might be attributed to the degradation of lignin and remaining proteins [43]. In the case of HC, the major weight loss occurred at a temperature range of 200-400°C, and only one sharp peak at 335°C was detected in Figure 1(b), indicating that the biopolymer fractions especially hemicellulose were decomposed after the hydrothermal carbonization. Similar phenomenon was also found in other studies [44]. For the mixture of HC and KOH, a total weight loss of 60% and three major stages in the thermal decomposition were found in Figure 1(c). The first stage mass loss from room temperature to 200°C was associated with the dehydration of KOH. The second stage in the wide temperature range of 200-600°C could be attributed to the decomposition of the biopolymer and KOH [45]. Besides, there is a significant weight loss in the final stage above 600°C, suggesting that the carbon is severely etched by KOH to form the well-developed porous structure [46].

3.2. Physical Properties of Activated Carbon. The morphologies of the S. horneri, HC, and AHC are shown in Figure 2. As shown in Figure 2(a), the surface of the S. horneri was smooth and exhibited a channel-like structure. After hydrothermal treatment, the surface of the HC became rough and showed an irregular and overlapping layered structure (Figure 2(b)). In addition, the HC surface also presented the cross-linked macropore structure which contributed to the diffusion of KOH. Moreover, the HC had good affinity to KOH solution due to its hydrophilic surface. After KOH activation, the original morphology of the HC was completely destroyed and transformed into honeycomb-like structures (Figure 2(c)). Obviously, neighboring pores were connected and distributed randomly in the AHC after the HTC and activation process (Figure 2(d)).

 $N_2$  sorption-desorption isotherms and pore size distributions for *S. horneri*, HC, and AHC are described in Figure 3, and the corresponding physical properties are presented in Table 1. It can be seen from Table 1 that HC had a low BET surface area  $(26.64\,\mathrm{m^2\cdot g^{-1}})$  and negligible micropore volume, corresponding to macropore porosity shown in Figure 2(b). This phenomenon was similar to hydrochar that originated from other biomass [34, 47, 48]. It is worth mentioning that the BET surface area of HC was

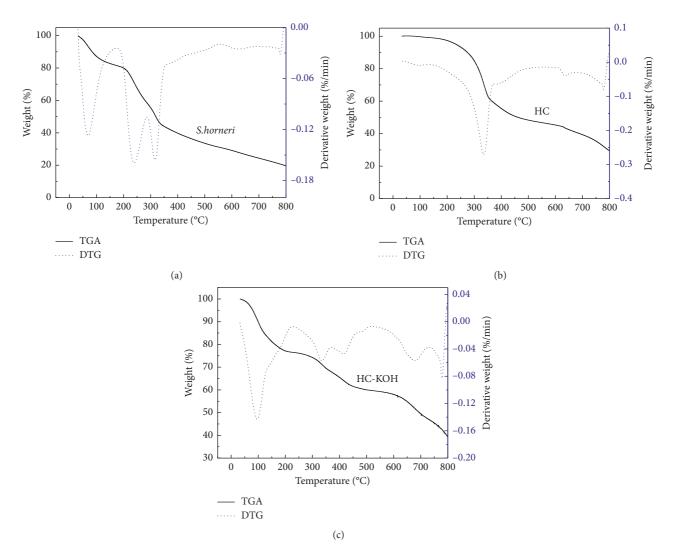


FIGURE 1: TGA and DTG curves for (a) S. horneri, (b) hydrochar (HC), and (c) the mixture of HC and KOH (HC-KOH) under N<sub>2</sub> flow.

higher than the hydrochars from other biomass such as Enteromorpha prolifera (1.4 m<sup>2</sup>·g<sup>-1</sup>) [34], maize silage  $(12 \text{ m}^2 \cdot \text{g}^{-1})$  [47], and pinewood  $(21 \text{ m}^2 \cdot \text{g}^{-1})$  [48], probably due to the special structure of S. horneri and the addition of catalyst. In Figure 3(a), the HC exhibited a typical type III isotherm with a H3 hysteresis loop at relative pressure  $(P/P_0 =$ 0.5-1.0), corresponding to a mesoporous or macroporous structure with slit-like geometry, which is formed by the accumulation of flaky particles. AHC showed a standard type I isotherm and a steep increase in nitrogen uptakes at low relative pressure ( $P/P_0 < 0.05$ ), indicating that KOH activation could promote the formation of abundant micropores in the carbon. To further investigate the porosity of the microporous carbon, the CO<sub>2</sub> adsorption experiment was carried out at 273 K. As shown in Figure 2(c), the pore size distribution showed that AHC possessed abundant narrow micropores (~0.50 nm). Cui et al. reported that the largest adsorption energy could be reached when the pore size of the adsorbent was 1-2 times larger than the kinetic diameter of the adsorbate molecule [49]. The kinetic diameter of CO<sub>2</sub> is 0.33 nm; hence, superior CO<sub>2</sub> adsorption capacity can be achieved by AHC with abundant narrow micropores of about 0.50 nm.

3.3. Chemical Properties of Activated Carbon. Elemental compositions of S. horneri, HC, and AHC are presented in Table 2. The hydrothermal carbonization of S. horneri significantly increased the relative carbon content from 41.25% to 52.77%. A van Krevelen diagram (in Figure 4) [50] was applied to analyze the reaction pathways of the carbonization process. The H/C atomic ratio decreased from 1.66 in the S. horneri to 1.13 in the HC, and the O/C atomic ratio descended from 0.89 to 0.54, indicating that the HTC process of S. horneri followed the pathways of dehydration and decarboxylation process [36]. After KOH activation, the relative carbon content of AHC increased from 52.77% to 71.40%, while the nitrogen content exhibited a small decrease, which might be related to the decomposition of unstable nitrogen-containing groups.

It has been proven that the CO<sub>2</sub> adsorption on activated carbon also depended on the surface functional groups. Therefore, the functional groups of HC and AHC were analyzed using FTIR spectroscopy as shown in Figure 5. For the HC, the adsorption peak in the 3000–3500 cm<sup>-1</sup> range was associated with H-bonded O-H vibration [51], and the band at around 2930 cm<sup>-1</sup> was assigned to C-H stretching.

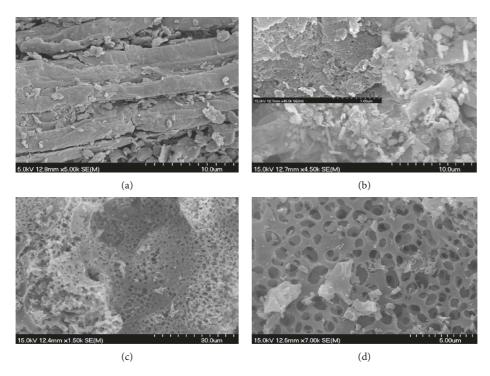


FIGURE 2: SEM images of the (a) S. horneri, (b) HC and (c, d) KOH-activated carbon (AHC).

The peak at 1620 cm<sup>-1</sup> corresponded to the C=C stretching vibration [52]. The absorption bands observed in the range of 1000-1450 cm<sup>-1</sup> represented the C-O stretching vibrations [53]. The bands at 500–800 cm<sup>-1</sup> region corresponded to out-of-plane N-H deformation vibration [34]. The characteristic peaks of HC were consistent with those of other biomass-based hydrochars [47]. Instead, as for AHC, only the weak O-H vibration band, C=C vibration band, and N-H deformation vibration were detected. The intensity of these characteristic peaks decreased dramatically due to the violent chemical reaction between HC and KOH. The abovementioned facts indicated that the CO2 adsorption of HC could be assigned to chemisorption that resulted from the rich oxygen- and nitrogen-containing functional groups, whereas the adsorption of AHC would be determined by the relative pore structure and residual chemical functional groups.

The XRD patterns of HC and AHC are shown in Figure 6. The XRD pattern of the HC displayed a sharp diffraction peak around  $2\theta = 22.5^\circ$ , corresponding to the (002) interlayer reflection. However, almost no sharp (002) diffraction peak has been observed in the hydrochars from other biomass [54]. This phenomenon indicated that the formation of graphitic structures was promoted by hydrothermal treatment in the presence of metal catalysts. Compared to HC, the (002) diffraction pattern of AHC exhibited a broad diffraction peak at around 25° and a week diffraction band at around 43°, attributing to the (002) and (100) planes, respectively. The broad (002) diffraction peak indicated that the graphitization degree decreased since KOH activation destroyed the graphite layer of HC.

3.4. Porosity Formation of Activated Carbon. Several pathways of porosity formation in AHC are proposed and described schematically in Figure 7. Firstly, the intrinsic channel-like structure of S. horneri contributes to the formation of macropores. As observed in Figure 2(b), the crosslinked macroporous structure is obtained by hydrothermal carbonization of S. horneri. The unique structure is ascribed to the special structure and component of S. horneri, hydrothermal carbonization and catalyst. S. horneri is mainly composed of hemicellulose, cellulose and lignin. In a structural context, the cellulose in S. horneri is mainly cross linked with hemicellulose and lignin [55]. Hemicellulose is easy to liquefy and degrades into smaller molecules under mild hydrothermal temperature (180°C) [56], while the cellulose and lignin significantly decomposes under hydrothermal conditions above approximately 200°C [57, 58]. Accordingly, the cellulose and lignin can be selectively retained at around 180°C and form a solid scaffold with the cross-linked structure, contributing to the opening and linking channel.

Secondly, iron ion can accelerate hydrothermal carbonization reaction and promote the formation of pores. Cui et al. [37] reported that metal ions, such as iron ions, could effectively accelerate the hydrothermal carbonization process, which shortened the reaction time to some hours. Moreover, Braghiroli et al. [38] pointed out that the iron ion had a catalytic effect on the production of gas, contributing to the production of carbon materials with higher porosity and surface area. In our previous experiments, we explored the effects of the ammonium iron (II) sulfate hexahydrate in the HTC process and hydrochar. The results showed that the reaction time of hydrothermal carbonization was shortened

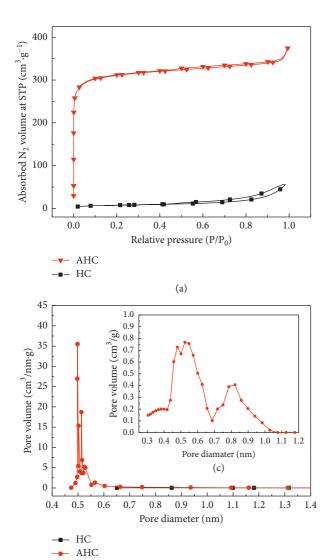


Figure 3: (a)  $\rm N_2$  sorption-desorption is otherms and corresponding pore size distributions derived from (b)  $\rm N_2$  adsorption and (c)  $\rm CO_2$  sorption.

(b)

TABLE 1: Textural properties of S. horneri-based carbon.

Sample	$S_{BET}$ $(m^2 \cdot g^{-1})$	$V_{ m total} \ ( m cm^3 \cdot g^{-1})$	$V_{\text{micro}} (\text{cm}^3 \cdot \text{g}^{-1})$	Average pore sizes (nm)
S. horneri	0.43	0.0051	0.00	21.77
HC	26.64	0.093	0.0007	13.96
AHC	1221	0.58	0.38	2.16

to 2 hours with the addition of catalyst in the HTC process; besides, the BET surface area and total volume of the hydrochar increased significantly.

Thirdly, KOH activation plays a vital role in pore evolution. A redox reaction has taken place during KOH activation, where the carbon is oxidized to CO or CO<sub>2</sub>, thus generating pores [59]. The developed porosity can be achieved through adjusting the activation conditions [24]. Compared with HC, AHC exhibited higher specific surface area (1221 m<sup>2</sup>/g), micropores volume (0.38 m<sup>3</sup>/g), and

narrower distributed micropores (~0.50 nm), indicating that the KOH activation contributes the most to the formation of micropore structures [60].

Finally, small gas molecules such as CO, CO<sub>2</sub>, CH<sub>4</sub>, and  $\rm H_2O$  are released via carbon gasification during the activation process with the increasing temperature, facilitating the development of pores. The combination of four proposed porosity formation pathways well explains the structure of AHC with abundant micropores ( $\sim$ 0.50 nm).

3.5.  $CO_2$  Uptake Capacity. The  $CO_2$  uptake capacities  $(q_e)$ of HC and AHC were studied at 30°C, 45°C, and 60°C. Although AHC had less nitrogen content, it showed higher CO<sub>2</sub> adsorption capacities of 101.7, 92, and 54 mg/g than HC at 30°C, 45°C, and 60°C and 1 bar, as shown in Table 3. This is due to the fact that the CO<sub>2</sub> uptake of activated carbon was not only contributed by functional groups on the surface, but also determined by the porous structure and specific surface area [61]. Though HC had more functional groups, the further CO<sub>2</sub> adsorption was limited as a consequence of its low porosity and negligible micropore volume. AHC exhibited a developed pore structure, such as high specific surface area and microporous volume. As shown in Table 1, the significant increase in micropore volume of AHC compared to HC indicates that the activation process primarily enhanced the CO<sub>2</sub> physical adsorption. Therefore, HC exhibited that certain CO<sub>2</sub> sorption capacity was mostly due to its functional groups on the external surface, while CO<sub>2</sub> adsorption on AHC was primarily attributed to abundant narrow micropores (~0.50 nm).

AHC exhibited  $CO_2$  adsorption capacity as high as  $101.7 \,\mathrm{mg/g}$  at  $30^{\circ}\mathrm{C}$  and decreased to  $92 \,\mathrm{mg/g}$  at  $45^{\circ}\mathrm{C}$  and  $54 \,\mathrm{mg/g}$  at  $60^{\circ}\mathrm{C}$ , respectively, caused by the exothermic nature of adsorption. In addition, AHC had a considerable  $CO_2$  adsorption capacity over other carbon materials as shown in Table 4. As a result, AHC was produced from marine waste via a facile method and was used as a  $CO_2$  adsorbent, alleviating the *S. horneri* golden tides.

3.6. Adsorption Kinetic. To assess the  $CO_2$  adsorption kinetic, the  $CO_2$  adsorption on AHC was conducted by TGA at 30°C under atmospheric pressure. The pseudo-first-order and pseudo-second-order models were used to fit the isotherm of AHC. The pseudo-first-order equation is applied to determine the kinetic parameters:

$$q_t = q_e (1 - e^{-k_1 t}),$$
 (1)

where  $q_t$  and  $q_e$  (mg·g<sup>-1</sup>) are the adsorption capacities at time t (min) and at equilibrium, respectively, and  $k_1$  (min<sup>-1</sup>) is the kinetic rate constant of the pseudo-first-order kinetic model.

The pseudo-second-order equation is expressed as follows:

$$q_t = \frac{q_{\rm e}^2 k_2 t}{1 + q_{\rm e} k_2 t},\tag{2}$$

where  $k_2$  (mg·min<sup>-1</sup>) is the rate constant of second-order-adsorption.

TABLE 2: Elemental analysis of S. horneri, HC, and AH	TABLE 2:	Elemental	analysis	of S.	horneri.	HC.	and AHC
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Samples	C (wt.%)	H (wt.%)	N (wt.%)	S (wt.%)	O*(wt.%)	H/C (atomic ratio)	O/C (atomic ratio)
S. horneri	41.25	5.70	3.43	0.68	48.94	1.66	0.89
HC	52.77	4.95	4.32	0.27	37.69	1.13	0.54
AHC	71.40	2.65	3.56	0.29	22.10	0.44	0.23

<sup>\*</sup>Calculated by the difference.

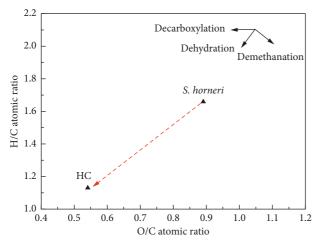


FIGURE 4: Van Krevelen diagram for S. horneri and its hydrochar.

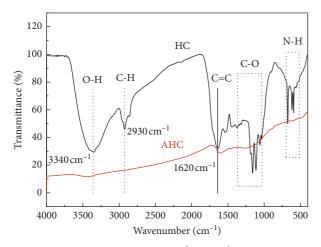


FIGURE 5: FTIR spectra of HC and AHC.

Figure 8 showed experimental  $CO_2$  uptake as a function of time on the AHC and the corresponding profiles obtained from the two adsorption kinetic models. Table 5 summarizes the related parameters of kinetic models. It was observed that the pseudo-first-order model gave a better fit than the pseudo-second-order model with the experimental data for  $CO_2$  adsorption on the AHC. This was further confirmed by higher  $R^2$  and lower error % values. Thus, the pseudo-first-order kinetic model provided a better description over the entire adsorption process. It showed two stages: in the first stage, approximately 70% of the total  $CO_2$  uptake reached within 6 min, and the adsorption process for the second stage was slow. This behavior could be attributed to the decreased unoccupied active

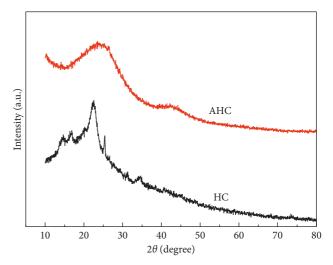


FIGURE 6: XRD patterns of HC and AHC.

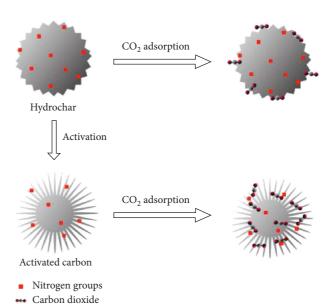


FIGURE 7: Schematic diagram of the porosity formation of AHC.

Table 3:  $\mathrm{CO}_2$  equilibrium adsorption capacities of carbon materials at different temperatures.

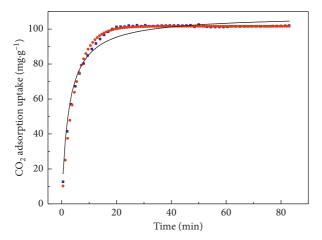
Sample	CO <sub>2</sub> uptake-1	$00\% \text{ CO}_2/\text{mg}\cdot\text{g}^{-1}$	(mmol·g <sup>-1</sup> )
Sample	30°C	45°C	60°C
НС	36 (0.8)	23 (0.5)	17 (0.4)
AHC	101.7 (2.3)	92 (2.1)	54 (1.2)

Sorbent	Temperature (K)	$CO_2$ uptake/mg·g <sup>-1</sup> (mmol·g <sup>1</sup> )	Reference
Enteromorpha prolifera-based activated carbon	298	61 (1.4)	[34]
Mesoporous sucrose-based activated carbon	298	76 (1.7)	[62]
Amino-modified peat-based activated carbon	298	96 (2.2)	[63]
A material composed by zeolite and activated carbon	298	116 (2.63)	[64]
A metal-rich wood-based activated carbon	298	83 (1.9)	[65]

303

303

TABLE 4: Comparisons of adsorbent capacity.



Waste ion-exchange resin-based activated carbon

Sargassum horneri-based porous carbon (AHC)

- Experiment
- · Pseudo-first-order fit
- --- Pseudo-second-order fit

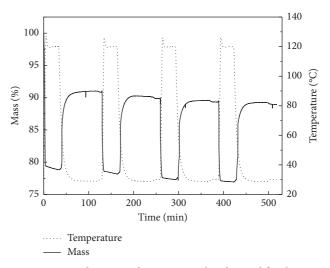
FIGURE 8: Experimental CO<sub>2</sub> uptake on AHC and corresponding fit to kinetic models at 30°C.

Table 5: The kinetic parameters of CO<sub>2</sub> adsorption on activated carbon.

	Kinetic parameters					
Kinetic models	$q_{\rm e} \pmod{\mathrm{mg}\cdot\mathrm{g}^{-1}}$	k	$R^2$	Error (%)		
Pseudo-first-order kinetic	101.6	0.21205 (min <sup>-1</sup> )	0.99218	3.57		
Pseudo-second-order kinetic	107.8	0.00355 (mg·min <sup>-1</sup> )	0.96796	6.09		

sites and the increased diffusion resistance [67]. The above facts illustrated that AHC had a rapid CO<sub>2</sub> adsorption rate, which was beneficial for industrial application.

3.7. Adsorbent Regeneration. Except for high CO<sub>2</sub> adsorption capacity, cyclic stability and ease of regeneration were also important criterions for efficient CO<sub>2</sub> capture in practical applications. A cyclic test was performed by alternatively repeating adsorption-desorption cycles at 30°C and 1 bar, as shown in Figure 9. It can be seen that the adsorbed CO<sub>2</sub> was easily desorbed by purging with N<sub>2</sub>. Actually, more than 94% of CO<sub>2</sub> could be desorbed within 3 min under desorption conditions. Besides, no noticeable changes in the CO<sub>2</sub> adsorption capacity were observed after four successive cycles of adsorption-desorption. Thus, the



81.2 (1.8)

101.7 (2.3)

[66]

This work

FIGURE 9: CO<sub>2</sub> adsorption-desorption cycles obtained for the AHC at 30°C (CO<sub>2</sub> concentration: 100%).

AHC could be successfully regenerated at 30°C and 1 bar and showed highly cyclic stability with ~99% of the initial adsorption capacity over multiple cycles, which is highly desirable for potential industrial applications.

#### 4. Conclusion

In summary, we reported a facile method for preparing microporous carbon from S. horneri via the hydrothermal carbonization and subsequent KOH activation, which shortens the hydrothermal reaction time and the dosage of the activating agent. It was found that the hydrothermal carbonization of S. horneri at 180°C for 2h is a suitable condition for the production of HC with high yield and macroporous structure. AHC with abundant microporous structure (~0.50 nm) has been synthesized using a KOH/HC ratio of 1 at 600°C. Then, the CO<sub>2</sub> uptake of HC and AHC has been studied under different temperatures. The result illustrated that AHC is more suitable as a CO2 adsorbent, and the low adsorption temperature facilitates the CO<sub>2</sub> uptake. The high CO<sub>2</sub> uptake of 101.7 mg/g has been achieved using AHC at 30°C. The high CO2 uptake is primarily ascribable to the presence of abundant narrow micropores (~0.50 nm). Moreover, the AHC exhibits a rapid CO<sub>2</sub> adsorption rate, excellent cyclic stability, and easy regeneration. As such, marine waste, S. horneri can serve as a potential raw material for developing a high-performance and cost-effective CO<sub>2</sub>

adsorbent. Our study also provides a feasible approach to alleviate the golden tides caused by macroalgae.

# **Data Availability**

The data used to support the findings of this study are included within the article.

#### **Conflicts of Interest**

The authors declare no conflicts of interest.

# Acknowledgments

This work was supported by the National Natural Science Foundation of China (grant nos. 21628601 and 51728902), the Zhejiang Provincial Natural Science Foundation of China (grant nos. LY16B060014 and LGF18D060002), and the State Key Laboratory of Chemical Engineering (no. SKL-ChE-08A01).

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