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Full Length Article

Adsorption of CO_2 from flue gas by novel seaweed-based KOH-activated porous biochars

Shuai Ding, Yangxian Liu*

School of Energy and Power Engineering, Jiangsu University, Zhenjiang, Jiangsu 212013, China

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ABSTRACT

Recently, environmental problems such as climate change and global warming caused by the greenhouse effect have become a worldwide topic of concern. In this article, two kinds of seaweed porous biochars were prepared by utilizing widely sourced seaweed (sargassum and enteromorpha) using single step KOH activation. The physical and chemical properties of the seaweed porous biochar adsorbents were characterized, and CO_2 adsorption performance over seaweed porous biochars was tested in a fixed-bed adsorption system. The textural properties and functional groups of the raw seaweed biochars are significantly improved by KOH activation. The seaweed porous biochars (SCK-800-1 and ECK-800-1) prepared with KOH/biomass weight ratio of 1:1 at 800 °C exhibit the maximum CO_2 capacity (reaching 1.05 mmol/g and 0.52 mmol/g at 25 °C, respectively). The adsorption capacity of CO_2 decreases with the increase of adsorption temperature, and increases with the increase of CO_2 initial concentration. The flue gas components such as O_2 and NO do not affect the adsorption capacity of CO_2 for SCK-800-1 and ECK-800-1, while SO_2 slightly inhibits the CO_2 adsorption performance. After ten cycles of adsorption-desorption, the adsorption capacities of seaweed porous biochars only decrease slightly. The pseudo-first order model better fits the experimental data, which demonstrates that the external mass transfer plays a dominant role in CO_2 adsorption over two kinds of seaweed porous biochars. The present results may inspire new research interests and provide necessary theoretical guidance for the application and research of seaweed biomass-based biochars for CO_2 capture, and effectively expand the utilization of marine biomasss.

1. Introduction

In recent years, major environmental problems such as climate change and global warming caused by the greenhouse effect have become a worldwide topic of concern. The increase of anthropogenic carbon dioxide (CO_2) concentration in the environment is the main cause of greenhouse effect. Greenhouse gas (GHG) CO_2 emissions are mainly derived from fossil fuels combustion and industrial production activities, which accounts for 76% of total greenhouse gas emissions in 2010 [1]. Therefore, reducing CO_2 emissions is the key to slowing down global warming. However, 90% of the world's energy is still supplied by fossil fuels, and the energy structure with fossil fuels as the main energy source is unlikely to change within a long time [2,3]. Accordingly, research on carbon capture and sequestration (CCS) from emission source has increased in recent years. CCS is considered to be the only technology that can significantly reduce CO_2 emissions from the combustion of fossil fuels [4]. CCS reduces CO_2 emissions through three steps, the most difficult and costly of which is the first step: separation of CO_2 [5]. CO_2 capture technology is mainly divided into pre-combustion capture, oxy-combustion system and post-combustion capture [6]. At present, in these three capture technologies, the most widely used one is the post-combustion capture [7].

The common separation methods of CO_2 include absorption [8], adsorption [9–11], membrane separation method [12], photocatalytic reduction [13] and electro-catalysis [14], etc. Among these, adsorption method has the advantages of simple equipment, low energy consumption and low corrosiveness, so it has a wide application prospect [15]. A series of adsorbents mainly used for CO_2 adsorption can be divided into non-carbonaceous adsorbents such as zeolites [16], metal oxides [17], metal-organic frameworks (MOFs) [18], alkali-metal based materials [19], silicas [20–22], etc., and carbonaceous adsorbents such as activated carbons (AC) [23], biomass-based carbons [24], ordered porous carbons [25], etc.

Among various carbon-based materials, biomass-based carbons have become a research hotspot in recent years due to its wide sources and low cost. Recently, several common terrestrial biomass materials, such as cotton stalks [26], coconut shells [27] and rice husks [28], etc., have been widely used as source materials of biomass-based carbons.

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* Corresponding author.
E-mail address: liuyx1984@126.com (Y. Liu).

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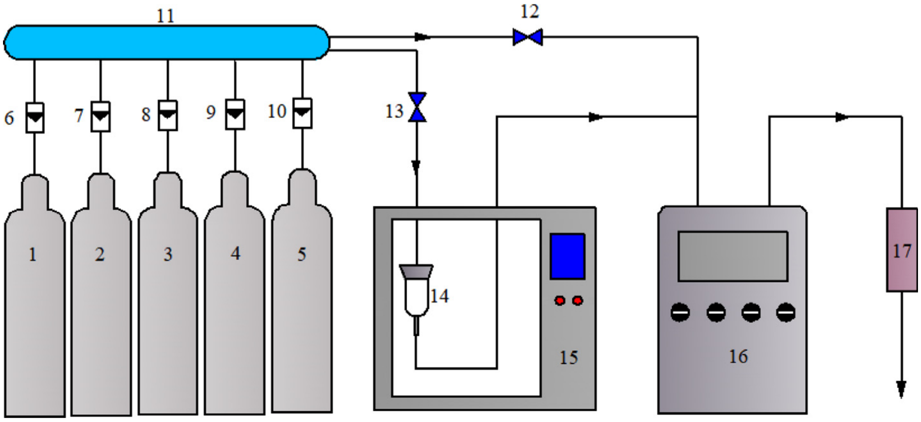

Fig. 1. Diagram of the experimental device. (1–5) $CO_2/N_2/O_2/SO_2/NO$ cylinders; (6–10) Flowmeters; (11) Mixed gas bottle; (12–13) Valves; (14) Fixed-bed column; (15) Thermostatic drying oven; (16) Flue gas analyzer; (17) Exhaust gas absorber.

However, most of these traditional biomass materials are subjected to factors such as geographical location and cultivated land yield, so the cost of large-scale recycling is quite high [29,30,31].

The development and utilization of marine biomass will be free of these limitations [32]. As we all know, there are a lot of seaweed resources in the ocean. Sargassum is a common seaweed widely distributed in warm water areas, and China is one of the main producing areas [33]. Enteromorpha is widely distributed in the world's oceans, also growing on the coast of China, and even causing large-scale green tide due to global climate change and eutrophication of water [34]. At present, these two kinds of seaweed have been studied for the preparation of bio-oil [35]. In the process of bio-oil production, a large amount of by-products (seaweed biochars) are produced. In order to reduce the pollution of solid waste, we propose for the first time to use seaweed biochar as raw materials to prepare CO_2 adsorbents.

So far, sargassum and enteromorpha have been used to prepare adsorbents for removing gaseous elemental mercury [36–38]. However, the use of these biomass to prepare adsorbents for CO_2 capture has been rarely reported. It is worth noting that raw biochars cannot adsorb CO_2 well because CO_2 belongs to a weak Lewis acid [39]. Thus in order to better adsorb CO_2, it can enhance textural parameters of biochars and increase alkaline sites at the same time by chemical activation. Chemical reagents, mainly including K_2CO_3 [40], KOH [41], HNO_3 [42], $ZnCl_2$ [43], H_3PO_4 [44], etc., are commonly used to activate biochars. Among these, KOH activation is one of the important ways to form well-developed pore structure and produce active functional groups on the surface of biochars [45]. Yaumi et al. [27] prepared the adsorbent using coconut shell, glucosamine and KOH as activators by carbonization and chemical activation, and found that it had a high specific surface area. Ganan et al. [46] reported that KOH activation increased the total pore volume of the sample, and indicated that it was due to the introduction of metallic potassium into the carbon matrix, thereby promoting the expansion of carbon atomic layers voids.

In this work, two kinds of seaweed porous biochars were prepared using sargassum and enteromorpha as precursors and KOH as a chemical activator, respectively, and were used to evaluate their CO_2 adsorption performance. The effects of preparation parameters and technological parameters on CO_2 adsorption capacity, CO_2 adsorption kinetics and regeneration stability were studied. The results may inspire new research interests and provide necessary theoretical guidance for the application and research of seaweed biomass-based biochars for CO_2 capture, and effectively expand the utilization of marine biomasss for gas purification.

2. Experimental

2.1. Preparation of adsorbents

Sargassum and enteromorpha were obtained from Weihai City, Shandong Province, China. The preparation method of the two materials was exactly the same, which can be described by preparation process of sargassum. Fresh sargassum was repeatedly washed with deionized water and then dried to remove possible impurities. The dried sargassum was crushed and sieved into powdered biomass materials of less than 50 mesh. Afterwards, sargassum powder and solid KOH were thoroughly mixed at different KOH/biomass weight ratios of 0, 1, 2 and 4. The mixtures were then calcined at different temperatures (400 °C, 600 °C and 800 °C) for 2 h in a tubular furnace protected with a continuous flow of N_2, which was called as a single step carbonisation and activation method. The obtained solid powders were washed by 1 M HCl to remove potassium residues completely, and then washed repeatedly with deionized water until the pH was about 7. Finally, wet black solid powders were dried in an oven at 95 °C for 6 h. The prepared materials are denoted as SCK-X-Y for sargassum activated chars and ECK-X-Y for enteromorpha activated chars, where X represents the activation temperature and Y represents for the weight ratio of KOH to biomass. And the sargassum and enteromorpha raw biochars are denoted as SC-Z and EC-Z respectively, where Z represents the pyrolysis temperature.

2.2. Fixed-bed adsorption and regeneration

The experimental device is shown in Fig. 1. The carbon dioxide adsorption-desorption was performed using a fixed-bed column (14 in Fig. 1) with a length of 4 cm and an inner diameter of 2.5 cm, which was placed in a constant temperature drying box (15 in Fig. 1). Before the start of the adsorption studies, a certain weight of adsorbent was placed in the adsorption column and then pre-heated to 110 °C under pure nitrogen flow of 30 mL/min for 1 h. This was to ensure complete removal of moisture and pre-adsorbed gases. Meanwhile, CO_2 and N_2 gases (1–2 in Fig. 1) at a certain flow rate (50 mL/min) were mixed in a bottle (11 in Fig. 1), with the inflow of each gas controlled by a flowmeter (6–7 in Fig. 1). The GHSV (hourly space velocity of gas) was about 3057 h^{-1}. Then the concentration of CO_2 was measured by a flue gas analyzer (FGA-4100M, Foshan, China) (16 in Fig. 1). It need to ensure that the mixed gas was composed of 12% CO_2 and 88% N_2 when it was passed into the adsorption column. Thereafter, the adsorption column was cooled to the desired adsorption temperature and stopped passing nitrogen. Furthermore, O_2, SO_2, and NO gases (3–5 in Fig. 1) were respectively introduced into the above basic flue gas components (12% CO_2 and 88% N_2) for contrast experiments. The effects of flue gas