Biochar reuse as adsorbent for post-treatment of hydrogen sulfide from microwave pyrolysis of sewage sludge

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Abstract The reuse of pyrolysis byproduct, biochar (BC), as adsorbent for post-treatment of hydrogen sulfide from microwave pyrolysis of sewage sludge was investigated in this study. Its adsorption performance was compared with one commercial activated carbon (AC) in the sealed desulfurization device. The porous structure and surface characteristics were studied using N_2 adsorption and desorption isotherms and SEM analysis. The results showed that BC had comparable adsorption performance with AC, in which the H_2S removal efficiencies of both adsorbents contributed to 78.4% and 90.3%, respectively. The adsorbent prepared by microwave pyrolysis had higher surface area than that of conventional pyrolysis, where SBET of BC reached 476.87 m^2/g in this study. The porous structure analysis found that H2S adsorption was mainly depended on the surface area of adsorbents. SEM characterization confirmed the reuse potential of biochar after H_2S adsorption, which provided a cost-effective way for post-treatment of H_2S from pyrolysis biosyngas.

Keywords: Biochar; Reuse; Hydrogen sulfide; Microwave pyrolysis; Sewage sludge

1. Introduction

The restrictive legislation and increase in the living standard contribute to the rapid production of sewage sludge during wastewater treatment in the plants. It was reported that in the EU above 10 million tons of dry solids were generated annually [Azuara *et al*., 2013]. The conventional application of sewage sludge on agricultural land and incineration faces significant difficulty due to health, environmental and social concerns. Consequently, alternative processes such as gasification or pyrolysis has raised increasing attentions for the recovery of energy from sludge [Bulushev and Ross, 2011; Chen *et al*., 2015; Zhang *et al*., 2013, 2014]. During pyrolysis, three products including the biosyngas, biochar and a liquid product are obtained. At high temperatures above 650 °C, the biosyngas is the main pyrolysis product in which H_2+CO accounts for more than 50 vol.% of the total gas yield [Zuo *et al*., 2011]. Thus, much attention in sewage sludge focuses on pyrolysis gaseous product which can be used for new renewable fuel.

The gas phase has a high hydrogen sulfide content limiting the application of pyrolysis biosyngas as fuel [Zhang *et al*., 2017a,b]. Therefore, the removal of sulfur-containing gas is an issue of particular concern. The application of an adsorbent for post-removal of hazardous gas is a common practice. In the study for adsorption of gaseous formaldehyde, sewage sludge based activated carbon was prepared and it showed excellent adsorption performance comparable with the commercial activated carbons [Wen *et al*., 2011]. In addition, efficient hydrogen sulfide adsorbents were obtained by pyrolysis of sewage sludge with spent mineral oil. The results found that the new adsorbent over performed by 230% coconut shell based activated carbon [Bagreev and Bandosz, 2004]. It was noted that most of the adsorbents were prepared under the conventional heating apparatus like electric furnace, while research in production of activated carbon by microwave pyrolysis was limited. Actually, the different heating mechanism between microwave and electrical pyrolysis might contribute to different characteristics of adsorbents prepared.

The main goal of this study is to know the effect of microwave pyrolysis on the porous characteristics and adsorption performance of biochar adsorbent. Moreover, the morphology analysis of biochar before and after adsorption of hydrogen sulfide was also conducted at the final section.

2. Material and methods

2.1. Materials

The dewatered sewage sludge was collected from the Taiping Municipal Wastewater Treatment Plant of Harbin city, P.R.China. All of the chemicals (including the commercial activated carbon) were of analytical grades and the characteristic of sewage sludge was shown in Table 1. The pyrolysis byproduct, biochar, was collected from the solid residue after pyrolysis experiments, in which dewater sewage sludge was used as raw material for microwave pyrolysis. Sludge pyrolysis was conducted in a microwave pyrolysis device and its detailed operation information was given in previous studies [Zhang *et al*., 2017a,b]. At last, the residual chars were collected and stored in airtight containers for next use.

Table 1. Characteristics of sewage sludge

Proximate analysis (wt%)				Ultimate analysis (wt%, daf)				
M	Ad	Vd	FCd	C	H	N	S	O
78	42	55	3	30.94	4.773	4.61	0.72	25.64

M, moisture content; A, ash content; V, volatile content; FC, fixed carbon; d, dried basis; daf, dried and ash-free basis.

2.2 Adsorption performance of hydrogen sulfide

The pyrolysis gases containing H2S was used as the vapor source in the experiments, where the virgin biosyngas first passed through the tar-collecting system to eliminate the influence of biotar on H2S adsorption. The desulfurization experiments were conducted in a rectangular fixed bed device with known amount of adsorbents and sealed during adsorption. The biosyngas entered the desulfurization device through the inlet valves and exited through the output valves.

2.3 Characteristics

The porous structure characteristics of adsorbents were determined from N2 adsorption and desorption isotherms using standard volumetric techniques (ASAP 2010, Micromeritics, USA). Surface morphology was observed by a scanning electron microscopy (JSM-6700F, Japan). Additionally, H2S concentration was analyzed in a gas chromatograph fitted with a TCD detector (HP 5890, Agilent China).

3. Results and discussion

3.1 Characteristics of the porous structure of adsorbents

The N2 adsorption and desorption isotherms of the prepared biochar (BC) and commercial activated carbon (AC) were shown in Fig. 1. For each isotherm, the lower and upper branches represented the adsorption and desorption curves, respectively. As can be seen from Fig. 1, both the BC and AC exhibited the isotherm of type Ⅰ in the BDDT classification, where a sharp rise displayed at low relative pressure and a hysteresis loop followed in the N2 adsorption curve. At the relative pressure of P/P0=0, the adsorption capacities of BC and AC reached 72 cm3/g and 100 cm3/g respectively, and increased gradually with the increase of P/P0 in the range of 0.1-0.75. The results indicated that the microporous carbonaceous structure was the major structure within the two adsorbents. The hysteresis loop could be associated with capillary condensation of mesoporous solids [Wen *et al*., 2011].

The structural parameters obtained from nitrogen isotherms were listed in Table 2. It was found that the SBET and SLangmuir of BC were 476.87 and 565.22 m2/g respectively, which was close to that of activated carbon. The surface area of biochar prepared in this study was significantly higher than those (55 and 49 m2/g) obtained from other researches [Ros *et al*., 2007]. This might be attributed to the fast release of volatiles during microwave pyrolysis of sewage sludge compared with the conventional pyrolysis, which contributed to the abundant and high porosity after pyrolysis. It was reported that the synchronous heating inside and outside of sludge during microwave pyrolysis resulted in the relative shorter time to achieve the high temperature desired than the conventional heating [Zhang *et al*., 2017a,b].

3.2 Adsorption performances of hydrogen sulfide by adsorbents

Based on our previous studies [Zhang *et al*., 2017a,b], H2S was identified as the main sulfur-containing pollutant in the pyrolysis biosyngas product. To further verify the post-removal efficiency of H2S by both adsorbents, a 50 L biosyngas produced by microwave pyrolysis of sewage sludge was tested passing through a fixed bed apparatus containing adsorbent with the same mass. The results were shown in Fig. 2. It was seen that AC had a higher desulfurization efficiency (90.3%) than that of BC (78.4%). This was consistent with the results of adsorbents surface area, where SBET of AC was also higher than that of BC (Table 2). According to the reports of other studies [Stüber *et al*., 2011], the adsorption performances of carbon adsorbents were significantly affected by their porous characteristics. In the study on the adsorption of gaseous formaldehyde by sludge based adsorbents, Wen *et al*. [2011] reported that the average pore diameter of adsorbents were another important parameter influencing the removal efficiency of adsorbents. From Table 2, the larger average pore diameter of BC (2.34 nm) was found than that of AC (1.67 nm). Generally, it was easier for adsorbate passing through the larger pores and arriving at the adsorption sites, accounting for higher removal efficiency. Thus, the above results indicated that H2S adsorption performance was mainly depended on the surface area of adsorbents.

3.3 Morphology analysis of H2S adsorption

The SEM analysis of the BC before and after adsorption was shown in Fig. 3. As shown in Fig. 3a, the surface porosity of BC prepared by microwave pyrolysis of sewage sludge developed well. This was mainly attributed to the following two aspects: In the microwave pyrolysis process, the macromolecular organic material of sludge at high temperature cracked and released abundant small-molecule gaseous substances, giving rise to the formation of porosity structure. On the other hand, sludge surface materials induced by the heating conduction of microwave absorbers [Zhang *et al*., 2017a] also experienced cracking reaction to generate pores, and these tiny pores greatly improved the pyrolysis biochar surface area and pore volume. Fig. 3b was the surface morphology of biochar after adsorption of H2S. It was found that parts of micropores of BC were blocked after adsorption and these microporous and mesoporous structure further etched into big pores, resulting in the decrease of pore volumes. Therefore, the regeneration of biochar after adsorption deserved further investigation and BC provided a cost-effective way for post-treatment of H2S from pyrolysis biosyngas.

4. Conclusions

In the present study, the characteristics and adsorption performance of sludge based biochar (BC) were investigated. For the treatment of 50 L of pyrolysis biosyngas, the desulfurization efficiency of BC could achieve 78.4% relatively lower than 90.3% of AC. The good adsorption performance of BC was owed to its higher surface area with SBET and SLangmuir of 476.87 m2/g and 565.22 m2/g respectively. The SEM analysis indicated that reuse of BC was deserved special attention due to its economical advantage.

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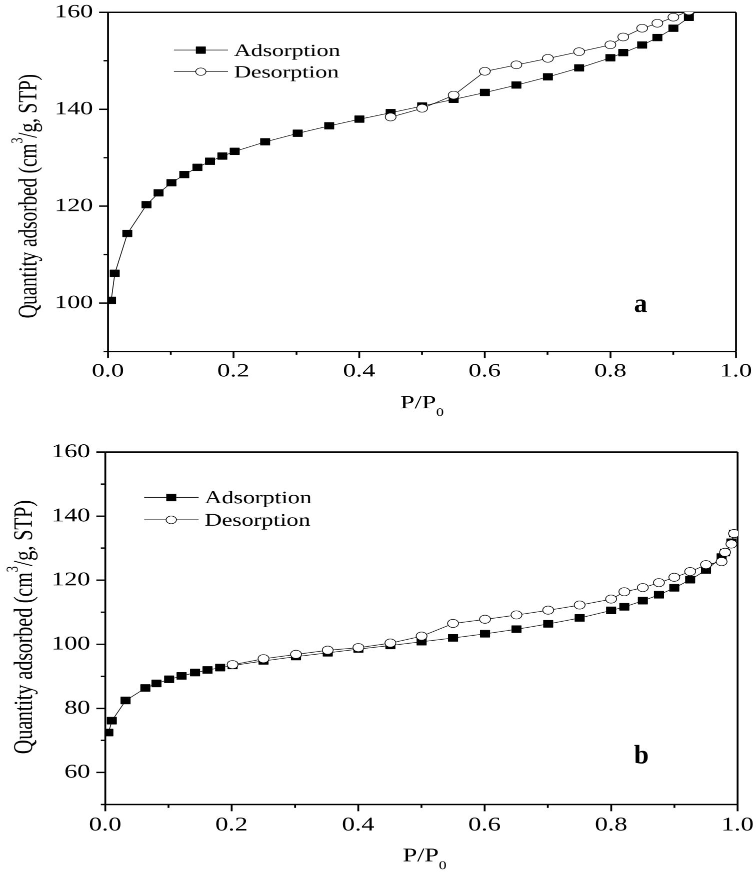

Fig. 1 N2 adsorption and desorption isotherms of AC (a) and BC (b)

Table 2. Characteristics of the porous structure of adsorbents

Samples	S_{BET} (m^2/g)	$S_{Langmuir}$ (m^2/g)	D_{Ave} (nm)	V_{Total} (cm^3/g)
AC	532.43	629.35	1.67	0.374
BC	476.87	565.22	2.34	0.212

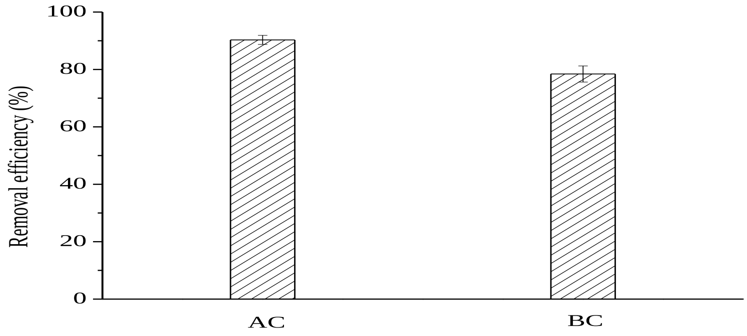

Fig. 2 H_2S adsorption performances of AC and BC adsorbents

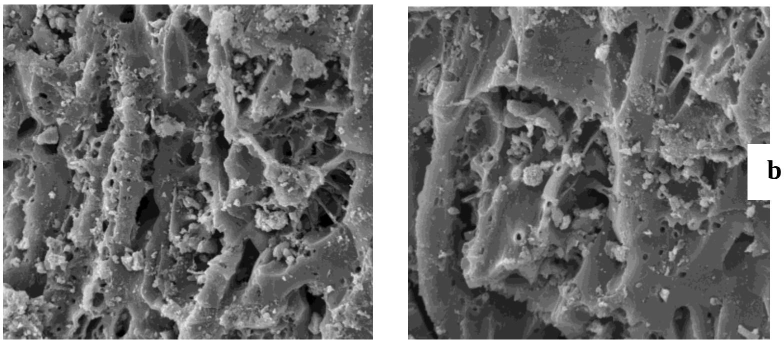

Fig.3 The scanning electron microscopy images of BC before (a) and after (b) adsorption

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