Characterization of Adsorbent from Hydrothermally Carbonized and Steam Activated Sewage Sludge

Pannarai Saetea, and Nakorn Tippayawong

Abstract **— Carbonaceous adsorbent was prepared by physical activation of hydrochars obtained from hydrothermal carbonization (HTC) of sewage sludge. Steam activation largely enabled porosity development in the hydrochars. The resultant activated carbon was characterized for chemical adsorption ability, specific surface area, and scanning electron microscopic images. The results indicated that the best quality sewage sludge activated carbon (SSAC) was obtained at activation time of 120 min. It was observed that the product had maximum iodine value of 612 mg/g, MB adsorption capacity of 162 mg/g, and specific surface area of 585 m^2/g. These properties were comparable to those from commercial activated carbon. HTC and physical activation with steam proved to be effective methods for preparation of low cost adsorbents from sewage sludge. The SSAC obtained from these processes showed good potential for adsorption or soil conditioning.**

Index Terms **— activated carbon, biomaterials, thermal conversion, subcritical water, waste valorization**

I. INTRODUCTION

Wastewater treatment process generates large amount of sewage sludge. Sewage sludge comprises mostly offensive, pathogenic and toxic substances. It must be disposed of or managed properly, otherwise, adverse effects on human health and the environments will occur. There are a number of safe and sustainable options with regards to disposal and utilization of these solid byproducts. Since sewage sludge contains large amount of organic materials, a popular treatment route for sewage sludge is to convert it into fuels or high value chemicals. Almost any carbonaceous materials can be used as a precursor for the preparation of activated carbon (AC). Sewage sludge has been suggested and demonstrated as a suitable raw material for the production of AC due to its richness in volatile components [1-9]. Typically, AC is generated using chars from pyrolysis of organic material, that undergo subsequent activation process with an agent (air, steam, CO_2) at high temperatures. Production cost of AC is directly associated to energy consumption. Hence, improvement of energy efficiency of the process would be beneficial.

A possible method to convert biomass into chars is by hydrothermal carbonization (HTC). The HTC process is relatively simple and low cost. It takes place effectively only in water. The products of the HTC are a carbon rich solid or “hydrochar” and a liquid filtrate. A small amount of gas is also produced. The process is considered to be more energetically efficient than pyrolysis, largely because (i) milder thermal conditions are employed, (ii) the process is exothermic, and (iii) wet materials can be used directly with no drying required [10-13]. Utilizing HTC to enhance production of AC from sewage sludge would be very interesting [14].

This work presents an attempt to improve hydrothermally carbonized sewage sludge using physical activation by steam to produce carbonaceous adsorbent. HTC of sewage sludge at mild condition followed by physical activation by hot steam was performed to prepare sewage sludge activated carbon (SSAC). Adsorption performances of produced AC were investigated to evaluate the effects of contact time on adsorbent dosage and specific surface area.

II. MATERIALS AND METHODS

A. *Raw Material*

Anaerobically stabilized sewage sludge from the treatment plant of Chiang Mai University, Thailand was used as starting material. The raw sewage sludge was dried at 105°C for 4 h to achieve constant weight, then comminuted and sieved into a uniform size. Dried sludge was milled to particle diameter of less than 1 mm and used as starting material.

B. *HTC Process*

Carbonization experiments were carried out in a 1000 ml pressure reactor equipped with an external resistance heater and internal sensors for pressure and temperature, shown in Fig. 1. 100 g of dried sewage sludge, 100 g of oxalic acid, and 300 ml of distilled water were mixed and shaken vigorously to create a homogeneous suspension. The mixture was then transferred to the reactor. Reactions were carried out at 200°C for 1 h. After the heater was turned off and the heat insulation was dismounted, the reactor was allowed to cool down to ambient condition. The reaction products were subsequently filtered. The hydrochar was washed well with deionized hot water. The slurry was

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Manuscript received February 20, 2013; revised March 11, 2013. This work was supported in part by the Graduate school, Chiang Mai University.

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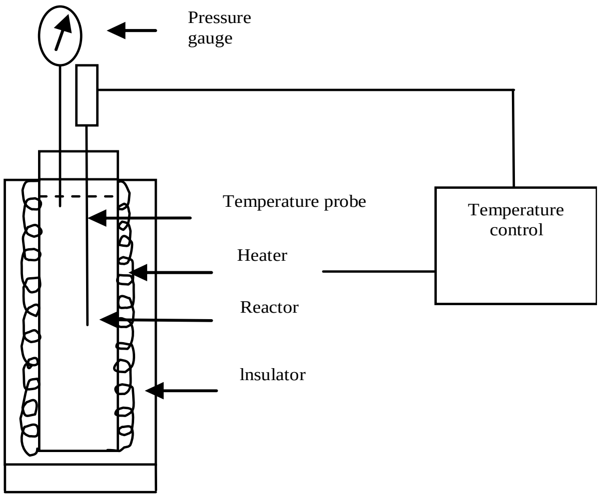


Fig. 1. Reactor for HTC process.

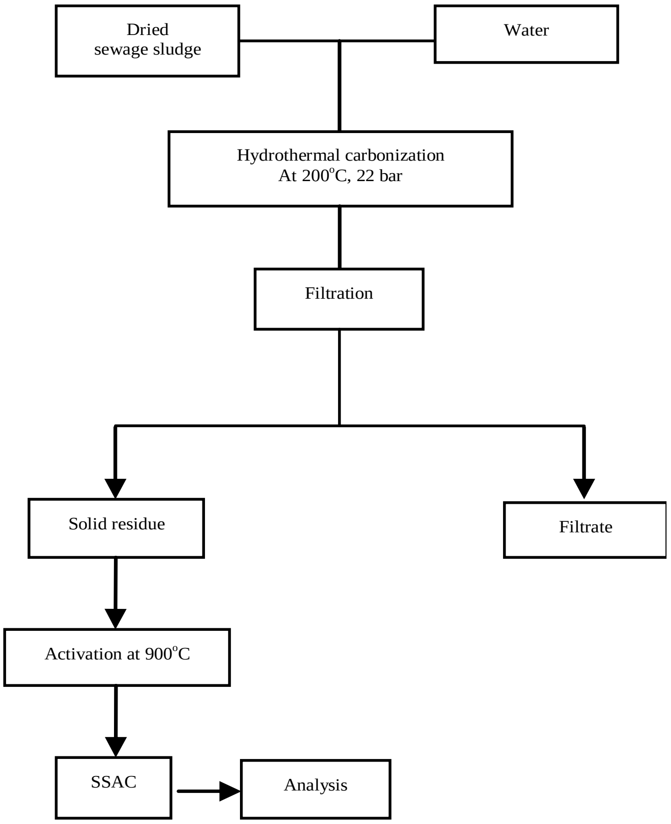


Fig. 2. HTC and activation procedure.

filtered through fluted filter paper and the solids were dried for 4 h at 105°C. The dry char was weighed.

C. Synthesis of Activated Carbon

After the dehydrated sewage sludge was hydrothermally carbonized, the hydrochar was physically activated in hot steam atmosphere. Overall procedure is summarized in Fig. 2. The hydrochar from HTC were crushed and sieved to particle sizes less than 1 mm. The hydrochar (10 g) was then charged into the fixed bed reactor. The heating rate supplied was 10°C/min and N_2 was continuously passed at an 80 m^3/min. Once the temperature was stabilized at 900°C, steam was fed at a flow rate of 20 cm^3/min for the activation time between 30, 60, and 120 min. The resulted product was subsequently dried at 105°C for 4 h to constant weight. It was then crushed and sieved into the desired particle size, which was designated as SSAC, and stored in vacuum desiccators for later analysis and characterization.

D. Characterization of SSAC

Tests were run on the adsorption of methylene blue (MB) and iodine onto the SSAC obtained. Iodine number in the characterization of AC was determined, based on ASTM D 4607-94. The adsorption of aqueous iodine was considered a simple and quick test for evaluating the surface area of the AC associated with pores larger than 1 nm [15]. The iodine value, defined as the amount of iodine adsorbed per gram of activated carbon at an equilibrium concentration of 0.02 N, was measured according to ASTM D 4607-94. Adsorption tests with MB were run discontinuously and with magnetic stirring at 25°C. Specific surface area was measured using BET method from the N_2 adsorption. The surface physical morphology of SSAC was inspected using a scanning electron microscope (SEM).

III. RESULTS AND DISCUSSION

A. Characteristics of Starting Materials

Raw sewage sludge was analyzed for fuel properties. Its gross heating value was about 19 MJ/kg, dry basis. It was observed that the dried sewage sludge high fractions of ash (40 %) and volatile matter (> 50 %). Because of its low fixed carbon content, carbonization was needed to develop higher fraction of fixed carbon before activation. After HTC, hydrochar yields obtained ranged between 77 – 85 %. Its iodine number and BET surface area were about 180 – 220 mg/g and less than 10 m^2/g, respectively.

B. Characteristics of SSAC

Yield was defined as a ratio between weight of dried activated carbon and that of hydrochar. The activation time had a negative influence on total yield of SSAC (Fig. 3). Over 80 % yield of SSAC was obtained at 30 min, and then decreased to about 65 % at 120 min. Volatile matter in the SSAC was progressively gasified by nitrogen and steam. Loss of volatile matter led to low yield. However, high temperature led to high porosity. Porosity development increases with an increase in time. The increase in reaction time, therefore, the removal of amorphous components which obstruct the pores, leading to a decrease in mass yield [15].

Fig. 4 showed that when the activation time was increased from 30 to 120 min, the iodine number increased sharply, showing maximum at 120 min. This may be contributed to the fact that tar-like matter in pores were removed or volatilized well by nitrogen, which generated porosity. In this study, it was found that iodine number of SSAC was about 470 – 612 mg/g, which was significantly higher than that of hydrochar (193 – 221 mg/g). Iodine number is considered as a simple and quick test for evaluating the surface area of activated carbon associated with pores with $d > 1$ nm [16], mesopores (2 nm $< d <$ 50

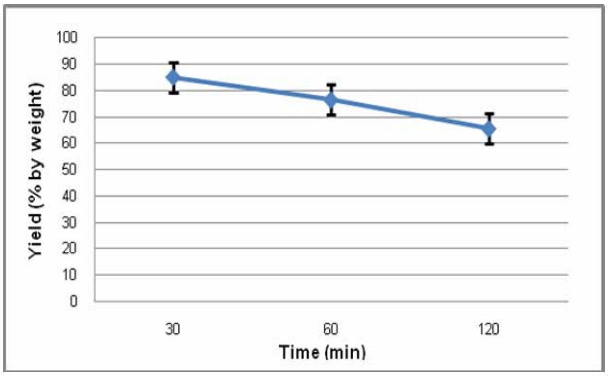


Fig. 3. Effect of activation time on yield of SSAC.

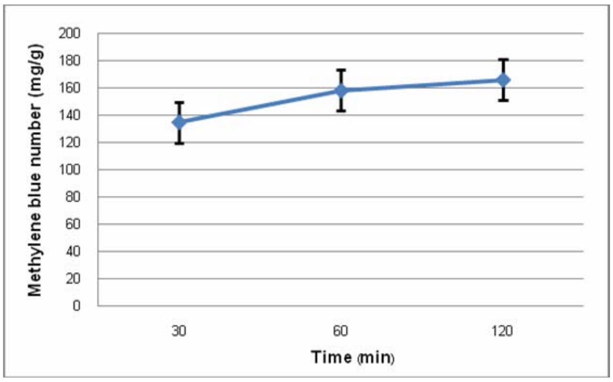


Fig. 5. Effect of activation time on MB adsorption of SSAC.

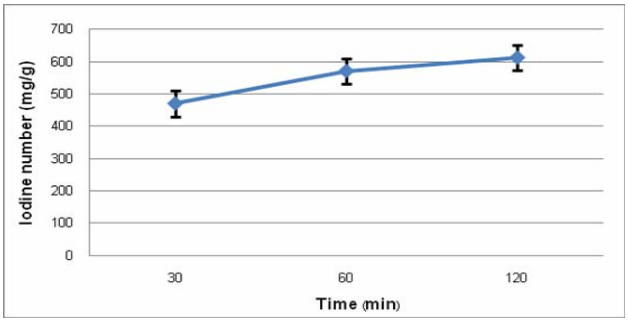


Fig. 4. Effect of activation time on iodine adsorption of SSAC.

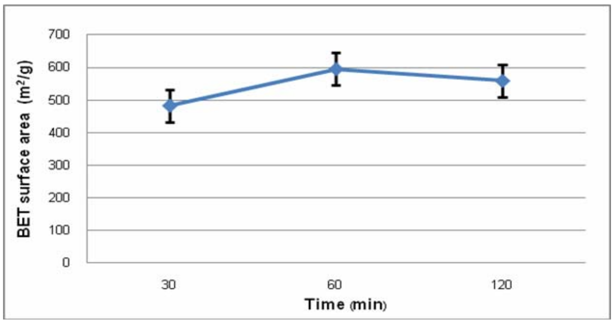


Fig. 6. Effect of activation time on specific surface area of SSAC.

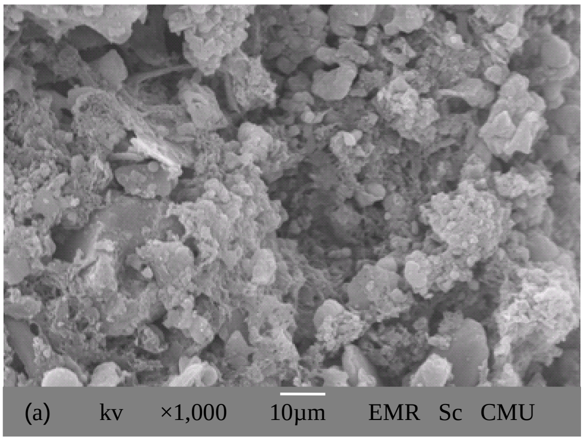
nm) were developed during physical activation with steam. Further increase in activation time may cause over-activation, accelerating surface erosion rather than pore formation. The observed trend agreed with those reported in the literatures [17].

The effect of activation time on adsorption of MB is shown in Fig. 5. The MB adsorption rates increased dramatically in the first 60 min, and reached equilibrium gradually at 120 min. The high adsorption rate during the initial period was due to a number of available adsorption sites. As these sites became progressively covered, the rate of adsorption decreased. This result is in agreement with the finding reported by [18]. As shown in Fig. 5, the amount of MB increased from 134 to 162 mg/g at 30 and 120 min, respectively. The maximum adsorption capacities of MB onto different adsorbents prepared from various solid wastes, are reported elsewhere [19]. Although the published values were obtained under different experimental conditions, they may be useful as a criterion for comparing the adsorption capacities. It can be seen that the adsorption capacity of SSAC obtained in this work was smaller than other adsorbents. The adsorption capacity of SSAC was 162 mg/g. It should be noted that, under the same processing conditions, the adsorption of SSAC was better than that used by [18]. The reason may be that SSAC was mainly of transition pore structure, and beneficial to adsorb the big member materials.

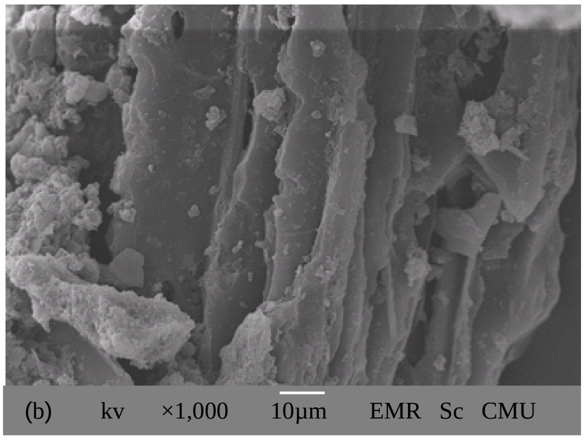
Specific surface areas of SSAC was about 483 – 595 m^2/g, shown in Fig. 6. An increase in specific surface area of SSAC was observed after carbonization and activation. Specific surface area of commercial activated carbon was about 500 – 1200 m^2/g, which was used as a standard material during the test. SSAC had a similar specific surface area to commercial activated carbon, indicating a great potential for surface adsorption.

At 120 min activation time, the SSAC appeared to have maximum MB and iodine number. The properties of the SSAC in this condition showed yield of 65.5 %, iodine number of 612.54 mg/g, MB number of 162.86 mg/g and BET surface area of 584 m^2/g, respectively. The iodine number, meets the standard of the commercial activated carbon of TS 900-1989 (over 600 mg/g).

Fig. 7 shows the SEM images of hydrochar product in comparison with SSAC. The structure of hydrochar product was dense and porosity was low (Fig. 7a). After activation process, it was noted that micropores were formed on the surface of SSAC, and its surface appeared to be coarser and rougher than hydrochar. The smooth surface observed for hydrochar was developed by the melting and fusion process of the organic substance and other small molecules compounds in sewage sludge, such as pectin and inorganic compounds [19]. Pores of different size and shapes can be observed, as shown in Fig. 7b. This may be attributable to decomposition of organic matters during activation process. The pores on the surface of SSAC were enhanced, as a result of drilling and expansion of steam to pores during activation. The vesicles on the rougher surface of SSAC resulted from the release of volatile gas contained in the softened biomass matrix during the pyrolysis process. The matrix became brittle and the collapses of part of vesicles were observed on the surface of hydrochar. As for SSAC, the vesicles were formed through chemical bonds decomposition and fragmentation release from sewage sludge matrix taking into account the fact that hydrolysis reaction was predominant for biomass hydrothermal treatment.



(a) hydrochar



(b) SSAC

Fig. 7. SEM images of hydrochar and SSAC

IV. CONCLUSION

In this study, the SSAC with remarkable adsorptive prosperities was successfully prepared from sewage sludge by HTC followed by physical activation with steam. The mild HTC condition proved to change proximate components of the hydrochars slightly with time, but improve pore structure, hence adsorption in terms of iodine number significantly. Activation with steam was shown to result in better adsorbent. However, at longer activation time, decreases in yield and micropores were observed. At optimum condition, the AC showed yield of 65 %, iodine number of 612 mg/g, MB number of 162 mg/g and specific surface area of 590 m^2/g, respectively. The maximum adsorption of MB, iodine number and specific surface areas of SSAC were found to be similar to commercial activated carbon. This study demonstrated that SSAC can be used as an effective, low cost alternative adsorbent.

ACKNOWLEDGMENT

The authors would like to thank the Department of Scientific Services, Ministry of Science and Technology, and the Mae Moh Laboratory, Electricity Generating Authority of Thailand for technical support.

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