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Original Research Paper

Preparation and analysis of activated carbon from sewage sludge and corn stalk

Yili Li *, Yanling Li, Liping Li, Xiujuan Shi, Zhan Wang

College of Environmental and Energy Engineering, Beijing University of Technology, Beijing 100124, China

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ABSTRACT

In this study, activated carbon (AC) was prepared using corn stalk and sewage sludge by chemical activation method, which not only solved the sludge's disposal problem, but recycled the agricultural waste (corn stalk). The effects of operating conditions (including activation reagent, activation temperature, concentration of activation reagent, pyrolysis time, impregnation ratio and corn stalk addition) on BET surface area and production yield of AC were investigated. The powder characters (like BET surface area, pore-size distribution and pore volume) were presented. Scanning electron microscope (SEM) and Thermo Gravimetric and Fourier Transform Infrared Spectroscopy (TG-FTIR) analysis were also used for the characterization of produced ACs. Results showed that the pure-AC with a higher BET surface area of 475.0 m^2/g could be obtained when the concentration of activation reagent ($ZnCl_2$) was 4 M, the activation temperature was 600 °C and the pyrolysis time was 60 min. If 25.0% corn stalk was added, the BET surface area reached to 769.0 m^2/g. Through the comparison between the production and the commercials, it can be seen that the two have almost equal methylene blue dye removal efficiency and adsorption. Besides, the sludge based AC is more economic.

1. Introduction

Sewage sludge, the inevitable by-product generated in wastewater treatment operations, is a kind of colloidal sediment containing harmful pollutants of pathogen, microorganism and heavy metals [1]. In China, large amounts of sewage sludge are produced every year, and the disposal cost account for 25–65% of the total operating cost [2]. Common disposal methods (including landfill, forestry, sea dumping, incineration and so on) have a lot of disadvantages, the harmful pollutants it contains can result second pollutions as well. Facing with the stricter regulatory pressure and increasing public opposition, an innovative, low-cost and environmental friendly alternative for sludge disposal is needed [3].

Activated carbon (AC), an inert porous carrier material, is widely used in air and wastewater decontamination since its capability of distributing chemicals on its large hydrophobic internal surface [4]. The commonly production methods were physical activation and chemical activation [5]. While, chemical activation is more popular since its combination of carbonization with activation, lower operating temperatures, higher yield [6], easier recovery of the activated reagents [6–8] and better production with higher surface area and better developed porous structure [9–12]. Many agriculture by-products or lignocellulosic materials, such as waste tires [13] and waste newspapers [14–19], were used for the production of AC.

It is worth mentioning that Beeckmans et al. [20] firstly put forward the idea that the sewage sludge could be used to prepare AC, since it contains carbonaceous structure and rich in organic materials. From then on, massive literatures have been reported about the sewage sludge-based AC [21–24]. Maria et al. [21] made sludge-based (SB) AC with biological sludge at a pyrolysis temperature of 700 °C in the presence of H_2SO_4. The obtained SB AC was with a surface area of 253 m^2/g and an average pore diameter of 2.3 nm. Li et al. [23] employed paper mill sewage sludge as the raw material for producing activated carbon by physical activation with steam. The highest iodine number and BET surface area of 186.36 mg/g and 135.49 m^2/g were obtained at a carbonization temperature of 300 °C, carbonization time of 60 min, activation temperature of 850 °C and activation time of 40 min.

Abbreviations: AC, activated carbon; pure-AC, AC prepared under optimum conditions based on pure sludge; mixed-AC, AC prepared under optimum conditions based on sludge mixed with 25.0% corn stalk.

* Corresponding author. Tel.: +86 10 67392080; fax: +86 10 67391983.
E-mail address: liyili@bjut.edu.cn (Y. Li).

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However, the industrial application of AC made by sewage sludge was limited due to the relatively low BET surface area [3,23,25]. To improve this quality of AC, some carbonaceous matters were added to sludge. Tay et al. [3] mixed coconut shell with sewage sludge, the BET surface area of final product obviously increased and reached 868.0 m^2/g. Some low-cost sawdust was blended with sludge to increase the carbon content, and the iodine value of AC reached 555.3 mg/g under the optimal activation temperature of 650 °C [26]. In the research of Kazemipour et al. [25], some materials such as pistachio, almond, hazelnut, walnut and apricot were respectively used to prepare AC and the BET surface area of the AC was between 635 m^2/g and 1208 m^2/g. Obviously, the addition of biomass materials into sludge truly increased the BET surface area of AC, on the other hand, it realized the resource utilization of agriculture wastes as well as sludge.

In this paper, corn stalk, a main agricultural residue in China, was added into sewage sludge from wastewater treatment plant to prepare AC with one-step pyrolysis method. It is a more economical way to boost the production yield of sludge based AC. The effect of activation reagents, activation temperature, pyrolysis time, impregnation ratio and corn stalk addition on BET surface area and production yield of the final product were investigated. SEM was used to scan the pore structure of AC, TG-FTIR was used to analyze the pyrolysis process and the emitted gases and the pore-size distribution was calculated to investigate the characters of final production.

2. Experiment

2.1. Materials

The main raw material, dehydrated sewage sludge, was from Gaobeidian wastewater treatment plant in China. And the additional raw material, corn stalk, was from Beijing Shengchang Green Energy Co. Ltd. The activation reagent solution were $ZnCl_2$, KOH and K_2CO_3 (Fuchen Chemical Reagent Factory, Tianjin, CN). Methylene blue (MB) was chosen as the adsorbate to evaluate the adsorption properties. All reagents were of analytical quality and the solutions were prepared using distilled water.

2.2. Preparation of AC

The process of preparing SAC was as follows (illustrated in Fig. 1): (I) Sewage sludge was pre-dried in a drying oven (WMZK-02, Beijing Dotrust Co. Ltd, Beijing, CN) at 110 °C to constant weight, then grinded to a uniform size of 1–3 mm; (II) corn stalk was dried at 80 °C for 18–20 h, then grinded to 1–3 mm; (III) mixed the samples obtained in (I) and (II) in a given proportion to generate the precursor for preparation, then immersed them into activation reagent solution at room temperature for 12 h; (IV) removed the supernatant liquid, then dried them at 110 °C to constant weight; (V) put the dried activated precursor into tubular furnace (TXAK6-II, Beijing Pyramid Technology Co. Ltd., Beijing, CN.) for pyrolysis with purified nitrogen as purge gas. The activation temperature and pyrolysis time were varied as parameters. The heating rate maintained at 10 °C/min and the nitrogen gas flow was 400 cm^3/min; (VI) took out the product from furnace, washed them with 3 M HCl solution and then repeatedly rinsed by hot distilled water (70–80 °C) to neutrality; (VII) the final product was obtained after dried at 105 °C to a constant weight and was stored in desiccators for characterization.

2.3. Characteristics of AC

To determine the performance of the obtained ACs, scanning electron microscope (SEM) (Hitachi S-4300) was used to scan the surface of AC, Thermo Gravimetric (STA 409, NETZSCH) and Fourier Transform Infrared Spectroscopy (NXU S609, NICOLET) (TG-FTIR) were used to analyze the pyrolysis process and the emitted gases, a surface area and pore size analyzer (Micromeritics Gemini VII 2390) was used to investigate the specific surface area (BET), pore volume and the pore-size distribution of the produced ACs. The concentration of the heavy metal in leaching liquor was measured using inductively coupled plasma mass spectrometry (ICP-MS) (Agilent 7500a).

3. Results and analysis

In this section, the effect of the activation reagent, activation temperature, pyrolysis time, the corn stalk addition and the impregnation ratio were investigated to determine the optimal operating conditions.

3.1. Activation reagent selection

Three kinds of activation reagents ($ZnCl_2$, KOH and K_2CO_3) were used to prepare AC. For comparison, the concentrations of three activation reagents were all 4 M. And the activation temperature, pyrolysis time and impregnation ratio were maintained at 600 °C, 60 min and 2.0, respectively. The influence of different activated regents on the BET surface area and the product yield of the final products were shown in Fig. 2(a).

Obviously, it was found that products' BET surface area was the highest (475 m^2/g) when $ZnCl_2$ acted as activation reagent. The impregnation with $ZnCl_2$ first degraded the cellulosic material and dehydrated the carbonization produces, resulting in building of the carbon skeleton and creating of the pore structure [27,28]. In contrast, when K_2CO_3-activated sample was heated in tubular furnace, K_2CO_3 molecules were decomposed to CO_2 and K_2O. As a result, the releasing of CO_2 and the catalysis activating of K_2O led to the porous structure [29]. When KOH was selected as activation reagent, KOH and carbon atoms react at high temperatures (600–900 °C) and form metallic K, K_2CO_3, CO and H_2, which was demonstrated by Marsh and Rodriguez-Reinoso [30] and Lillo-Ródenas et al. [31]. The generated metallic K infiltrated into layered carbon structures, which provided additional amount of pores in AC [32,33]. As for yield, three activation reagents didn't show much difference. Therefore, $ZnCl_2$ was selected as the optimal activation reagent.

3.2. Effect of activation temperature

To study the effect of activation temperature on BET surface area and yield, the sludge was activated by 4 M $ZnCl_2$ at different temperatures for 60 min and the impregnation ratio was 2.0. The activation temperature increased gradually from 450 to 650 °C. Fig. 2(b) revealed the BET surface area and the yield of AC under different active temperatures.

With the increasing of the activation temperature, experimental data showed that 600 °C provides a better condition for making activated carbon with highest BET surface area (475.0 m^2/g). This can be explained as follow: with the increasing temperature, much more activation reagent molecules diffused to the precursor, which developed a wide range of pore network [23]; while exorbitant temperature might widen the micropore to mesopore or macropore since the over etching effect [34], besides, $ZnCl_2$ may be evaporated from the precursor at higher temperature. Product yield strongly decreased from 42.6% to 36.8% when temperature increased from 450 °C to 650 °C. This is because that the bound moisture, hard decomposition components and volatile matters were escaped from the raw material at a higher temperature