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Effects of ammonization on the surface physico-chemical properties of sludge-based activated carbon

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ABSTRACT

In this paper, sludge-based activated carbon (SAC) was treated by HNO_3 and NH_3 in turns. Under the conditions of ammonization temperature and residence time, the surface physico-chemical characteristics of modified SAC were characterized by SEM, BET, FTIR and XPS. The research results show that modification of SAC leads to beneficial effect on the porous structure, the maximum surface area and micro-pore volume reached to 273 m^2/g and 0.082 cm^3/g at 750 °C, respectively. After ammonization, N—CH_3 and C═N groups were detected on the surfaces of all the modified SACs. Moreover, XPS study indicated that the nitrogen content increased from 1.65% in origin sample to a larger content range of 2.93–4.69% at different treatment conditions and found that lower ammonization temperature and longer residence time will produce higher nitrogen content. The nitrogen introduced mainly in the forms of amines, pyridine nitrogen (N-6), pyrrole nitrogen (N-5), quaternary nitrogen (N-Q) and N-pyridine oxide (N-O_x). The sample of SAC-650-90 obtained the highest content of N-6 with the value of 1.46%. The highest content of N-5, N-Q and N-O_x which obtained in the sample of SAC-750-120 in the same time were 1.22%, 0.98% and 1.21%, respectively. Compared to the ratios of five kinds of nitrogenous substance, the highest ratios of N-O_x, N-5, N-Q and N-6 obtained among different samples were 27.11%, 29.09%, 33.14% and 31.11%, respectively. And they can transform from one type to another.

1. Introduction

Sewage sludge, which is carbonaceous in nature and rich in organic materials, is an inevitable by-product during the wastewater treatment. The potential of sewage for producing sewage sludge-based activated carbon (SAC) was first recognized in 1971 by Kemmer et al. [1]. So far, a lot of studies have demonstrated the feasibility of transform sewage sludge into activated carbon due to SAC has the similar surface structure to activated carbon after pyrolysis. Furthermore, it was successfully adopted as adsorbent in many fields [2–6]. The attractive properties of SAC are determined not only by the well-developed surface area but also by the type, number and mode of bonding of different heteroatos (oxygen, sulphur, nitrogen, boron, phosphorus, chlorine) on the carbon's surface [7–10]. Nitrogenous functional groups are playing important role in the adsorption process for removing sulphur oxide [11] and hydrogen sulfide [12]. Nitrogenated active carbon also found to have good performance in disposal of nitrogen (II) oxide [13] and perchlorate [14].

Ammonization has been widely applied to introduce nitrogen functional groups into activated carbon and contributed to significant changes in the physico-chemical structure of the latter, which can be enhanced or reduced, depending on the temperature, time and atmosphere condition of treatment [15–17]. In previous studies [18–22], the chemical agent used to activate sludge including potassium hydroxide, zinc chloride, nitric acid, sodium hydroxide, sulfuric, phosphoric acid and so on. All these agents could enlarge the BET surface area of SAC and eventually lead to better adsorption capacity [23–25]. The modified SAC which pretreated with nitric acid would improve the content of oxygen functional groups on the surface and it was conducive to the introduction of nitrogen and conversion of nitrogen functional groups [26–29]. Robert Pietrzak obtained activated carbon surface area of 2600–2800 m^2/g and pore volume of 1.29–1.60 cm^3/g for high volatile bituminous coal by subjected it to the process of ammonization. It was performed by a mixture of ammonia and air at the ratio 1:3 (flow ratio 250:750 mL/min) at 350 °C. In addition, the greatest amount of nitrogen (6.6%) was introduced in the sequence process of carbonization–activation–ammoxidation. The ammonization process leads to the formation of amines, pyridine nitrogen (N-6),

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pyrrole nitrogen (N-5), quaternary nitrogen (N-Q) and N-pyridine oxide, directly grafted in the graphene planes [30]. Fatemi et al. [31] concluded that multi-walled carbon nanotubes functionalized with ammonia improved the adsorption capacity and selectivity of CO_2/CH_4 in gas adsorption process at ambient temperature and moderate pressures. Chen et al. [32] made activated carbon react with NH_3 at temperatures higher than 700 °C, it got higher nitrogen content and effectively enhanced the adsorption capacity for perchlorate. However, Cao et al. [33] concluded that high temperature especially surpassed 800 °C during pyrolysis leaded to the decrease of nitrogen which was similar to the introduction of nitrogen during ammonization.

This study was aimed at exploring the effects of ammonization time and temperature on the surface physico-chemical properties especially nitrogen functional groups of SAC. In addition, the present study attempts to carry out a comprehensive study with respect to the chemical and physical properties of SAC obtained after ammonization so as to provide fundamental knowledge for its application for pollutants removal.

2. Experimental

2.1. Sample preparation

Dewatered sewage sludge from the second urban wastewater treatment plant of Changsha (Hunan province) was used for the production of SAC.

The sludge sample was first dried at 105 ± 5 °C for 24 h up to constant weight. The sample was then ground and sieved to a particle size in the range of 0.35–0.83 mm. Then 10 g of sludge was pyrolyzed in a tubular resistance furnace which was electrically heated. The heating rate of the furnace was 20 °C/min and the purge gas (N_2) was continuously supplied at a flow rate of 200 mL/min. The temperature maintains for 5 min when reached at 105 °C and then went up to the final heating temperature of 500 °C and lasted for 90 min. Following pyrolysis, the solid product was obtained and then washed with distilled water and dried at 105 °C for 2 h.

The SAC was put into the following treatments (including a and b) in turns. Process (a) is the HNO_3 activation, 10 g SAC was added into a conical flask with 200 mL of HNO_3 (7 mol/L), and then the mixed solution was moved into thermostat water bath oscillated for 10 h at 70 °C. Process (b) was an ammonia treatment of the materials obtained from process (a). The ammonization was carried out in NH_3 (flow rate = 10 mL/min) atmosphere at a heating rate of 15 °C/min up to different working temperatures (650 °C, 750 °C, 850 °C) and retention time (60 min, 90 min, 120 min) (Table 1).

The process route can present as follows :

pyrolysis → HNO_3 activation → ammonization

2.2. Characterization

The proximate analysis was determined by thermo-gravimetric analyzer (TGA, STA 409 PC, NETZSCH, Germany) and the results were presented in terms of moisture, ash, volatile matter and fixed carbon contents. The composition of inorganic material was obtained by inductively coupled plasma optical emission spectroscopy (ICP-OES720, Agilent, AUS). The Brunauer–Emmett–Teller (BET) surface areas and pore structure parameters of the samples were determined from the adsorption–desorption isotherm of nitrogen at −196 °C with automatic specific surface and pore size analyzer (Micromeritics ASAP2020, USA). Surface physical morphology was observed by a scanning electron microscopy (SEM, Hitachi TM3000. Japan). Fourier transform infrared spectroscopy (FTIR) was chosen to qualitatively identify the surface functional groups. The spectra were measured from 4000 to 400 cm^{-1} and recorded on a FTIR-8400S Spectrometer (USA) using the KBr pellets containing 1% of SAC samples. The chemical state of selected elements and surface composition of the samples were determined by X-ray photoelectron spectroscopy (XPS) using FRR spectrometer (XSAM800 KRATOS Ltd., England) .The XPS spectra were recorded with an Mg Kα source operating at 192W to analyze individual elements. Samples were passed through a desorption chamber maintained at ultra-high vacuum (6×10^{-7} Pa) in order to desorb any volatile matter present on the samples.

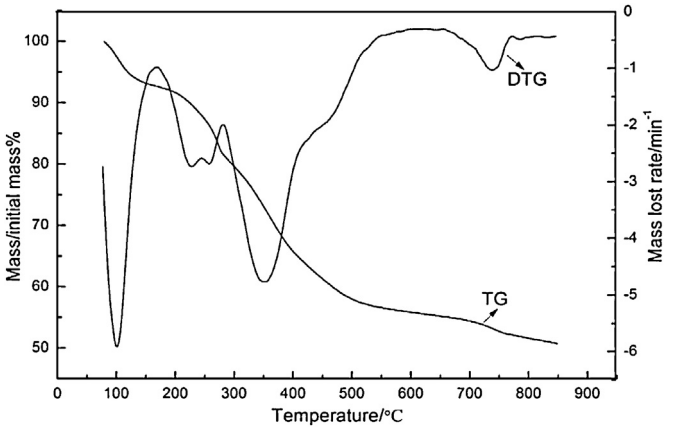

Fig. 1. TG–DTG curve of sludge sample.

3. Results and discussion

3.1. Chemical characteristics and inorganic composition of sewage sludge

The results of chemical characteristics and inorganic composition of the sewage sludge were obtained from the achievements provided by other members in our research group. Detailed data is represented in Tables 2 and 3.

3.2. Thermal gravimetric analysis of sewage sludge

Fig. 1 presents the TG and DTG analysis of sewage sludge. It can be seen from Fig. 1 that the pyrolytic process of sewage sludge can be divided into three stages, that is, dehydration (80–180 °C), devolatilization (180–500 °C) and fixed carbon burning (500–850 °C). And most of the impurities and ash dislodged from sewage sludge at 500 °C. In addition, pyrolysis at this temperature can effectively make use of organic matter and nitrogen compounds containing in sewage sludge and obtain desired SAC through specific treatments [10]. Previous study [33] showed that nitrogenous gases were detected during pyrolysis with the increasing temperature and sharply decreased when temperature surpass 550 °C. So pyrolysis at 500 °C is the best choice.

3.3. Surface morphologies of sludge-based activated carbon

Fig. 2 shows the SEM micrograph of the origin SAC (a) and modified SAC (b–f) which magnified to 8000 times. The samples modified with nitric acid and ammonization orderly. It depicts that the origin sample SAC has no obvious pore structure. However, it appeared to have a lot of deeper grooves and apertures in the surface after modifications which due to the removal of ash and the change of carbon frame structure at high temperature. The observations suggest that the modified SAC samples have more composite structure than