



Surface modification of activated carbon for siloxane adsorption

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ABSTRACT

The presence of siloxanes challenges the use of landfill gas (LFG) as a fuel for energy recovery, due to the formation of microcrystalline silica deposits during combustion. Activated carbon (AC) is often selected as an adsorbent for removing siloxanes from LFG. In order to find the key characteristics that affect the siloxanes adsorption capacity of AC, this paper studied the effects of AC textural structure and surface chemistry on siloxane adsorption. Anthracite AC was respectively treated by aqua ammonia, hydrochloric acid and heat to obtain modified AC with different surface properties. Adsorption capacities of the original and modified AC for octamethylcyclotetrasiloxane (D4) were measured. Results showed that most of the modified AC had a higher D4 adsorption capacity than the original AC. Several approaches were adopted to characterize the AC. The results obtained by nitrogen adsorption experiment revealed that all the employed modification methods changed the AC pore size distribution to some extent. The narrow mesopores on the AC surface are more desired for the siloxane adsorption. As for the AC surface functional groups, the results obtained by Boehm titration revealed that the alkaline and phenolic groups are favorable for siloxane adsorption, while the carboxylic groups are undesired for siloxane adsorption.

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1. Introduction

Landfill gas (LFG) is a valuable source of renewable energy. It has been exploited as a fuel to substitute fossil fuels in boilers, internal combustion engines, fuel cells and so on [1–3]. The existence of siloxanes in LFG is of particular concern as this class of substances is converted to microcrystalline silica deposits during combustion, and the siliceous deposits on valves, cylinder walls and liners are the cause of the extensive damage by abrasion or blockage. Moreover, silicon compounds are also found in the lubrication oils, resulting in frequent change of oil [4]. Hence, it is imperative to develop economical and effective siloxane removal technologies for LFG to increase the feasibility of using it as a fuel.

In recent years, growing importance is attributed to siloxane removal from LFG and digester gas, as the increase of publications

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and patents can be found. Dewil et al. [5] described the fundamentals of siloxanes and the variety of problems related to the presence of siloxanes in biogas. Schweigkofler and Niessner [6] tried several methods for the removal of siloxanes in biogas including solid adsorption and liquid absorption. In their study, various solid adsorption materials and liquid absorption solutions were evaluated for their siloxane elimination efficiency. A review presented by Ajhar et al. [7] summarized the commercial siloxane removal technologies and patents and discussed the siloxane removal concepts as found in the literature. Various siloxane removal technologies and concepts were reported by different research groups such as solid adsorption, liquid absorption, cryogenic condensation, biological degradation, membrane separation, and so on [6–12]. Among these technologies, adsorption on activated carbons (AC) is the most widely used method in commercial operation. Research has been carried out to study siloxane adsorption characteristics of different kinds of AC [13–17]. In order to select suitable AC for the removal of siloxanes from LFG, some research groups tried to find out the key textural characteristics of

AC that determine its siloxane adsorption capacity. Matsui and Imamura [15] observed that the AC with higher BET surface area, pore volume, and pH value showed higher siloxane (D4) adsorption capacity. Oshita et al. [16] concluded that higher external specific surface areas and relative wider pores of the adsorbents are desired for the removal of siloxanes. From the results of our previous study, the pores with diameters of 1.7–3.0 nm are the most favorable pores for siloxane (D4) adsorption [17].

In addition to the textural structure, the surface chemistry of AC is also responsible for its adsorption performance. Atoms other than carbon also exist on the surface of AC, and they occur in various forms to determine the surface chemical properties of the AC. To our knowledge, until now no research has been carried out to study the effect of the AC surface chemistry on siloxane adsorption. Therefore it is required to develop a rational framework for the selection of AC, and an improved understanding of the textural structure and surface chemistry effects on siloxane adsorption from LFG. On the other hand, the nature and concentration of surface functional groups could be modified by suitable thermal or chemical treatments. AC treated with acids could not only reduce the mineral matter content, but also change the surface area and porosity. Moreno-Castilla et al. [18] treated an AC with very low ash content from olive stones using different acids. They observed that the AC treated with hydrochloric acid (HCl) resulted in some chlorine chemisorbed on the surface and a slight decrease in the micropore volume and width, while that treated with nitric acid (HNO_3) brought about a decrease in surface area and microporosity, a slight increase in the micropore diameter, and a large increase in oxygen content. Oxidation in the gas or liquid phase could increase the concentration of AC surface oxygen groups, while heating under inert atmosphere could selectively remove some of these functional groups [19]. AC could acquire an alkaline character upon high-temperature heat treatment in an inert atmosphere followed by exposing to air below 200 °C [20]. Ammonia treatment at 400–900 °C could not only remove some acidic oxygen-containing functional groups but also introduce alkaline nitrogen-containing groups onto the AC surface [21,22].

The first objective of this paper was to study the effects of AC pore structure and surface chemistry on siloxane adsorption, and thus develop simple descriptors of the AC characteristics that facilitate the selection of suitable AC for the removal of siloxanes from LFG. The second objective was to propose proper modification methods for a specific AC to improve its siloxane adsorption capacity. To achieve these objectives, anthracite AC was treated by different methods to obtain modified AC with different surface properties, and then the original as well as the modified AC were characterized by several approaches. The siloxane (D4) adsorption capacities of the AC were also measured. As the siloxanes existing in LFG are hydrophobic and weak polar organic compounds, it is rational to believe that AC with a more hydrophobic surface has higher adsorption capacity for siloxanes. In this study aqua ammonia ($\text{NH}_3 \cdot \text{H}_2\text{O}$) and HCl was respectively selected as the chemical modification reagent for the AC to reduce the mineral matter content, as well to modify the surface textural structure and functional groups. Besides, all of the AC, including the original and the chemically modified AC, were thermally treated in a nitrogen atmosphere at high temperature to increase their alkalinity and hydrophobicity by removing some surface oxygen-containing functional groups. The major elemental compositions were measured by elemental analysis (EA) and X-ray fluorescence (XRF) analysis respectively. The surface acidic and alkaline properties were characterized by chemical titration (Boehm titration). The textural properties were determined by N_2 adsorption/desorption isotherm measurements at 77 K.

2. Material and methods

2.1. Materials

A chunk of commercial anthracite AC supplied by Xinhua Active Carbon Co., Ltd. (Shanxi, China) was used for chemical and/or thermal modifications. Octamethylcyclotetrasiloxane (D4, 99%) used for testing the adsorption capacity of the AC was obtained from Acros (NJ, USA). The AC modification reagents $\text{NH}_3 \cdot \text{H}_2\text{O}$ (27%), HCl (37%), and the solvent dodecane (98%) for D4 adsorption were obtained from Shanghai Reagent Station (Shanghai, China).

2.2. Sample preparation

The original AC was ground and sieved, and then the particles with the size of 0.3–1 mm were used for the following liquid phase modification and/or thermal modification. Liquid phase modification was performed by putting about 20 g original AC into 200 mL aqueous solution of $\text{NH}_3 \cdot \text{H}_2\text{O}$ or HCl with different concentrations and the suspension was oscillated for 24 h at 30 °C. After the liquid phase treatment, the sample was washed with distilled water until OH^- or Cl^- could not be detected by phenolphthalein or AgNO_3 in the washing water. Then the sample was dried at 200 °C under vacuum for 24 h. All of the products were kept in a desiccator for further use. Thermal modification was carried out in a 5 cm i.d. quartz boat inside a horizontal tubular furnace. About 2.0 g original or the liquid-phase treated AC was placed in the quartz boat. Prior to the thermal treatment, the tube was purged with ultra-high-purity N_2 for 10 min at air temperature, and then the sample was heated to the desired temperature (600 °C or 800 °C). After keeping this temperature for 6 h, the sample was cooled to air temperature. All the process was in an ultra-high-purity N_2 atmosphere. After the thermal treatment, the product was stored in a desiccator for further characterization and siloxane adsorption experiment. In this paper, the original AC is referred to as AC-origin, while the samples modified by $\text{NH}_3 \cdot \text{H}_2\text{O}$, HCl, and heat are referred to as AC-(wt%) NH_3 , AC-(wt%)HCl and AC-N(temperature) respectively. The two-step treated samples are referred to as AC-(wt%) NH_3 -N(temperature) and AC-(wt%)HCl-N(temperature) respectively.

2.3. Sample characterization

The elements of carbon, hydrogen, and nitrogen contents of the AC were determined by an elemental analyzer (Perkin–Elmer 240C, USA). Inorganic elementary compositions were determined from XRF analysis. The AC samples were calcined at 960 °C for 5 h in an electric muffle furnace to eliminate the carbon and some other organic elements such as H and N. The ashes were afterwards analyzed by an ARL-9800 XRF (ARL, Switzerland).

The textural characterization of the AC was determined from the N_2 adsorption/desorption isotherm at 77 K by a JW-BK122W static nitrogen adsorption apparatus (JWGB Science and Technology Company, China). The BET (Brunauer–Emmet–Teller) standard equation was used to calculate the specific surface area in the relative pressure (P/P_0) range of 0.01–0.2. The total pore volume, mean diameter of the pores and pore size distribution were calculated by BJH (Barrett–Joyner–Halenda) model. All these results were calculated from the obtained N_2 adsorption/desorption isotherm data using the software of the apparatus.

The acidic and alkaline properties of the AC samples were studied by the method of Boehm titration. According to the Boehm method [23–25], the acidic group content is determined by neutralization with some alkalis of increasing strength, while the alkaline group content is measured by neutralization with HCl. The titrations were carried out using a T90 potentiometric titrimeter

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