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Adsorption characteristics of methyl mercaptan, dimethyl disulfide, and trimethylamine on coconut-based activated carbons modified with acid and base

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ABSTRACT

The influence of surface modification of activated carbon on the adsorption of methyl mercaptan (MM), dimethyl disulfide (DMDS), and trimethylamine (TMA) was investigated by treatments with 1N-HNO_3 solution and 1N-NaOH solution. The surface modifications changed the concentrations of functional groups on the surface of activated carbon. Also, the surface modifications changed breakthrough time and equilibrium adsorption capacity of MM, DMDS, and TMA. The adsorption capacities of MM and DMDS were increased by acid treatment, but decreased by base treatment. On the other hand, the adsorption capacity of TMA was decreased by both acid and base treatments. But the difference ranges of equilibrium adsorption capacities according to acidity and basicity of the surface were relatively small.

1. Introduction

Nowadays, odor problems have become a serious concern as environmental and public nuisance with high economic growth and improvement of living standard. Odor has been recognized as one type of sensory pollution that gives an unpleasant and disgust feeling and it is often linked directly to the quality of life.

The mercaptans, sulfur compounds, amines, organic acids, aldehydes, and ketones are examples of representative malodorants. The mercaptans, amines, and ketones are generated from industrial activities. And the organic acids, aldehydes, and ketones are generated during the decomposition of hydrocarbons in food garbage. Among the malodorous gases, volatile sulfur compounds (VSCs) produced from various industrial and municipal sources can cause unpleasant feeling even at low concentrations [1].

In domestic realm, the most prominent volatile compounds generated in home refrigerator are methyl mercaptan (MM), dimethyl disulfide (DMDS), and trimethylamine (TMA). MM is an organic compound with the formula CH_3SH. It is a colorless gas with a rotten cabbage-like smell and has a low threshold of 0.007 ppm. DMDS is an organic compound with the formula $(CH_3)_2S_2$. It occurs naturally in certain foods and has a low threshold of 0.0028 ppm. TMA is an organic compound with the formula $N(CH_3)_3$. It is colorless, hygroscopic, and this flammable tertiary amine has a strong fishy odor at low concentrations and an ammonia-like odor at higher concentrations. It has a low threshold of 0.001 ppm.

Activated carbon can be considered as a good adsorbent in pollutants control. Their large adsorption capacity is linked to their well-developed internal pore structure, surface area, and the presence of a wide spectrum of surface functional groups. To effectively adsorb those odorous gases, adsorbents with specific chemical properties are needed. Recent research on activated carbons has focused on the surface modification to tailor the surface chemistry for a specific use such as for air and water treatments. The surface modification methods could be in the forms of impregnation [2–4], acid/base treatment [5], heat treatment [6], and oxidation by gas [7]. The impregnation is not favorable since materials used for modification could block pore entrance, and decrease specific surface area and total pore volume [8]. Acid/base modification can create functional groups on the surface of activated carbon without variations in specific surface area and total pore volume. So it is seen more advantageous since the adsorption characteristics by modification are improved according to the concentration of the functional groups. The existence of surface functional groups on the carbon matrix can also be manipulated by thermal and chemical treatments. Many researchers have successfully employed oxidation reactions to produce activated carbons that possess weakly acidic functional groups [9,10]. The presence of heteroatoms can be regarded as an important contribution to the chemical nature of the carbon surface. The most important heteroatoms are oxygen, nitrogen,

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Table 1
Characteristics of the malodorants used as adsorbate.

Properties	Methyl mercaptan	Dimethyl disulfide	Trimethylamine
Symbol	MM	DMDS	TMA
Formula	CH_3SH	$(CH_3)_2S_2$	$(CH_3)_3NH_2$
Molecular weight, g/mol	48.1	94.2	59.1
Dipole moment[a], Debye	1.764	0.001	1.020
Critical volume[a], cm^3/mol	145.5	255.5	221.5
Vapor pressure at 25 °C, mm Hg	1510	28.7	1610

[a] Calculated by MOPAC. About 1.8 Debye for water.

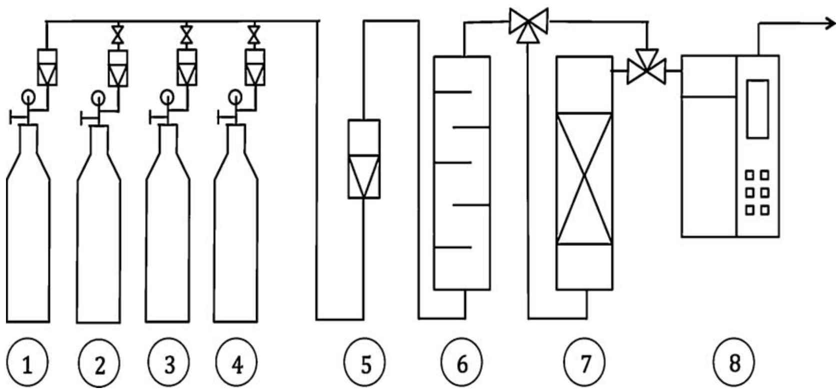

Fig. 1. Schematic diagram of experimental apparatus (① air, ② MM, ③ DMDS, ④ TMA, ⑤ flow meter, ⑥ mixing chamber, ⑦ adsorption bed, ⑧ GC).

hydrogen, and phosphorus. Some of these, such as nitrogen and hydrogen are residuals from the organic precursors, whereas oxygen is introduced via a chemisorption process when carbon is exposed to air. Other heteroatoms, such as phosphorus have their origin in the agent used during chemical activation. All of these species have an important impact on the adsorption behaviors of acidic, basic, or polar adsorbates.

There are numerous studies on the adsorption abilities according to the surface chemical changes after modifications. However, the studies for the relations between adsorption ability and the concentrations of the functional groups created on the surface were scarce. Among the functional groups that contain oxygen on the surface of activated carbon are carboxyl acid, phenol, quinone, lactones, carboxyl anhydride, cyclic peroxide, etc. [11]. Based on the literature reports the adsorption ability is closely related to the specific surface area, the adsorbate size, and pore structure. As the concentrations of the oxygen groups are increased, the chemical properties of active sites on the surface changed [11,12]. Lee et al. [13,14] compared the adsorption intensity and polarity differences between adsorbate and activated carbons. Lee et al. [15] also studied the adsorption characteristics of benzene and acetone vapor according to acidity and basicity changes after modifications to compare the adsorption ability according to chemical changes on the surface of activated carbon.

The objective of this work is to investigate the effect of surface modification on the adsorption of malodorants such as MM, DMDS, and TMA. Relations between equilibrium adsorption capacity and the acidity and basicity of the surface of activated carbon were also investigated.

2. Experimental

Coconut-based granular activated carbon was obtained from Calgon, U.S.A. in the particle size of 8–12 mesh. A similar size range was used in the previous work [15]. The sample was washed with pure water, and dried at 105 °C overnight and cooled down in a desiccator to room temperature for modification. The prepared activated carbon was modified by agitating with 1N-HNO_3 solution or 1N-NaOH solution for 8 h at 70 °C. The virgin activated carbon was denoted as AC and the modified activated carbons with 1N-HNO_3 solution and 1N-NaOH solution were denoted as AC-AN and AC-BN, respectively. The elements on the surface of activated carbon were analyzed by X-ray photoelectron spectroscope (XPS, Thermo VG Scientific, MultiLab 2000). BET specific surface area, total pore volume, and average pore diameter were measured by BET analyzer (Quantachrome Autosorb). The malodorants used as adsorbate were MM, DMDS, and TMA. The characteristics of the malodorants are listed in Table 1. The adsorbates were diluted with air to obtain a certain concentration needed in the experiments. Adsorption experiments were carried out in laboratory controlled at 20 °C using the apparatus used in the previous work [15] shown in Fig. 1. And the adsorption experiments were carried out in the following conditions: activated carbon 0.1 g, inlet concentration 300 ppmv, flow rate 100 ml/min. The concentrations of adsorbates were measured by gas chromatograph (Shimadzu GC-9A). The analysis conditions of GC are as Table 2. The equilibrium adsorption capacity was calculated by measuring the area of the breakthrough curve.

3. Results and discussion

3.1. Effects of modification on characteristics of activated carbon

The characteristics of virgin activated carbon and modified activated carbons with acid and base were compared in Table 3. The results showed that the BET specific surface area and the total pore volume of AC-AN activated carbon modified with 1N-HNO_3 solution decreased, but those of AC-BN activated carbon modified with 1N-NaOH solution were increased. It was thought that the specific surface area and the total pore volume of AC-AN activated carbon decreased because some surface functional groups created by nitric acid modification blocked the entrance of the pores [16,17]. Although the specific surface area and the total pore volume were affected by modifications, the average pore diameter was nearly the same. It indicates that the pore structures of activated carbon are unchanged by these modification conditions.