A-2.2.5 Recovery and Emission Control of Methyl Bromide by Adsorption

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Total Budget for FY1996-FY1997 25,634,000 Yen (FY1997; 13,009,000Yen)

Abstract Manufacturing techniques of activated carbon fiber as well as adsorption system for recovery of dilute methyl bromide have been studied.

As for manufacturing of activated carbon fiber , activated carbon fiber of high adsorbability can be prepared by controlled gasification of carbonized fiber derived from polyvinylidene chloride , phenol resin and coal tar pitch with carbon dioxide or steam.

As for adsorption system, it was found that microwave irradiation for desorption has some advantages over usual hot gas heating.

Key Words Adsorption, Activated Carbon Fiber, Methyl Bromide, Microwave

1. Introduction

Methyl bromide is considered as a significant ozone-depleting chemical, whose ozone depleting potential is calculated to be about 0.6. Therefore it seems to be important to stop releasing methyl bromide into the atmosphere. Adsorption method is considered to be one of the most efficient methyl bromide recovery processes. The efficiency of adsorption method is influenced by adsorbents and adsorption process.

The purpose of this study is to establish manufacturing techniques of activated carbon fiber as well as adsorption process for recovery of dilute methyl bromide.

2. Experimental

2.1. Production of Activated Carbon Fiber

Fibers derived from polyvinylidene chloride, phenol resin and coal tar pitch were used as starting materials. The procedure for the production of activated carbon fiber is shown in Fig. 1.

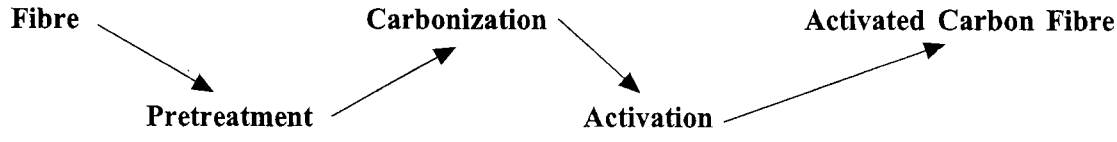
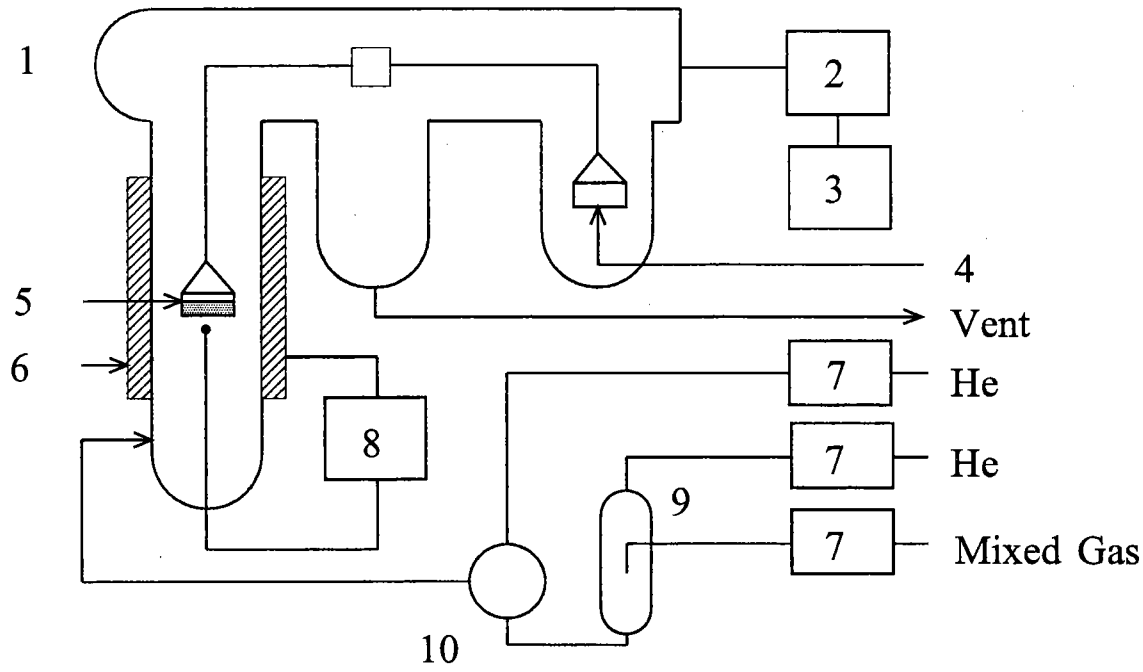


Fig.1 Procedure for the production of activated carbon fibre

Before carbonization pretreatment of fiber is conducted, if necessary. For example, coal tar pitch based fiber is oxidized in order to avoid melting. Carbonized raw materials were partially gasified with carbon dioxide or steam. The carbon is subjected to controlled gasification at 1073-1273K.

Nitrogen adsorption isotherms at 77K were used to calculate the surface area of activated carbons using BET equation. Adsorption isotherms of methyl bromide were measured gravimetrically at 308K using a CAHN microbalance. Figure 2 shows the experimental apparatus.



1 CAHN electrobalance, 2 Controller, 3 Recorder, 4 Couterweights
5 Sample, 6 Heater, 7 Mass flow controller, 8 Temperature controller
9 Mixer, 10 Three-way valve

Fig.2 Adsorption apparatus

2.2. Adsorption System

Breakthrough curves of methyl bromide were measured using a gas chromatograph with PID detector for representative commercial activated carbons to clarify the dynamic adsorption properties of methyl bromide.

The experiment was conducted in combination with adsorbing apparatus capable of flowing through multi-component gas with a microwave irradiation system.

The microwave irradiation apparatus used in this study had the specification of 2.45GHz, 600W.

3. Result and Discussion

3.1. Activated Carbon Fiber for Methyl Bromide Recovery

The performance of adsorption apparatus is influenced by adsorbents. Therefore

selection of adsorbents is very important. The purpose of this work for adsorbents is to get data of basic adsorption properties of commercial activated carbons and to clarify the preparation conditions of activated carbon fibers with high adsorption ability.

Figures 3 illustrates the relationship between the adsorption amount(q) of methyl bromide at 308K and the specific surface area(S) of commercial activated carbon.

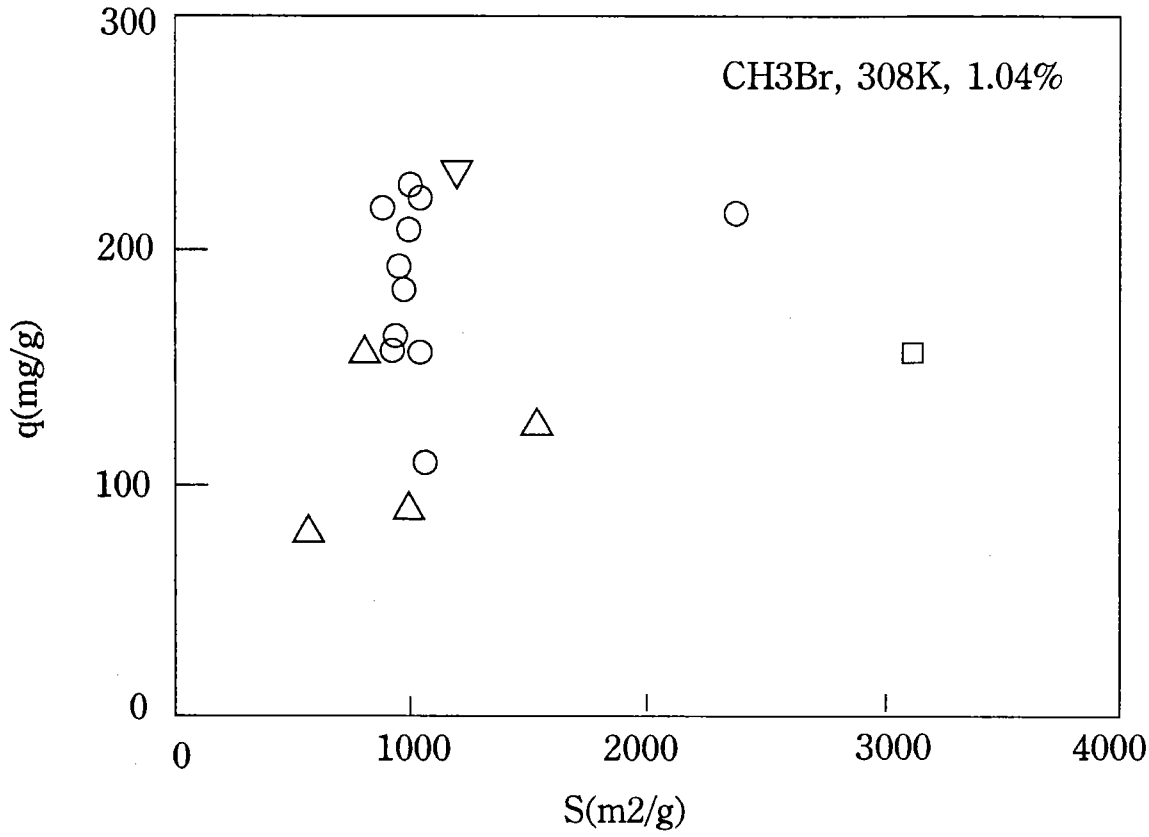


Fig.3 Relation between amount adsorbed (q) and surface area(S) for commercial activated carbons

The results demonstrate that the adsorption of methyl bromide in the low concentration range has no correlation to surface area.

Activated carbon fibers of high adsorbability have been prepared by controlled gasification of each carbonized fiber. An example of the relationship between the adsorption ability for methyl bromide and the burn-off of carbon fiber are shown in Figure 4 . This is the case for production of activated carbon from polyvinylidene chloride by activation with carbon dioxide.

Adsorption of methyl bromide passed through a maximum and then decreased. Optimum burn off was relatively low. This indicates that activated carbon fiber of high adsorption ability can be produced at relatively low cost. It was found that optimum burn off increased with increase of methyl bromide concentration. For concentrations of 605 ppm of methyl bromide, activated carbon fiber of high adsorbability, compared to commercial activated carbons, can be prepared by gasification of carbon fiber with carbon dioxide in the weight loss range of 0.17 - 0.65.

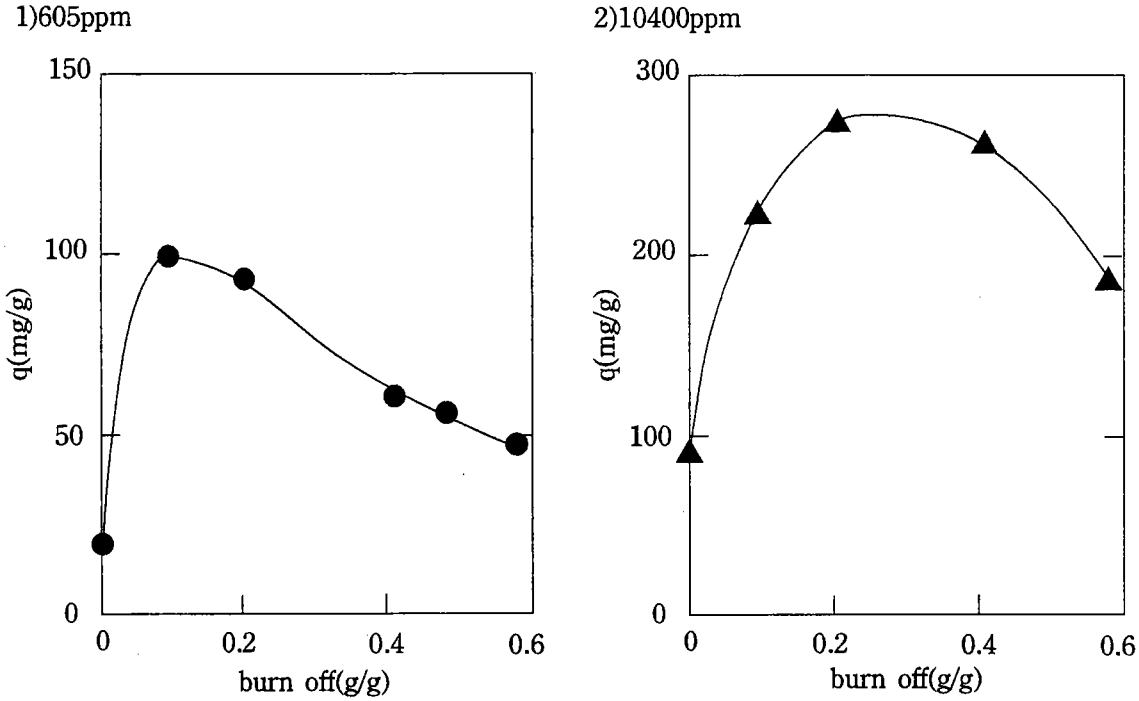


Fig.4 Relationship between adsorption amount and weight loss of carbon

3.2. Adsorption System

An example of the breakthrough curves of adsorption of methyl bromide from helium is shown in Fig.5. Experiments were carried out on commercial activated carbons at 279-281K under dynamic conditions at a flow rate of 34.4cm/sec. The inlet concentration of methyl bromide was 530 ppm.

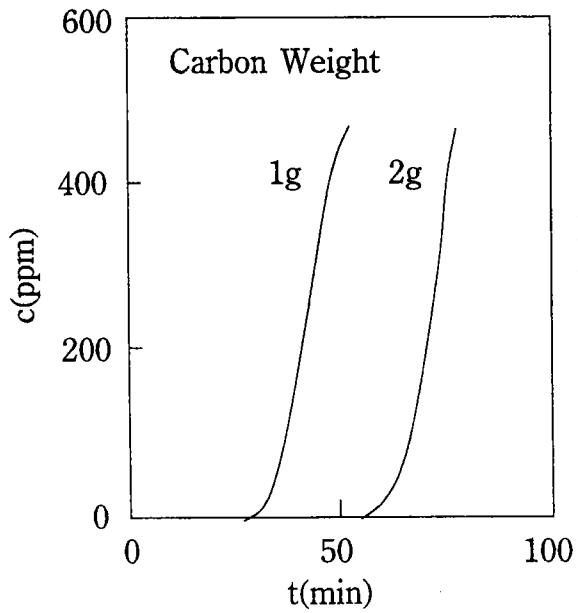


Fig.5 Breakthrough curves of methyl bromide

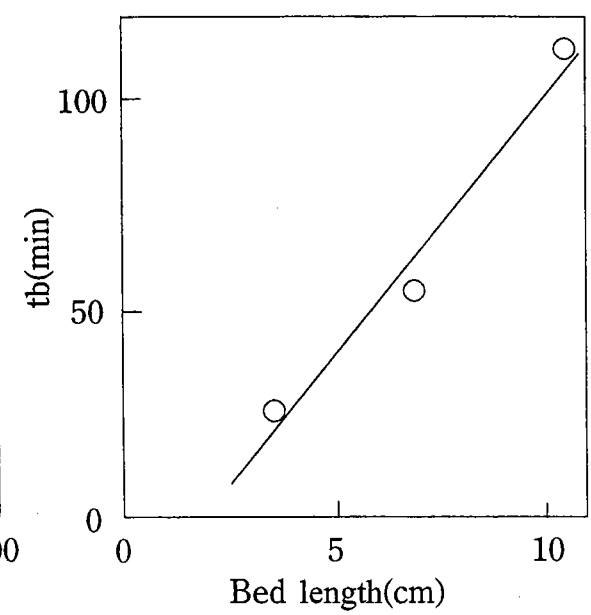


Fig.6 Breakthrough time vs. bed length

When breakthrough time of methyl bromide was plotted against bed length of carbon, as shown in Fig.6, straight line resulted. This relationship will be applied effectively for the design of an adsorption apparatus for methyl bromide.

Typically, there must be at least two beds of adsorbents for the adsorption process to be carried out. In each bed, adsorption and desorption must be changed periodically. In the desorption(regeneration of adsorbents)step, hot gas, such as steam, is used to desorb highly concentrated organics. In this study, irradiation of microwave was employed instead of hot gas regeneration.

Fig. 7 shows the schematic diagram of the new adsorption system using microwave irradiation. The advantages of microwave heating over hot gas heating are the high efficiency and the compact size of heating section.

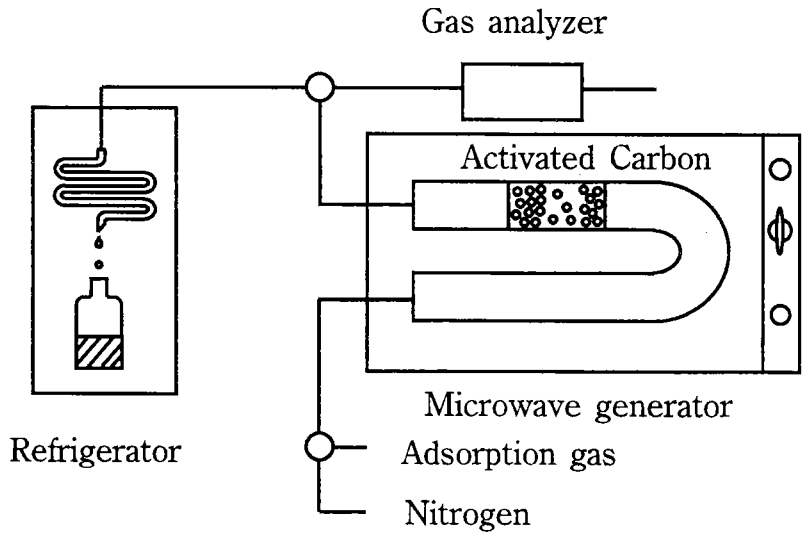


Figure 7 Adsorption apparatus with microwave irradiation

4. Conclusion

Activated carbon fiber of high adsorbability can be prepared by controlled gasification of char with carbon dioxide or steam.

We made sure of a basic concept for a new adsorption system which uses microwave irradiation for desorption instead of hot gas heating.

List of Publications

1) S. Kobayashi et al., "Control of adsorption by microwave irradiation" , Chemistry Letters, 1996, 769-770
2) H. Kitagawa , "Studies on Production and Adsorption Properties of Activated Carbon Fiber", Shigen Kankyo Taisaku, 33, No.2, 139(1997)
3) H. Kitagawa, "Adsorption Techniques for Hazardous Air Pollutants", Kagaku Souchi, 39, No.6, 49(1997)