

Improvement of VOCs Adsorption on Carbon Materials Derived from Sewerage Sludge by Treating Various Acids

Hidekazu Komatsu¹, Takashi Suzuki^{1*}, and Atsushi Narisawa²

Gunma Prefectural Industrial Technology Center¹,
884-1, Kamesato-machi, Maebashi 379-2147, Japan

Gunma Prefectural Government²,
1-1-1, Ote-machi, Maebashi 371-8570, Japan

Sewerage sludge sampled at Gunma Prefectural Central Sewage Disposal Plant was carbonized at 500 °C and activated at 850 °C. The resulting carbon material contained 55 wt.% of ash and its specific surface area was around 126 m²/g. When the carbon material was treated with nitric acid, sulfuric acid, hydrochloric acid, it was suggested that the ash content was reduced to 24~25 wt.% and that nitric acid showed slightly superior performance for the modification. It was also observed that the formation of meso-pores (5 ~ 10 nm), and increase of gross pore volume were made on the material treated with nitric acid. Finally the specific surface area was reached 263m²/g and as a result the adsorbed amount of benzene on the treated material was improved 2.0 fold as much as that in the untreated one. The additional formation of meso-pores may suggest that the bi-modal structure was appeared in the carbon materials.

Keywords: Recovery of VOCs, Utilization of Sewerage Sludge, Treatment with Acids, Bi-modal structure

1. INTRODUCTION

It has been pointed out that the volatile organic compounds (VOCs) are the noticeable causes which enhance global warming and air pollution¹⁾. It is reported that about 60 % of the discharge sites of VOCs are concerned with the medium and small sized industrial business establishment in our country²⁾. Therefore development of the facility to reduce VOCs which is adapted for such enterprises is important.

On the other hand, sludge from sewage disposal plant reached 1,500,000t/year in Japan^{1, 3)}. In Gunma Prefecture, 8,000 t/year of the sludge was generated from sewage disposal plant^{1, 4)}. Considerable budget is, hence, desired for the processing of sewerage sludge despite the situation with low diffusion rate of sewers around 40% in Gunma Prefecture at the present time^{2, 5)}. Hence it is considered that the utilization of sewerage sludge becomes important with increasing spread of sewers.

From the environmental and industrial viewpoints, utilization of the carbon materials derived from sewerage sludge for recovery of exhausted VOCs will be one of indispensable technologies. However, the physico-chemical properties of the carbon material are not enough to recover VOCs. Therefore the improvement of the properties has been continued.

In this work, when the carbon materials activated around 850 °C was further treated with various acids, physicochemical properties such as the specific surface area, pore volume, and pore size distribution were improved. Moreover, it was suggested that the bi-modal structure was newly appeared in the material. Finally, the static adsorbed amount of benzene to the treated carbon materials was improved 2.0 fold as much as

that in the untreated one.

2. EXPERIMENTAL

Carbon materials;

The sludge supplied from Gunma Prefectural Central Sewage Disposal Plant contained ca. 20 wt.% of water was used as starting material. The sludge was carbonized and activated at 500 °C and 850 °C for several hours, respectively. The specific surface area of the carbon material was ca. 126 m²/g. Ash content of the material was 55 wt.%.

Treating with acids;

The carbon material mentioned above was soaked in various inorganic acids at 60 °C for 3 h with agitating. The concentration of acid was varied from 0 to 2 mol/L. Rinsing of the resulting slurry was continued until pH of the solution was reached around 3 using de-ionized water. Finally the specimen was dried in oven at 150 °C for 2 hours.

Static and Dynamic Adsorption of VOCs;

Static adsorption and dynamic adsorption of VOCs were performed by using a gas mixture of benzene and nitrogen which contains 26,000 vol.ppm of benzene for static adsorption, 20,000 vol.ppm of benzene for dynamic adsorption as simulated vapor at room temperature. Static adsorption was made in the brief apparatus which was based on a method as in the report⁶⁾, that is, 0.5 g of the carbon material was set in a gas bag. 1.6 L of the gas mixture was introduced to the bag and it was held until further concentration change of benzene was not recognized.

Dynamic adsorption was carried out in the continuous flow fixed bed adsorption system as described in Fig. 1. 16.8 g (20.0 ml) of the sample was set in the adsorption

* author to whom correspondence should be addressed.

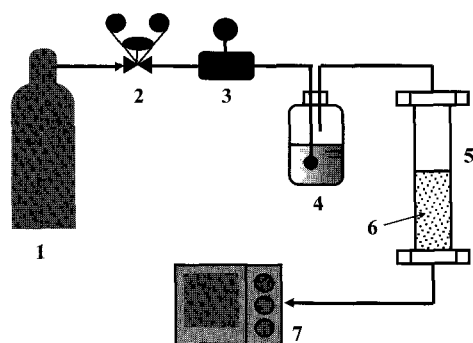


Figure 1. Continuous flow fixed bed adsorption system.

- | | |
|-------------------------------|------------------------------|
| 1. N ₂ in cylinder | 5. adsorption vessel |
| 2. regulator | 6. carbon material |
| 3. mass flow controller | 7. gas chromatograph (GC323) |
| 4. benzene vaporizer | |

vessel. The benzene vapor was fed onto the sample with GHSV (gas hourly space velocity): 1,200 (vol/vol) h⁻¹. The feeding rate was regulated by using mass flow controller (Model 5850 E, Emerson Co.) which was calibrated by using soap thin film flowmeter.

In static and dynamic adsorption, the change of the concentration of benzene was monitored by means of gas chromatograph (GC323, GL Science Co.) equipped with stainless steel column (2m × 1/8inchφ) packed with a Gaschropack-54 (GL Science Co).

3. RESULTS AND DISCUSSION

Condition of acid treatment;

Fig. 2 shows the ash content in the carbon materials as a function of the concentration of nitric acid used for treatment of the carbon materials. When 0.05 mol/L of nitric acid was used, the ash content showed 35 wt.%. Upon increasing the concentration of the acid, the content was less than 25 wt.% as seen in the figure. Thus the ash was reduced by treating with nitric acid. In addition, it is inferred from the results that the minimum required concentration was 0.2 mol/L and slightly more.

In order to confirm the reduction performance on acids, the carbon material was treated with various inorganic acids. When the specimen was treated with nitric acid (2 mol/L), sulfuric acid (1 mol/L), and hydrochloric acid (2 mol/L), the ash content was 24.0, 24.8, and 24.9 wt.%, respectively as shown in Fig. 3. Thus the ability regarding removal of ash was almost the same but nitric acid showed slightly superior performance in these acids.

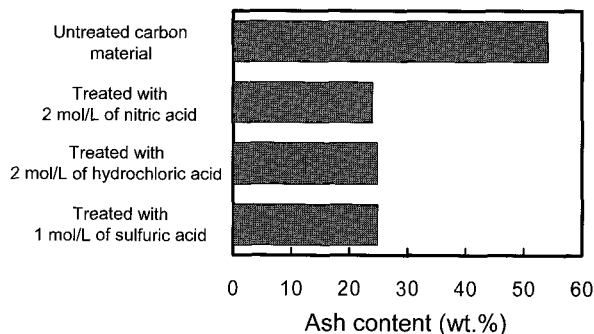


Figure 3. Ash content by treating with various acids at 60°C for 3 hours.

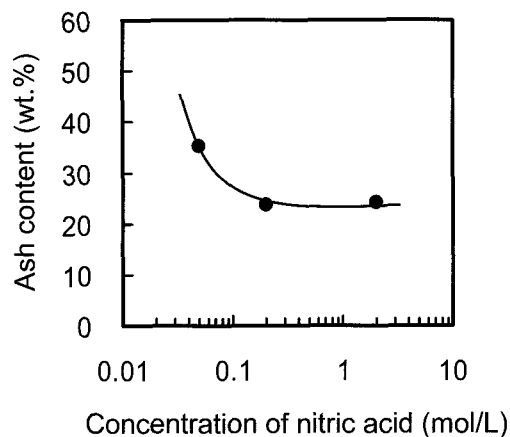


Figure 2. Ash content as a function of the concentration of nitric acid, where ash content of the untreated carbon material was 55wt.%.

Upon clarifying the change of ash component during the treatment, the element distribution in the ash was analyzed by EPMA (electron probe micro analysis). Table I shows chemical composition in the ash before and after treating with 2 mol/L of nitric acid. Aluminum, phosphorus, and calcium were preferentially decreased from 15.0 to 4.9wt.%, 12.9 to 0.8wt.%, 6.4 to 1.4wt.%, respectively. Here one can point out that the some element, such as silicon, was increased after the treatment. It was conjectured that this phenomenon was caused by the reduction of the whole weight which was induced by extraction of acid soluble elements as aluminum, phosphorus, calcium and so on.

Improvement of adsorption capacity;

It is considered that specific surface area of the adsorbent plays important role for the physisorption of VOCs. The specific surface area of ash was very small such as ~1m²/g, therefore, it was worthy to mention that the adsorption capacity would be dependent on the carbon content in the material. As described above, the ash content was reduced to 24.0 wt.% by treating with nitric acid, then it might be simply expected that the surface area was improved 1.7 times relative to that of the untreated carbon material. Actually, specific surface

Table I. Chemical composition in the ash.

Element	Content of each elements (wt. %)	
	(a) Untreated carbon material	(b) Treated with 2 mol/L of nitric acid
Al	15.0	4.9
P	12.9	0.8
Si	10.9	40.6
Fe	6.5	9.5
Ca	6.4	1.4
Zn	1.7	N.D.
Cu	1.3	1.1
Mg	0.8	1.2
O	42.3	37.7
Other	2.0	2.9

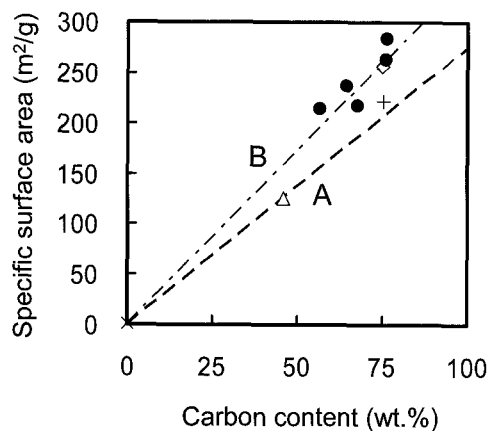


Figure 4. Specific surface area as a function of carbon content.

where (Δ); untreated carbon material, (\bullet); treated with nitric acid, (+); treated with 1 mol/L of sulfuric acid, (\diamond); treated with 2 mol/L of hydrochloric acid, (\times); ash.

area of untreated and treated carbon material was $126\text{m}^2/\text{g}$, and $263\text{m}^2/\text{g}$, respectively (improved 2.0 times).

Fig. 4 shows specific surface area of the carbon materials as a function of carbon content. It can be noticed that the line B to link original point and group B was slightly steep to the line A. It was deduced that the reason why the specific surface area rose was the removal of ash and the change of structural factors.

In order to clarify the change of structural factors, pore size distribution of the carbon materials before and after treating with nitric acid was measured by a BJH (Brett-Joyner-Halenda) method. Fig. 5 shows BJH plots of untreated and treated materials. When untreated specimen was subjected to the measurement, single narrow peak was appeared alone at 4 nm. In contrast to this, using the specimen treated with 2 mol/L

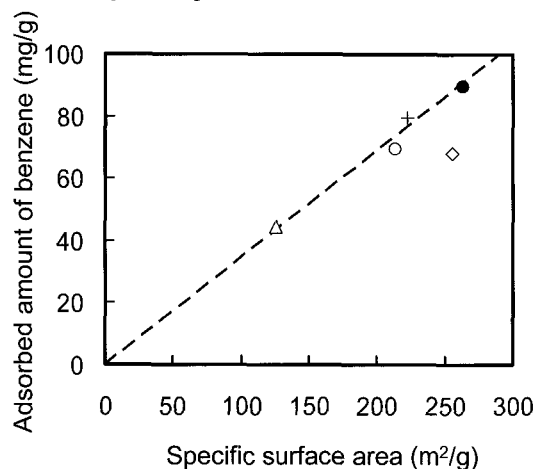


Figure 6. Adsorbed amount of benzene as a function of the specific surface area in static adsorption.

where (Δ); untreated carbon material, (\bullet); treated with 2 mol/L of nitric acid, (\diamond); treated with 0.05 mol/L of nitric acid, (+); treated with 1 mol/L of sulfuric acid, (\diamond); treated with 2 mol/L of hydrochloric acid. Concentration and volume of the benzene contacted: 26,000 vol.ppm, and 1.6L, carbon material: 0.5g

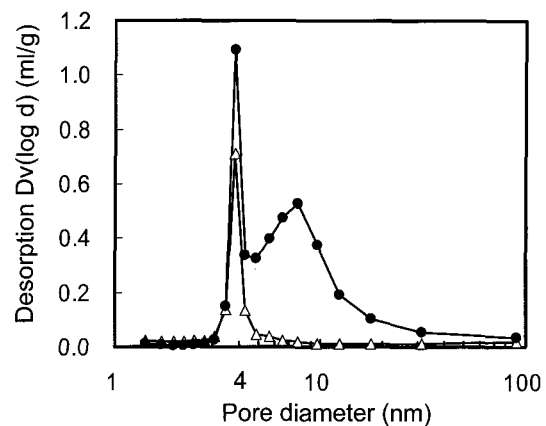


Figure 5. Pore size distribution of the carbon material untreated (Δ), and treated with 2 mol/L of nitric acid (\bullet).

of nitric acid, additional broad peak centered around 5~10 nm was newly appeared. It was deduced that the bi-modal structure might be formed in the specimen by the treatment.

In addition, the peak height revealing amount of pore volume was increased in the treated one. These results led us to the trial of adsorption of VOCs using simulated vapor.

Trials of static and dynamic adsorption of VOCs

0.5 g of carbon material was set in a gas bag and the 26,000 vol.ppm of benzene in N_2 was contacted to the specimen until the adsorption was saturated at room temperature. Static adsorbed amount of benzene was summarized in Fig. 6. The adsorbed amount was proportional to the specific surface area and the amount reached 90 mg/g on the specimen treated with 2 mol/L of nitric acid. The adsorbed amount was 2.0 times larger than that in the case using untreated material.

In industrial VOCs recovery process, adsorption of VOCs should be carried out in dynamic adsorption, e.g., adsorption in continuous flow. The sample treated with 2 mol/L of nitric acid was subjected to dynamic adsorption under flowing 20,000 vol.ppm of benzene in N_2 with GHSV: $1,200\text{ (vol/vol) h}^{-1}$ at room temperature.

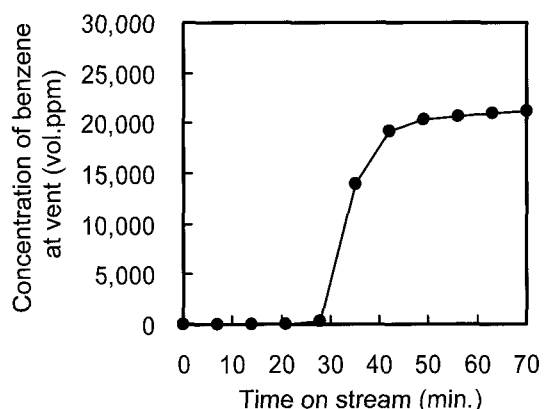


Figure 7. Break-through curve on the treated specimen in dynamic adsorption.

Concentration of the feed benzene: 20,000 vol.ppm, GHSV: $1,200\text{ (vol/vol) h}^{-1}$

Fig. 7 shows the break-through (BT) curve on the treated specimen in dynamic adsorption.

If the adsorption process is made insufficiently, the bleed of benzene is recognized even in the first stage of the adsorption and the shape of the BT curve is broad. As seen in the figure, benzene vapor was hardly detected before 28 min and the BT curve was suddenly up to the 20,000 vol.ppm. This means, at least, that the adsorption of the benzene was rationally carried out in our experimental conditions.

Actually, for instance, in medium-small scale dry cleaning facilities, the exhausting term of VOCs is about 10 min or less. If our result is met with the actual conditions, modified carbon materials derived from sewerage sludge in our laboratory may have a potential to apply to adsorbent for recovery of VOCs in the industrial use.

Acknowledgement

Authors indebted to Mr. R. Yamamoto (registered P. E. Jp. in chemical physics) of Gunma Pref. Ind. Tech. Ctr. for his stimulating discussion in regard with determination of pore size distribution.

References

1. T. Suzuki, *Kagaku Souchi (Chemical Plant Engineering)*, **40**, 58 (2007).
2. H. Komatsu, T. Suzuki, Y. Fukushima, H. Kashimoto, *Bull. Gunma Industrial Technology Center*, **18**, 20 (2007).
3. K. Matsunaga, K. Morita, M. Kondoh, T. Itatani, T. Mori, K. Shishido, M. Ohbu, *Jpn. Soc. Waste Management Experts*, **6**, 89 (1995).
4. "Utilization plan of biomass resources", Gunma prefectural government (2005).
5. "Annual report of Gunma prefectural sewerage disposal plants", Gunma prefectural government (2002).
6. M. Sugiura, K. Fukunaga, and S. Inagaki, *R&D Rev. Toyota Central Res. Labs.*, **28**, 43 (1993).

(Received December 28, 2007; Accepted May 8, 2008)