Deodorization of Ammonia by Coffee Grounds

Naohito KAWASAKI^{*1}, Hideo KINOSHITA², Takashi OUE², Takeo NAKAMURA¹
and Seiki TANADA¹

¹ School of Pharmaceutical Sciences, Kinki University
(3-4-1 Kowakae, Higashi-Osaka, Osaka 577-8502, JAPAN)

² Kokubu Hospital
(4-672 Asahigaoka, Kashiwara, Osaka 582-0026, JAPAN)

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Abstract: Coffee grounds are a vegetable biomass that can be efficiently burned. The carbon dioxide generated by burning coffee grounds is affecting global warming. On the other hand, ammonia generated in the places such as toilets or farms produces a bad smell. In the present study, we have analyzed the possibility of ammonia elimination using the carbonaceous materials produced from coffee grounds. Carbonaceous materials were prepared by the microwave treatment of coffee grounds. We observed that the saturated amounts of ammonia adsorbed by some of the carbonaceous materials produced from coffee grounds were greater than that adsorbed by activated carbon. In contrast, the activated carbon adsorption rate for ammonia was higher than those of the carbonaceous materials. Therefore, carbonaceous materials produced from coffee grounds could be utilized for the removal of ammonia in the gaseous phase.

Key words: adsorption rate, ammonia, coffee ground, vegetable biomass

1 Introduction

In recent years, we have been required to think about environmental problems on a global scale. Current socio-economic activities such as mass production, mass consumption and mass abandonment are all related to consumption. The amount of waste has increased due to the development of these activities. Moreover, most vegetable biomasses are being burned, leading to a global warming generated by excessive accumulation of atmospheric carbon dioxide. The amount of carbon dioxide discharge linked to Japanese economic activities will be restricted by enforcement of the Kyoto Protocol, an amendment to the United Nations Framework Convention on Climate Change. Therefore, to enable the society to continue advancing, it is necessary to qualify the organic wastes as if they were “unused

organic materials”, and to develop the technology for promoting material circulation. Organizing a carbon circulation-type society is especially required. Coffee grounds are vegetable biomass being burned for disposal, but they will have to be reused in a circulation-type society. We have already reported lead, dyes and formaldehyde removal by coffee grounds based toxic removal technologies (1-3). In these studies, the activated carbons were prepared from coffee grounds and rice hulls by chemical activation using sodium hydroxide, potassium hydroxide and zinc chloride (4). Besides, the production of adsorbents from Sugi sapwood was achieved by oxygen-nitrogen activation (5). However, chemical activation is not good because there is the danger of environmental pollution.

Ammonia, which is generated in places such as toilets or farms, has a strange odor and its environmental

*Correspondence to: Naohito KAWASAKI, School of Pharmaceutical Sciences, Kinki University, 3-4-1 Kowakae, Higashi-Osaka, Osaka 577-8502, JAPAN
E-mail: kawasaki@phar.kindai.ac.jp

concentration is being controlled by the Offensive Odor Control Law in Japan. Ammonia is a polar molecule which is difficult to eliminate using activated carbon because the activated carbon surface is hydrophobic.

In this study, coffee grounds have been regarded as a useful unused material, and the possibility to use them following their carbonization was examined. The carbonaceous materials from coffee grounds were prepared by the microwave treatment, and the adsorption of ammonia onto the carbonaceous materials was examined based on the amount of ammonia adsorbed at the saturation level, the adsorption rate, and the physico-chemical properties of the carbonaceous materials.

2 Materials and Methods

2.1 Materials

The aqueous ammonia solution was purchased from Wako Pure Chemical Industries, Ltd. Activated carbon (AC) made from steam-activated coconut shell, Shirasagi G was obtained from Takeda Chemical Industries, Ltd. Coffee grounds used here were originated from beans of *Coffea robusta* produced in Thailand. Carbonaceous materials of coffee grounds, CG0, CG10, CG15 and CG20, were prepared by carbonizing the wetted coffee grounds in air by the microwave treatment for 0, 10, 15 and 20 min at 2450 MHz and the output of 500 W, respectively. All carbonaceous adsorbents (AC, CG0, CG10, CG15 and CG20) were dried for 15 h at 190°C before use.

2.2 Acid and Base Consumption of AC and CGs

Acid and base consumptions by the AC and CGs

were measured using the acid-base titration method (6). The AC or CGs were added to 100 mL of an aqueous hydrochloric acid solution (0.1 mol/L), and the suspension was shaken for 15 h. The base consumption was determined by titrating the filtered solution with an aqueous sodium hydroxide solution (0.1 mol/L). On the other hand, either the AC or CGs were added to 100 mL of an aqueous sodium hydroxide solution (0.1 mol/L), and the suspension was shaken for 15 h. The acid consumption was determined by titrating with an aqueous hydrochloric acid solution (0.1 mol/L).

2.3 Specific Surface Area of AC and CGs

The AC and CGs were dried for 3 h at 190°C. The specific surface area of the carbonaceous materials was measured using a FlowSorb II 2300 (Micromeritics Co., Ltd.).

2.4 Saturated Amount of Ammonia Adsorbed by AC and CGs

Approximately 0.1 g of either the AC or CGs was placed in a weigh bottle and stored in a desiccator containing a 35% ammonia aqueous solution in a 100-mL beaker for 72 h at 15 or 25°C. The saturated amount of ammonia adsorbed by the AC and CGs was estimated from their weight before and after the adsorption. The weight was measured using an A&D GR-120 electronic balance.

2.5 Adsorption Rate of Ammonia by AC and CGs

The device to determine the adsorption of ammonia by the AC and CGs is shown in Fig. 1. The concentration of ammonia in the absorption liquid was deter-

Fig. 1 Device to Determine Adsorption of Ammonia.

mined by the standard analytical method for hygiene chemists, that is, the indophenol method (7). A 5.0 mL sample was added to a test tube along with 2.5 mL of a phenol sodium nitroprusside aqueous solution and 2.5 mL of a NaClO aqueous solution, which then was incubated for 60 min at 25°C. The ammonia was measured at the maximum absorbance wavelength (640 nm) using a Hitachi U-1100 spectrophotometer (Hitachi Ltd.), with water as the blank, and NH₄Cl as the standard for the calibration curve.

3 Results

The base and acid consumptions of the AC or CGs and the yield of the carbonaceous material by the microwave treatment are shown in **Table 1**. The acid consumption of the AC and CGs were similar. In contrast, the base consumption of AC was the lowest and that of CG0 was the highest, and having a value 8 times greater than that of AC. Results of the elemental analysis and measurements of the specific surface area of the AC and CGs are shown in **Table 2**. The N/C values of the CGs did not change by the microwave treatment, but the H/C values decreased. The specific surface area of the CGs is lower than that of AC due to the lack of activation.

The saturated amounts of ammonia adsorbed by the AC and CGs are shown in **Table 3**. The amounts of adsorbed ammonia increased in the following order: CG20, CG15, AC, CG10 and CG0. The amounts of ammonia adsorbed at 15°C were greater than those adsorbed at 25°C, and the difference increased with the longer microwave treatment. In spite of AC and CG0 having the highest and the lowest specific surface areas, the saturated amounts of ammonia adsorbed by AC and CG0 resulted in the lowest and highest values, respectively.

The amount of ammonia adsorbed by CG0 did not increase with the longer microwave treatment. The amount of ammonia adsorbed by CG15 is lower than that by AC. However, the saturated amount of ammonia adsorbed by CG0 was twice as much compared to that adsorbed by AC.

The amounts of ammonia adsorbed by the AC and CGs versus time are shown in **Fig. 2**. The adsorption rate of ammonia increased in the order of CG10, CG20 or CG15, CG0 and AC. The ammonia adsorption by AC reached an equilibrium after 8 min. We believed

Table 1 Physical and Chemical Properties of Carbonaceous Materials.

Sample	Consumption (mmol/g)		Yield (%) ^{a)}
	Base	Acid	
AC	1.4	0.048	—
CG 0	11.7	0.040	—
CG 10	5.0	0.032	25.5
CG 15	7.8	0.049	6.9
CG 20	8.2	0.058	5.3

^{a)} (Weight of carbonaceous material after carbonization/weight of wetted coffee grounds) × 100.

Table 2 Physical and Chemical Properties of Carbonaceous Materials.

Sample	N/C ^{a)}	H/C ^{b)}	Specific surface area (m ² /g)
AC	---	---	1119
CG 0	4.3	12.6	< 1
CG10	4.3	9.7	< 1
CG 15	4.5	4.5	< 1
CG 20	4.1	2.6	5

^{a)} {N (nitrogen content, %)/C (carbon content, %)} × 100

^{b)} {H (hydrogen content, %)/C (carbon content, %)} × 100

Table 3 Saturated Amounts of Ammonia Adsorbed onto Carbonaceous Materials.

Sample	S.A.A (mg/g) ^{a)}		A.P (%) ^{b)}
	15°C	25°C	
AC	234	181	77
CG 0	606	365	60
CG 10	508	275	54
CG 15	175	86	49
CG 20	145	68	47

^{a)} Saturated amount of ammonia adsorbed.

^{b)} (Amount of ammonia adsorbed at 25°C/amount of ammonia adsorbed at 15°C) × 100.

Fig. 2 Amount of Ammonia Adsorbed onto Carbonaceous Materials vs. Time.

●, CG 0; ▲, CG 10; ■, CG 15; ▼, CG 20; ○, AC.

Table 4 Adsorption Rate Constants of Carbonaceous Materials for Ammonia.

Sample	Adsorption rate constant ^{a)} ($\times 10^{-3}$ mg/g/min)	$r^{b)}$
AC	2.72	1.000
CG 0	0.14	0.988
CG 10	0.25	1.000
CG 15	0.13	0.988
CG 20	0.59	1.000

^{a)} Adsorption rate constants were obtained based on Samejima's equation.

^{b)} Correlation coefficient.

that the results shown in **Fig. 2** followed Samejima's equation, which is an adsorption rate equation derived from the Langmuir adsorption rate equation. For the early stage of adsorption, Samejima's equation (8) takes the following form:

$$Ve \times \ln \{Ve / (Ve - V)\} - V = kt \quad [1]$$

where t is the elapsed time in minutes, Ve and V represent the milligram amount of adsorbate adsorbed per gram of adsorbent at equilibrium and at a given time t , respectively, and k is the adsorption rate constant expressed in mg/g/min. Equation [1] is represented by a straight line when $[Ve \times \ln \{Ve / (Ve - V)\} - V]$ is plotted versus t , and the adsorption rate constant k is given by the slope of the line. The adsorption rate constant and the correlation coefficient are shown in **Table 4**. The experimental results fit to the Samejima's equa-

tion yielding the regression lines

$[Ve \times \ln \{Ve / (Ve - V)\} - V]$ versus time for $t < 5$ min with correlation coefficients from 0.988 to 1.000. From the slopes of these lines, the adsorption rate constants of the different CGs were estimated to be from 0.13 to 0.59 mg/g/min, while the AC adsorption rate constant was 2.72 mg/g/min.

4 Discussion

The production of activated carbon includes both carbonization and activation processes. In general, based on the carbonization process using a rotary kiln or an electric muffle furnace employs an output power of 1500 W and a period of 150 min. For the microwave treatment, the output power and the period were 500 W and 15 min, respectively. The amounts of electricity needed to manufacture the carbonaceous materials by carbonization using an electric muffle furnace and a microwave apparatus are 3750 Wh and 125 Wh, respectively. The Ministry of Environment reported in 1999 that the amount of carbon dioxide produced per kilowatt-hour was 0.550 kg. According with this, the amount of carbon dioxide produced by the electric muffle furnace and the microwave apparatus is 2.06 kg and 0.07 kg, respectively. Results of elemental analysis were used to evaluate the carbon dioxide discharge associated to carbonization of the CGs.

Acid consumptions by the AC and CGs were similar. In contrast, the CG0 base consumption is the highest, being about 8 times greater than that of the AC. Base and acid consumptions by the adsorbents indicate the number of carboxyl or phenolic hydroxyl groups and the number of amino groups on the adsorbent's surface, respectively (6). The number of AC and CGs amino groups did not change. In contrast, the number of carboxyl or phenolic hydroxyl groups changed. The yield of CG10 by microwave treatment is the highest. However, it decreased with an increasing the treatment period due to the occurrence of excessive carbonization.

The saturated amounts of ammonia adsorbed increased in the order CG20, CG15, AC, CG10 and CG0. In addition, the saturated amount of ammonia adsorbed at 15°C was greater than at 25°C. The saturated amount adsorbed at 15°C compared to that at 25°C decreased with the increasing microwave treatment period. Thus, ammonia adsorption abilities of the AC and CGs might be related with the adsorbent's physical

properties. CG0 had the highest level of base consumption, and therefore it could easily adsorb the base materials. In spite of the fact the specific surface area of AC and CG0 were the highest and the lowest, their saturated amounts of ammonia adsorbed were the lowest and the highest, respectively.

In general, the removal of hazardous materials by adsorbents is better when the absorption rate is faster. However, the adsorbents with a faster adsorption rate sometimes cannot be used for a long time. In spite of the fact that the CG0 adsorption rate was slower than that of AC, the saturated amounts of ammonia adsorbed by CG0 and CG10 was greater than that adsorbed by AC. Hence, CG0 and CG10 can be used as deodorants for a much longer time than AC.

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