Activated carbon from municipal waste

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Abstract

A refuse derived fuel (RDF) was carbonized by partial combustion at 623 K and the carbonized RDF (cRDF) was steam-activated at 1123 K. The cRDF was also treated by 3.3 or 5.2 N nitric acid at a boiling temperature for 3 h prior to the steam-activation. Porous properties of the activated carbons prepared were determined by the nitrogen adsorption method. The porous structure of the carbon prepared without the pretreatment of nitric acid was not so developed as a commercial carbon for dioxin adsorption. On the other hand, the carbons prepared via the nitric acid treatment had BET surface areas of 515 and 828 m^2/g and more mesopore volumes than the commercial carbon. During the acid treatment, the ash dissolution from cRDFs to nitric acid was observed and resulted in the formation of activation sites for developing mesopores. Hence, the carbons prepared could be used to remove dioxins from the incinerators. © 2000 Elsevier Science Ltd. All rights reserved.

1. Introduction

More and more municipal solid wastes are produced by society, and landfill sites are becoming full and hard to find. Since municipal wastes contain a relatively high percentage of organic compounds, such as papers, plastics, woods, garbage, etc., a huge amount of municipal waste is reduced by volume in incinerators. If activated carbons are produced from the waste, their production costs may be low. The usage of the carbons in waste water and waste gas treatments can be a two-fold solution to environmental problems and effective reuses of the wastes.

Activated carbons are produced from raw materials that contain rich carbon [1–6]. Although industrial and household wastes contain relatively rich carbon, the composition is variable and inhomogeneous. The waste have been considered to be unfavorable raw materials for activated carbons. Raw materials are carefully chosen for the usage of activated carbons in adsorption processes from the viewpoint of pore size, pore size distribution, surface area, chemical property of surface, mechanical strength, particle size, etc. [6]. The authors, however, are interested in establishing a preparation procedure of activated carbons from municipal wastes though the wastes have not been recognized to be favorable raw materials for activated carbons.

Recently, the emission of dioxins from municipal solid waste incinerators has become a social problem in Japan. Dioxins generally indicate polychlorinated dibenzo-*p*-dioxins and polychlorinated dibensofurans and have more than 200 kinds of isomers. The Ministry of Health and Welfare of Japan took a permanent countermeasure for the dioxin emission from small-scaled incinerators. According to the countermeasure, incinerators whose capacities are less than 100 t/day will be changed to plants of a refuse derived fuel (RDF) to reduce the dioxin emission.

RDFs are produced from municipal solid wastes via crushing, magnetic separation of iron, air classification of aluminum and incombustibles and briquetting by an extruder. In briquetting, calcium hydroxide $(Ca(OH)_2)$ or calcium oxide (CaO) is added to the waste to remove chlorine. Although the construction of RDF plants will increase in the near future, the usage of RDF has not been fixed yet. Hence, it is important to change RDFs to valuable chemicals. If activated carbons are produced from RDFs and used to remove dioxins from incinerators, the usage can be a two-fold contribution to waste management policies.

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RDF is used for the generation of electric power. In a power plant the RDF is pyrolyzed, gasified and melted by fluidized beds, rotary kilns, etc. Although chars exhausted from a pyrolysis furnace are usually forwarded to a gasification furnace, they can be utilized to produce activated carbons by an activation furnace built along side the power plant. On the other hand, the RDF can be also transported to remote chemical factories to produce activated carbons.

In this paper, the molecular size of the dioxins are estimated by a molecular orbital (MO) calculation and information on pore size of activated carbon to adsorb dioxins is obtained. Activated carbons are produced from carbonized RDF (cRDF) by steam-activation. The cRDF is also treated by nitric acid (HNO_3) before the steam-activation. Porous properties of carbons prepared are compared with those of a commercial activated carbon. A novel pretreatment method is proposed to develop mesoporosity of carbons.

2. Experimental

2.1. Refuse derived fuel

A raw material for activated carbons is a municipal solid waste produced in a city of Japan. Garbage in the municipal waste is composted and the others are changed to a RDF. Table 1 shows the composition of the waste. One can see that the waste contains mainly plastics, woods, and papers, but no garbage.

RDF has been produced from the waste. The RDF is cylindrical (diameter: ca. 2 cm, length: ca. 5~6 cm) and the composition is listed in Table 2. The carbon content of RDF is ca. 54 wt.% (daf base) and the content is increased further by carbonization. Fig. 1 shows the photograph of RDF used in the present work.

2.2. Preparation of activated carbon

The RDF was carbonized by partial combustion at 623 K for 8 h and the carbonized RDF (cRDF) were obtained. The photograph of cRDF is shown in Fig. 1. Table 3 shows metal contents in the cRDF. The cRDF contains various metals of low content as an ash. Especially the

Table 1
Composition of municipal solid waste

Wastes	wt.% (raw waste base)
Plastics	22.0
Combustibles (woods and papers)	72.7
Garbages	0.0
Incombustibles	1.6
Others	3.7

Table 2
Composition of RDF

Analysis of RDF	wt%
Proximate analysis	
Water	1.9 (raw RDF base)
Ash	11.3 (dry RDF base)
Combustibles	88.7 (dry RDF base)
Elemental analysis	
C	53.7 (daf base)
H	7.7 (daf base)
N	0.7 (daf base)
O	36.5 (daf base)
S (combustible)	0.1 (daf base)
Cl (combustible)	1.3 (daf base)

content of Ca, which is added to the waste in producing RDF, is more than 7 wt.% (dry cRDF base). The metals influence the porosity of activated carbons.

The cRDF was set in a quartz reactor and activated in a N_2–H_2O flow to develop their porous structures. The weight of cRDF was 1.0 g, the gas flow rate was 200 cm^3/g, the steam concentration was 1.0×10^{-2} kg/m^3 and the activation temperature was 1123 K. On the other hand, the cRDF was chemically treated by the following methods prior to steam-activation.

2.2.1. HNO_3 treatment

5.0 g of cRDF was immersed in 300 cm^3 of HNO_3 aqueous solution (3.3 or 5.2 N) at a boiling temperature for 3 h. The cRDF was washed by distilled water until the pH of the water became ca. 5.0 and then was vacuum-dried at 353 K.

2.2.2. O_2 oxidation

The cRDF was oxidized in air at 573 K for 2 h and vacuum-dried at 353 K. The weight of cRDF was 0.5 g and the air flow rate was 200 cm^3/min.

2.2.3. H_2O oxidation

The cRDF was oxidized in N_2–H_2O at 573 K for 2 h and vacuum-dried at 353 K. The weight of cRDF was 1.0 g, the gas flow rate was 200 cm^3/g and the steam concentration was 1.0×10^{-2} kg/m^3.

2.3. Porous characterization of activated carbons

Adsorption and desorption isotherms of N_2 were measured on the activated carbons at 77 K using an adsorption apparatus (BELSORP28, BEL Japan Inc., Japan). BET surface area S_{BET}, mesopore size distribution and microporosity were determined. The pore size distribution was estimated by applying the Dollimore–Heal method [7] to the desorption isotherms measured and the microporosity was evaluated by the *t*-plot method [8]. Then, the
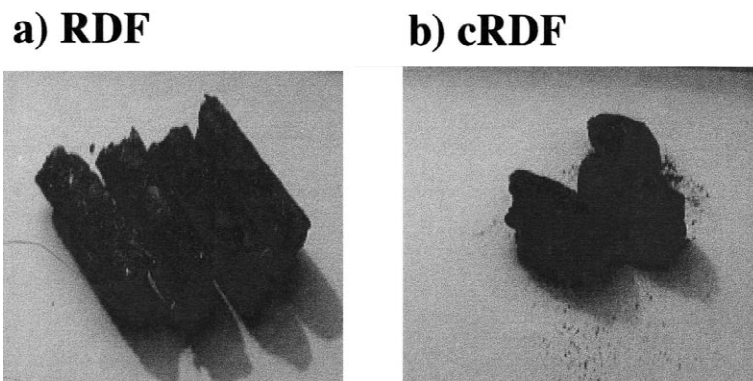
a) RDF

b) cRDF

Fig. 1. Photograph of RDF and cRDF.

mesopore volume V_{mes}, the surface area S_{mic} and the volume V_{mic} of micropores were determined. Here, the adsorption isotherm of N_2 on Spheron 6 was adopted, which had been measured by BEL Japan Inc. as the standard isotherm

3. Results and discussion

3.1. Molecular size of the dioxins

It is important to evaluate the molecular size of the adsorptive when preparing activated carbons. Hence, the molecular size of the dioxins were first calculated using a nonempirical (ab initio) MO method. Gaussian 92 and 94 programs [9] were used and the geometries of dioxins were optimized by Hartree-Fock level and STO-3G basis set. The molecular sizes were estimated by the bond length, bond angle and van der Waals radii.

Since dioxins have more than 200 kinds of isomers, 2,3,7,8-TCDD and 2,3,7,8-TCDF have been picked up. 2,3,7,8-TCDD is known as the most harmful compound. The molecular sizes of the dioxins are shown in Fig. 2. The figure suggests that the longer axis of dioxins is 1.4 nm, the shorter axis is 0.74 nm and the thickness is 0.35 nm. One can see that mesopores of activated carbons are necessary for adsorption of dioxins.

3.2. Porous structure of prepared activated carbon

Activated carbons were prepared without the chemical treatments of steam-activation. Fig. 3 shows the relation between activation time and the BET surface area S_{BET}. Here, the activation time of 0 h indicates the original cRDF. The carbon activated for 5 h (AC1) has a maximum S_{BET}. The value of S_{BET} is increased four times of that of the cRDF by steam-activation. Hence, the activation time was fixed to be 5 h.

Table 3
Metal content in cRDF

Metal	wt% (dry cRDF base)
As	1.3×10^{-4}
Cd	3.4×10^{-4}
Cr	4.7×10^{-3}
Pb	8.3×10^{-3}
Zn	9.0×10^{-2}
Hg	1.0×10^{-6}
Al	3.3
Cu	2.3×10^{-2}
Fe	0.48
Mn	5.0×10^{-2}
Ni	2.3×10^{-3}
Ca	7.3
K	0.26
Mg	0.83
Na	0.48

a) 2,3,7,8-TCDD

b) 2,3,7,8-TCDF
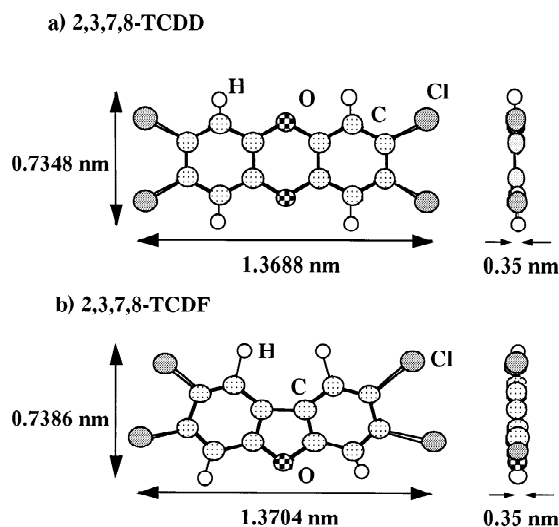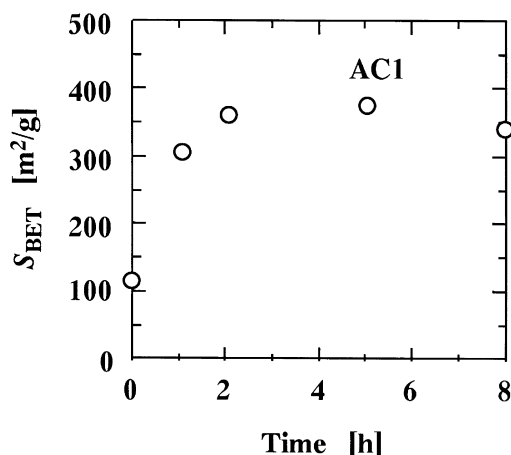

Fig. 2. Molecular size of dioxins.

Fig. 3. Influence of activation time on BET surface area of steam-activated carbons without pretreatment.

Table 4
BET surface area and pore volumes of activated carbon[a]

Carbon	S_{BET} (m^2/g)	V_{mes} (cm^3/g)	V_{mic} (cm^3/g)
AC1	378	0.21	0.18
D-AC	607	0.26	0.31
W-AC	785	0.07	0.44

[a] AC1=Steam-activated for 5 h, D-AC=commercial carbon for dioxin adsorption, W-AC=commercial carbon for waste water treatment.

on D-AC, the amount of N_2 adsorbed on AC1 is smaller than that on D-AC.

The values of S_{BET}, V_{mes} and V_{mic} of AC1 are shown in Table 4. The pore size distribution of AC1 is shown in Fig. 5. The mesopores of AC1 are not so developed as D-AC. D-AC has mesopores of ca. 2 nm-radius to adsorb dioxins. Although AC1 has more mesopores than W-AC, it has fewer mesopores than D-AC.

3.3. Improvement of mesoporosity of carbon by pretreatment prior to steam-activation

It is expected to develop mesoporosity of activated carbon by chemical modification of cRDF prior to steam-activation. Table 5 shows S_{BET}, V_{mes}, and V_{mic} of the carbons using several pretreatments of activation. Porous properties of ar_AC and vp_AC suggest that the O_2 or H_2O oxidation of cRDFs cannot improve the mesoporosity of the carbon. On the other hand, the carbons prepared by HNO_3 treatments (n_AC1 and n_AC2) had BET surface areas of 515 m^2/g and 828 m^2/g and more mesopore volumes than D-AC.

Adsorption and desorption isotherms of N_2 on AC1,

The adsorption and desorption isotherms of N_2 on AC1 at 77 K are shown in Fig. 4. Here the amount of N_2 adsorbed q is plotted against the relative pressure p/p_0 (p=pressure, p_0=saturated vapor pressure) of N_2. The isotherms on commercial activated carbon for dioxin adsorption (D-AC) and for waste water treatment (W-AC) are also shown in this figure. One can see that the isotherm on W-AC is typical I type and that W-AC has mainly micropores. On the other hand, the amount of N_2 adsorbed on D-AC increases with p/p_0 in the range of $p/p_0>0.1$. Since dioxins are relatively large molecules (e.g., $1.4\times0.74\times0.35$ nm), mesopores of D-AC are developed. Although the shape of the isotherm on AC1 is similar to that
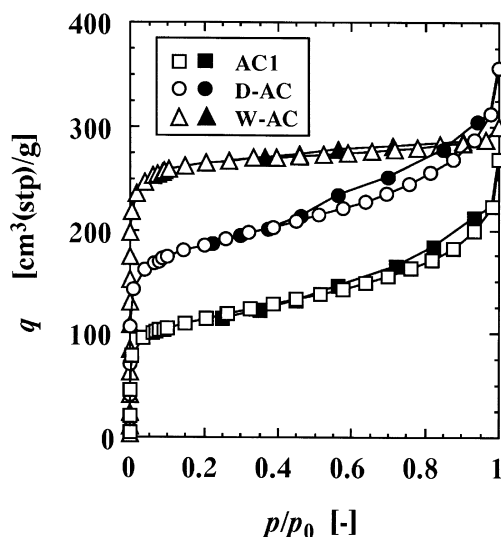

Fig. 4. Adsorption and desorption isotherms of N_2 on activated carbons at 77 K; open symbols: adsorption, closed symbols: desorption.
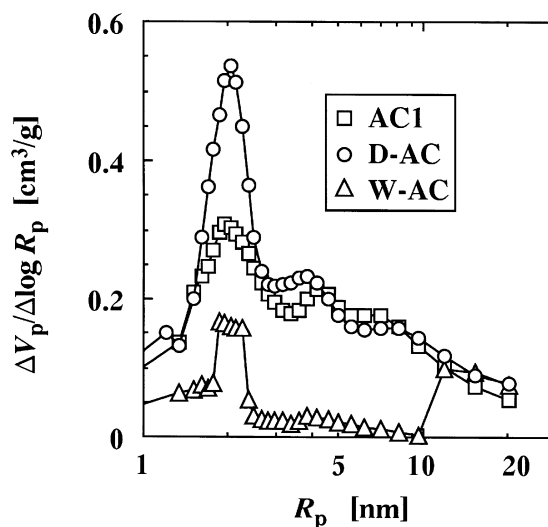

Fig. 5. Pore size distributions of activated carbons.

Table 5
BET surface area and pore volumes of activated carbon[a]

Carbon	S_{BET} (m^2/g)	V_{mes} (cm^3/g)	V_{mic} (cm^3/g)
ar_AC	74	0.09	0.02
vp_AC	272	0.21	0.13
n_AC1	828	0.30	0.43
n_AC2	515	0.48	0.25
D-AC	607	0.26	0.31

[a] ar_AC=Activated after O_2 oxidation, vp_AC=activated after H_2O oxidation, n_AC1=activated after 3.3 N HNO_3 treatment, n_AC2=activated after 5.2 N HNO_3 treatment, D-AC=ommercial carbon for dioxin adsorption.

n_AC1, n_AC2 and D-AC at 77 K are shown in Fig. 6. One can see that the shapes of these isotherms are similar. The amount of N_2 adsorbed on AC1 is smaller than that on D-AC as described above. On the other hand, the amount of N_2 adsorbed on n_AC1 or n_AC2 is much larger than that on AC1 and is also larger than that on D-AC. The results suggest that the mesoporosity of activated carbon is improved by HNO_3 treatment prior to steam-activation.

Fig. 7 shows pore size distributions of n_AC1 and n_AC2. The distribution of D-AC is also shown in this figure. The n_AC1 and n_AC2 have more mesopores of ca. 2 nm radius than D-AC. Hence, the carbons are available for adsorption of dioxins.

The authors have prepared activated carbons from another RDF including garbage, which has been produced from a municipal waste in another city. When one prepares the carbons by the conventional steam-activation without pretreatments, the carbons have quite different porous
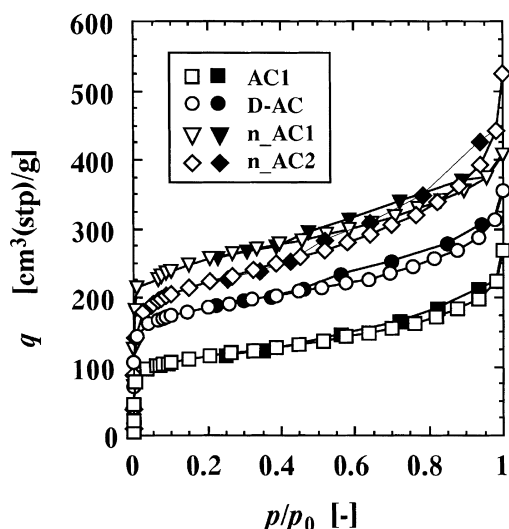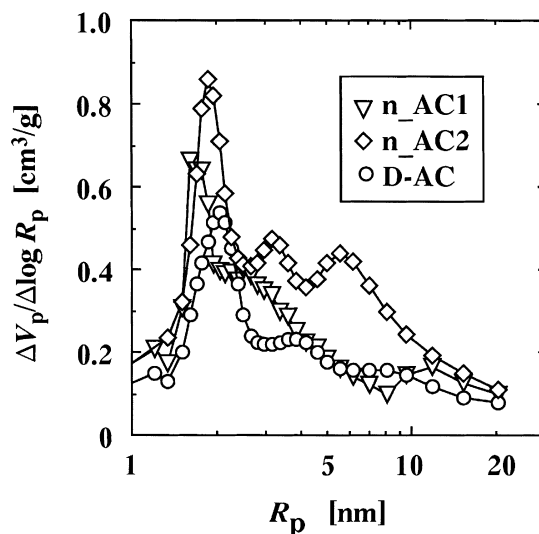

Fig. 7. Pore size distributions of prepared activated carbons.

properties from the carbons reported in the present article. The results suggest that the conventional steam-activation gives no consistency of product because the source material can vary from region to region and with the season of the year. On the other hand, the carbons prepared via the HNO_3 treatment of cRDF and steam-activation have almost same porous properties independent of different municipal wastes. The results will be reported in a subsequent article.

3.4. Effect of HNO_3 treatment

We discuss the porosity of the carbons steam-activated without the pretreatment. The mesoporosity of the carbons is not developed compared with the carbons prepared via the HNO_3 treatment. It is well known that pores of activated carbon increase with decreasing the yield of carbon because the activation reaction proceeds. Fig. 8 shows the relation between the yield and the activation time. AC1 has been obtained by 5-h activation. Although its S_{BET} is the largest, the yield is relatively large also.

Table 6 shows ash contents of cRDFs. One can confirm that the ash content of cRDF treated by HNO_3 decreases by less than half of the original cRDF because 3.3 or 5.2 N HNO_3 is relatively strong. Table 7 shows the porous properties of the activated carbons calculated by carbon basis. One can see that S_{BET}, V_{mes} and V_{mic} of n_AC1 and n_AC2 are much larger than those of D-AC even for carbon basis. Hence, the results suggest that ash is dissolved into the HNO_3 solution during the pretreatment and that many activation sites (edges of graphene layers of carbons) are formed inside the carbon structure by the dissolution of the metal compound. The mechanism for developing mesopores will be elucidated in the near future.
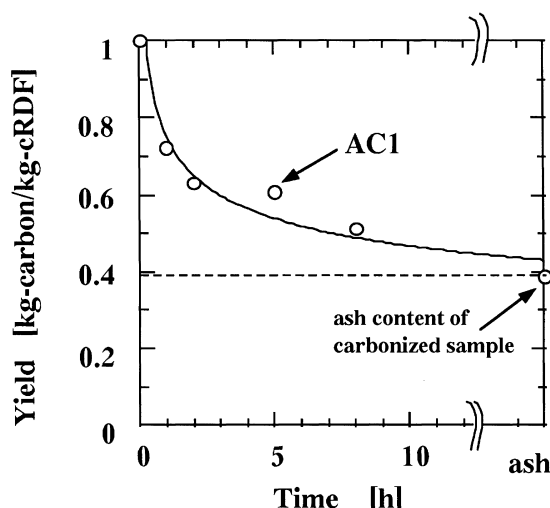

Fig. 6. Adsorption and desorption isotherms of N_2 on activated carbons prepared at 77 K; open symbols: adsorption, closed symbols: desorption.

Fig. 8. Time change of the yield of the steam-activated carbon without pretreatment.

Table 6
Ash content of carbonized substance

Carbonized substance	Ash content (kg-ash/kg-dry cRDF)
cRDF	0.39
cRDF treated with 3.3 N HNO$_3$	0.17
cRDF treated with 5.2 N HNO$_3$	0.18

4. Conclusion

The carbonized RDF (cRDF) produced from municipal waste was steam-activated at 1123 K. The cRDF was also treated by 3.3 or 5.2 N HNO$_3$ at a boiling temperature for 3 h prior to the steam-activation. The carbons were compared with a commercial activated carbon for dioxin adsorption and the following conclusions were obtained.

Table 7
BET surface area and pore volumes of activated carbon (carbon basis)[a]

Carbon	S_{BET} (m^2/g)	V_{mes} (cm^3/g)	V_{mic} (cm^3/g)
AC1	808	0.44	0.39
ar_AC	308	0.38	0.10
vp_AC	893	0.70	0.42
n_AC1	1249	0.45	0.66
n_AC2	907	0.85	0.43
D-AC	607	0.26	0.31

[a] Ash content of D-AC is neglected.

1. Since the molecular sizes of dioxins determined by ab initio MO calculations are relatively large, the mesopores of activated carbons are necessary for adsorption of dioxins.
2. The porosity of the carbon prepared without the pretreatment of nitric acid was not so developed as the commercial carbon for dioxin adsorption.
3. The carbons steam-activated after the HNO$_3$ treatment have more mesopore volumes than the commercial carbon and are effective for adsorption of dioxins.
4. The ash dissolution from cRDFs by HNO$_3$ results in the formation of activation sites for developing mesopores.

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