**RESOURCES
PROCESSING**

Original Paper

Adsorption Properties of Activated Carbon Prepared from Waste Beer Lees by KOH Activation and CO_2 Activation

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Abstract

Activated carbon was successfully produced from beer lees which are the main waste material from a beer-production process, when KOH and CO_2 were used as oxidizing agents in activation process. KOH activation produces well-developed porous structure. CO_2 activation deserves attention in ecological and economical aspects. Adsorptions of 1,2-dichloroethane and 1,2-dichloropropane onto the obtained activated carbon in aqueous solutions were studied. Adsorptions are found to be affected by the solubility of adsorbate and the porous properties of adsorbent such as specific surface area and total pore volume. KOH-activated carbon shows distinguished performance for adsorption of 1,2-dichloropropane. Applicability of the obtained activated carbon was examined with McCabe-Thiele analysis which calculates the specific amount needed for removal of the above organic contaminants in aqueous solutions to meet a given standard.

Key words: Carbon, Activation, Adsorption, McCabe-Thiele analysis

Introduction

According to a report in 1996, about 20 million ton of food waste was being discharged annually in Japan. Only a small portion is utilized as feed for domestic animals or as fertilizer and most of it is just burned up into ashes. Beer-making industry is one of the main producers of food waste and it contributes nine hundred thousand ton annually. Lees, mud from drainage, glass waste form 80%, 10% and about 7% in the waste, respectively. Beer lees are fibriform and mainly composed of barley husks. It is being used in part as feed for animals but complete consumption is not achieved yet. Finding a new usage for beer lees that is the main constituent in the waste of beer production is required for 'zero emission of waste'.

Recently, activated carbon is expanding its application and diversifying its consumption rapidly, for example, solvent recovery, waste water treatment, adsorbents for pollutants and adsorbents for medical purpose. Keeping pace with this current, various kinds of waste materials have been studied on their fitness for the production of activated carbon. Agricultural wastes such as wood[1] and nutshells[2], municipal waste[3] and mineral waste materials related with the coal or petroleum[4] have been examined. Waste plastic or waste tires are also investigated[5].

The purpose of this study is to examine feasibility of obtaining activated carbon from waste beer lees and evaluate applicability of the obtained activated carbon. KOH activation and CO_2 activation were used and compared in this study. Chemical activation is known to have some advantages over physical activation, such as lower activation temperature, higher development of porosity and reduction of ash content while it also has disadvantages like expensive activating agents and additional washing process[6]. Using CO_2 is meaningful in the economical point of view because CO_2 is a widely used activating agent and discharged from a beer-making process as a waste material.

Applicability of the obtained activated carbon as an adsorbent for organic contaminants in aqueous solutions was studied using 1,2-dichloroethane and 1,2-dichloropropane as adsorbates. 1,2-dichloroethane and 1,2-dichloropropane are harm-

ful for human body due to two chloro-ligands included and need to be kept under a certain level in concentration in city water. The amount needed to satisfy the environmental standard by removing the organic materials was calculated using Ma-Cabe-Thiele analysis.

Experimental

Beer lees carbon obtained using beer lees from Asahi Beer Co. was used in this study. Beer lees carbon used in this study has cylindrical shape with a diameter of 5 cm and a length of 25 cm when it is obtained through drying, compressive forming and carbonization of beer lees. It was pulverized to a particle size of 0.5~1.0 cm in diameter before it is taken to activation process.

Five grams of the mixture of beer lees carbon and KOH with the carbon/KOH weight ratio of 1:1 was put in an alumina boat, heated to 500°C at a rate of 10°C/min in an electric furnace under N_2 gas flowing at a rate of 250 cm^3/min and kept at the temperature for 1 hour. Activation was completed by subsequent heating to 800°C at a rate of 5°C/min and keeping the condition for 1.5 hours. The product was cooled down to room temperature under N_2 atmosphere and washed with distilled water several times until a constant pH was obtained for the slurry. Yield of production was calculated using the weight of sample measured after drying. The sample is designated as K800H1.5 referring to the activation temperature and time.

For CO_2 activation, five grams of beer lees carbon put in an alumina boat was heated in an electric furnace to 900°C at a heating rate of 30°C/min under N_2 atmosphere and kept at the temperatures for 1 hour under the CO_2 flow of 100 cm^3/min. Yields of production were calculated with the weight of sample after cooling to room temperature under N_2 atmosphere. The sample is named C900H1.

Porous structure was analyzed using N_2 adsorption and desorpsion isotherms recorded on an automatic gas adsorption measurement apparatus (AS1MP-LP2, Quantachrome Instruments). Physical properties such as specific surface area, total pore volume and pore size distribution were calculated with the isotherms.

Adsorption of 1,2-dichloroethane and 1,2-dichloropropane onto the obtained beer lees activated carbon in aqueous solutions was examined. Powder samples obtained by pulverizing and sieving the activated carbon to a particle size of less than 106 μm were used as adsorbents. A quantity of 0.02 g of the activated carbon was put into 20 cm^3 of aqueous 1,2-dichloroethane solutions with the concentration of 200~800 mg/dm^3 or aqueous 1,2-dichloropropane solutions with the concentration of 200~800 mg/dm^3 and the resulting mixture was agitated for 6 hours. Adsorption amount was calculated by measuring the concentration of the remaining adsorbate in the solutions with capillary gas chromatography (GC-17A, Shimazu) after removal of the adsorbent.

Using the obtained adsorption isotherms, required amounts of activated carbon for removal of 1,2-dichloroethane and 1,2-dichloropropane in aqueous solutions to satisfy the related standards were calculated by McCabe-Thiele analysis. Permissible levels for the concentrations of 1,2-dichloroethane and 1,2-dichloropropane in city water in Japan are 0.004 mg/dm^3 and 0.06 mg/dm^3, respectively. Taking the standards into consideration, an initial adsorbate concentration of 10 mg/dm^3 and a target adsorbate concentration of 0.001 mg/dm^3 were assumed.

Results and discussion

Figure 1 shows N_2 adsorption-desorption isotherms for the obtained activated carbons. The isotherms are identified as type I corresponding to microporous solid having small external surface area according to IUPAC classifications. Small hyteresis is found in the desorption branches, which is a feature of type IV curves implying the existence of mesopores. The initial steep rise in adsorption comes from micropore filling and the opening at the knees of the isotherms corresponds to the breadth of pore size distributions[7,8]. The ini-
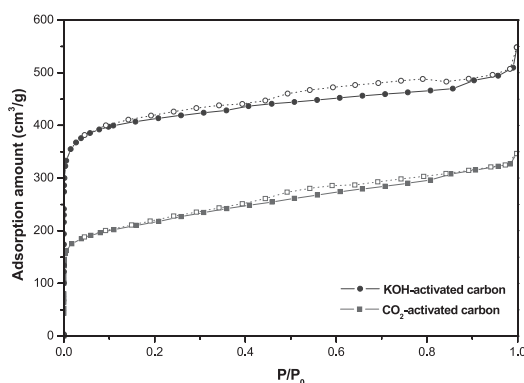

Fig. 1 N_2 adsorption and desorption isotherms of activated carbon obtained from beer lees using KOH or CO_2 as an activating agent. Dotted lines and open symbols mean desorption isotherms.

tial rise and the opening of the knee in the isotherm are greater in the activated carbon prepared by KOH activation method. Figure 2 shows the pore size distributions calculated from the isotherms. Pores of about 6 Å diameter are mainly developed in C900H1, whereas K800H1.5 mainly contains pores of about 8 Å diameter. The peak in the pore size distribution appears stronger and broader with K800H1.5 as can be forecasted from N_2 adsorption-desorption isotherms. Physical properties concerning porous structure calculated from N_2 adsorption-desorption isotherms are given in Table 1 where the properties of a commercial activated carbon are shown together for comparison. KOH-activated carbon shows larger specific surface area and larger total pore volume than CO_2-activated carbon. K800H1.5 has the specific surface area of 1560 m²/g which is found larger than that of the commercial activated carbon. However, the commercial activated carbon has larger total pore volume than K800H1.5. It implies that K800H1.5 contains more amounts of small pores than the commercial activated carbon.

Adsorption onto the obtained activated carbon was examined using 1,2-dichloroethane and 1,2-dichloropropane as adsorbates. Figure 3 and Fig-
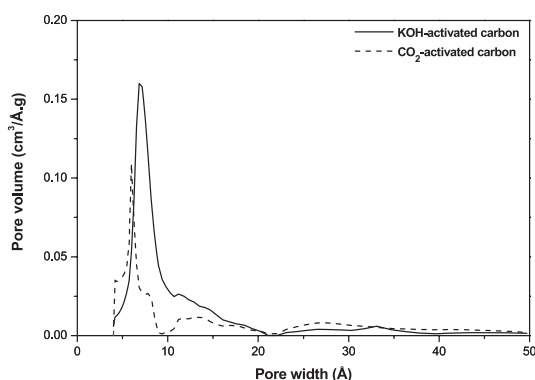
ure 4 present the adsorption isotherms of the adsorbates using CO_2-activated carbon and KOH-activated carbon, respectively. The isotherms approach to a saturated value after an abrupt increase below the concentration of 100 mg/dm³ in general. K800H1.5 shows faster increase in adsorption to a greater value than C900H1 for any adsorbates used in this study due to the larger specific surface area and larger total pore volume. It is considered that most pores in the activated carbon can serve as the available sites for the adsorption of 1,2-dichloroethane and 1,2-dichloropropane, because their molecular sizes are much smaller than the average pore size. It is found, however, that their adsorptions take place to different extents in spite of their similar molecular sizes. 1,2-dichloropropane shows more than twice as much adsorption as 1,2-dichloroethane. 1,2-dichloroet-
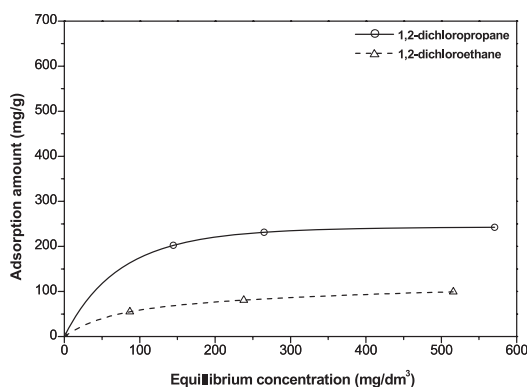

Fig. 3 Adsorption isotherms of 1,2-dichloroethane and 1,2-dichloropropane onto activated carbon obtained from beer lees using CO_2 as an activating agent.

Fig. 2 Pore size distributions of activated carbon obtained from beer lees using KOH or CO_2 as an activating agent.

Table 1 Specific surface area and total pore volume of commercial activated carbon and activated carbon obtained from beer lees using KOH or CO_2 as an activating agent.

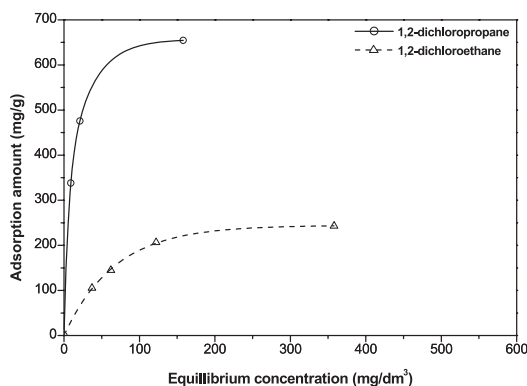|	Specific surface area (m²/g)	Total pore volume (cm³/g)
C900H1	795	0.54
K800H1.5	1560	0.85
Commercial activated carbon	1370	1.56

Fig. 4 Adsorption isotherms of 1,2-dichloroethane and 1,2-dichloropropane onto activated carbon obtained from beer lees using KOH as an activating agent.
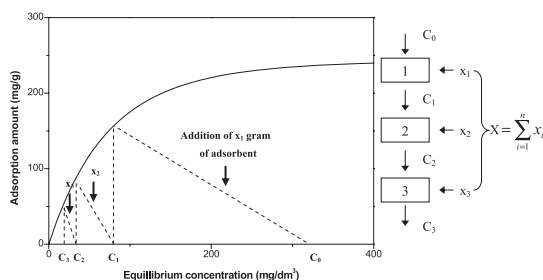
Fig. 5 McCabe-Thiele analysis for a 3-stage operation.

hane and 1,2-dichloropropane have solubilities of 8.53×10^3 mg/dm^3 and 2.80×10^3 mg/dm^3 in water at 20°C, respectively. The solubility of 1,2-dichloro-

ethane is more than 3 times as high as that of 1,2-dichloropropane. Higher solubility implies higher affinity between solvent and solute, and then solute with higher solubility is thought more difficult to be captured by adsorbent. Strong attraction toward 1,2-dichloroethane by water is supposed to interrupt its adsorption to adsorbent.

Serviceability of the obtained activated carbon in removal of 1,2-dichloroethane and 1,2-dichloropropane in aqueous solutions was examined by McCabe-Thiele analysis using the adsorption isotherms in Figure 3 and Figure 4. Figure 5 describes flow of the analysis for a 3-stage process as an example. To reduce adsorbate concentration to a target value, adsorbent is added and removed from the solution by stages. The total amount of

Table 2 McCabe-Thiele analysis results for removal of 1,2-dichloroethane and 1,2-dichloropropane by multi-stage processes.

Removal of 1,2-dichloropropane by KOH-activated carbon								
Number of stages	C_1[a] (mg/dm^3)	C_2[a] (mg/dm^3)	C_3[a] (mg/dm^3)	x_1[b] (g)	x_2[b] (g)	x_3[b] (g)	x_4[b] (g)	X[c] (g)
1				1370				1370
2	0.100			13.71	13.56			27.27
3	0.464	0.022		2.954	2.825	2.809		8.588
4	1.000	0.100	0.010	1.363	1.246	1.234	1.233	5.076

Removal of 1,2-dichloroethane by KOH-activated carbon								
Number of stages	C_1 (mg/dm^3)	C_2 (mg/dm^3)	C_3 (mg/dm^3)	x_1 (g)	x_2 (g)	x_3 (g)	x_4 (g)	X (g)
1				21340				21340
2	0.100			211.6	211.3			422.9
3	0.464	0.022		44.20	43.93	43.75		131.88
4	1.000	0.100	0.010	19.51	19.24	19.21	19.21	77.17

Removal of 1,2-dichloropropane by CO$_2$-activated carbon								
Number of stages	C_1 (mg/dm^3)	C_2 (mg/dm^3)	C_3 (mg/dm^3)	x_1 (g)	x_2 (g)	x_3 (g)	x_4 (g)	X (g)
1				15720				15720
2	0.100			156.0	155.6			311.6
3	0.464	0.022		32.68	32.36	32.23		97.27
4	1.000	0.100	0.010	14.49	14.18	14.15	14.15	56.97

Removal of 1,2-dichloroethane by CO$_2$-activated carbon								
Number of stages	C_1 (mg/dm^3)	C_2 (mg/dm^3)	C_3 (mg/dm^3)	x_1 (g)	x_2 (g)	x_3 (g)	x_4 (g)	X (g)
1				85720				85720
2	0.100			849.5	848.7			1698.2
3	0.464	0.022		177.0	176.4	175.7		529.1
4	1.000	0.100	0.010	77.92	77.23	77.16	77.15	309.46

[a] C_1, C_2 and C_3 mean adsorbate concentrations in the solution after each stage.
[b] x_1, x_2, x_3 and x_4 mean amounts of activated carbon addition in each stage.
[c] X means total amount of activated carbon required for a given multi-stage process.

adsorbent needed to achieve the target concentration can be minimized by proper combination of C_1 and C_2 or x_1, x_2 and x_3, where C_i and x_i are adsorbate concentration in the solution after stage i and the amount of activated carbon addition in stage i, respectively. The purpose of the analysis is to find out the minimum amount of adsorbent needed for a given process. The optimum combination is found using the rule of trial and error. Solution amount of $10\,dm^3$, an initial adsorbate concentration of $10\,mg/dm^3$ and a target adsorbate concentration of $0.001\,mg/dm^3$ were assumed in this study. Results of analysis for several multistage processes are summarized in Table 2. Adsorbate concentration after each stage, C_i is found to be independent of the kinds of adsorbate and adsorbent. It is only dependent on the initial and target adsorbate concentrations and the number of stages, mathematically. Total amount of activated carbon required for the removal process decreases rapidly with the number of stages in a process in general. Required amount of activated carbon reflects efficiency of the material as an adsorbent. Removal of 1,2-dichloropropane using K800H1.5 is the most effective in this study. The amount of $8.588\,g$ of K800H1.5 is needed to reduce 1,2-dichloropropane concentration of $10\,mg/dm^3$ to $0.001\,mg/dm^3$ in $10\,dm^3$ of aqueous solution by applying a 3-stage process. A multi-stage process also can be a solution for utilization of a low-grade adsorbent like CO_2-activated carbon. Much more amount is needed when using C900H1 but low production cost is expected for CO_2-activated carbon because CO_2 is discharged from a beer-making process as a waste material.

The amount of adsorbent required for a column operation can be estimated by the calculation result for a multi-stage process where C_i's are decided by equally dividing the gap between the initial adsorbate concentration and the target adsorbate concentration. A 200-stage process may be a typical example to estimate the required amount of adsorbent in a column operation. The total required amount of activated carbon in a 200-stage operation is calculated to be $7.79\,g$, $119.50\,g$, $88.15\,g$ and $479.50\,g$ for removal of 1,2-dichloropropane and 1,2-dichloroethane by KOH-activated carbon and removal of 1,2-dichloropropane and 1,2-dichloroethane by CO_2-activated carbon, respectively. The required amounts are found to be about the same measure as those for the 3-stage operations in the above. The 3-stage process is thought to be adequate in the practical point of view because the number of stages in the process is practicable and the required amount of adsorbent is as small as that for a column operation.

Summary

Activated carbon was obtained from beer lees by activation with KOH or CO_2. Porous structure was studied with the adsorption-desorption isotherms of nitrogen. Adsorption property was studied using 1,2-dichloroethane and 1,2-dichloropropane as adsorbates and the examples of usage of the obtained activated carbon for removals of the adsorbates were examined by McCabe-Thiele analysis according to the environmental standard. The following results can be obtained.

1) KOH activation produces more developed porosity than CO_2 activation. Reduction of mineral residue is another advantage of KOH activation over CO_2 activation. However, CO_2 activation is advantageous in economical and ecological point of view because it is a waste material discharged from a beer-making process.

2) The extent of adsorption is found to be affected by the porous structure of adsorbent and the solubility of adsorbate. Adsorption takes place more actively with KOH-activated carbon due to its highly developed porous structure. Adsorption of 1,2-dichloropropane is found to be more active because it is less soluble in water than 1,2-dichloroethane.

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