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Adsorption and Desorption Characteristics of Maltooligosaccharide for the Surface Treated Activated Carbons

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Abstract. The adsorption and desorption characteristics of maltooligosaccharide for raw and surface treated activated carbons were studied experimentally. The TLC imaging densitometry method was used in determining the sugar concentration in the maltooligosaccharide. Adsorption amount of larger molecules, such as maltopentaose and maltoheptaose on F400 were greater than those of smaller molecules. On the other hand, Adsorption amount of smaller molecules, such as maltose and maltotriose on SLS103 were greater than those of larger molecules. Acid treatment of the GAC increases the carboxyl group, but did not affect much on the adsorption rate of saccharides. Heat treatment decreases the adsorption time of F400 due to substantial surface area increase. For the desorption of the adsorbed saccharides with ethanol, the amount of ethanol in the solution was more important than the concentration.

Keywords: activated carbon, adsorption, desorption, maltooligosaccharide, thin-layer chromatography (TLC)

1. Introduction

Oligosaccharides are carbohydrate compounds containing 2-20 sugar units, with molecular weights ranging between 300 and 2,000. Oligosaccharides are usually water soluble, have little influence on rheological properties of food, mild in sweetness, not degraded by human digestive enzymes. Oligosaccharides can be easily modified chemically and biochemically, and are highly stable, nontoxic, and hydrophilic. Maltooligosaccharide is a mixture of various glucose monosaccharide, which can be separated from maltooligosaccharide. It is useful in a wide variety of applications. For example, maltopentaose (G5) is used as a food additive, and it can restrain blood sugar and the cholesterol (Francesca et al., 2004). It can be used as an aging agent for starch food and is highly functional material.

For the separation of maltooligosaccharide, silica gel and ion exchange resin were used in general. However, it is too expensive for commercial scale application, thus an inexpensive separation method is required. Activated carbon is a powerful adsorbent because it has a large surface area and pore volume.

The separation and quantitative analysis of oligosaccharides are important in a wide variety of applications such as food analysis and analysis of the products obtained from hydrolysis of polysaccharides. The quantitative determination of carbohydrate density directly from the "spots" on the TLC plate by densitometry has been appeared in the literature (Han and Robyt, 1998; Robyt and Rupendra, 1994), and recent development of computerized TLC densitometric instrumentation increased sensitivity and precision. The TLC method

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for the quantitative determination of relatively small amounts of sugars and maltooligosaccharide are very convenient.

In this work, the adsorption and desorption characteristics of maltooligosaccharide for raw activated carbons and surface treated activated carbons were studied experimentally using TLC method.

2. Experimental

Two kinds of commercial granular activated carbons (GACs), SLS103 (Samchully Activated Carbon Co. Ltd., Korea) and F400 (Calgon Carbon Corp., USA), were used in this study. SLS103 and F400 are made from coconut shell and pitch coal, respectively. They were ground and sieved to 0.42–0.59 mm. Both GACs were boiled in distilled water for 1 h to remove impurities, then dried at 105°C and stored in a desiccator. Prior to thermal or acid treatment, the physical properties of these activated carbons were characterized. For acid treatment, 200 g of GAC was placed in a bottle, and 1 litter of 0.5 N HNO_3 solution was added. The bottle was then placed in a shaking incubator and agitated for 24 h. The GAC was then placed in an oven at 80°C and dried for 3 h. The HNO_3-treated activated carbon was washed with distilled water several times and then dried in an oven at 105°C for 24 h, and kept in a desiccator. Thermogravimetric analysis (TGA) data of the SLS103 and F400 were used to determine the optimum temperature for heat-treatment. Based on the TGA data, the optimum heat treatment condition obtained for the two GACs were 24 h at 350°C. The surface area and average pore size of the GACs were measured by desorption experiments of N_2, and are listed in Table 1.

Commercial maltooligosaccharide (Daesang Co., Ltd., Korea) was used as an adsorbate. Maltooligosaccharide solutions were diluted with distilled water to a concentration of 2.7% (w/v) for batch experiment and a concentration of 1.35% (w/v) for column experiment. The concentrations of G1 (glucose), G2 (maltose), G3 (maltotriose), G5 (maltopentaose) and G7 (maltoheptaose) in the maltooligosaccharide solution of 2.7% (w/v) are 6.21, 5.57, 5.56, 4.13 and 1.94 g/L, respectively. G1 is a single sugar, and G2–G7 are oligosaccharides with linear (1-4)-linked glucosides. Standard solution for each sugar (Sigma Chemical Co., USA) was used for the quantitative determination of sugar concentration.

Table 1. Physical properties of activated carbons used.

	Unit	SLS103	F400
Diameter	mm	0.42–0.59	0.42–0.59
Density (dry)	kg/m^3	1,240	1,430
Density (wet)	kg/m^3	1,410	1,460
BET surface area	m^2/g	1,650	1,610
Pore diameter (average)	Å	24,0	29.9

3. Results and Discussion

The physical properties of the GACs used in this study are listed in Table 1. The density of F400 is higher than SLS103, and the density differences of F400 in dry and wet states are very small. The surface areas of the two GACs were practically the same, but the average pore diameter of F400 was larger than that of SLS103. The meso-pore volume of SLS103 is much smaller than that of F400, and most of the pore volume is distributed in the range of 30–45 Å in diameter. And the range of pore size distribution for F400 is much wider, 30–400 Å. The surface area and pore volume of the raw and heat or acid treated GACs are listed in Table 2. By treating the raw GACs at 350°C for 24 h, the weights of SLS103 and F400 were decreased by 2.40 and 1.75%, respectively, but the BET surface areas of SLS103 and F400 were increased by 19.4 and 16.8%, respectively. The effect of 0.5N HNO_3 treatment on the BET surface area was very small. By the heat treatment, the total pore volumes of SLS103 and F400 were increased by 19.6 and 13.0%, respectively. However, the effect of 0.5N HNO_3 treatment on the pore volumes of the two GACs are not great, 4.4% increase for SLS103 and 3.4% decrease for F400.

Figure 1 shows the adsorption capacity of maltooligosaccharide onto raw GACs. As can be seen in this figure, adsorption amount of larger molecules, such as maltopentaose and maltoheptaose for pitch

Table 2. Surface area and pore volume of the activated carbons used.

	$S_{BET}(m^2/g)$	V (cm^3/g)
SLS103	1,290	0.459
SLS103 (350°C)	1,540	0.547
SLS103 (0.5 N HNO_3)	1,320	0.479
F400	1,370	0.532
F400 (350°C)	1,600	0.601
F400 (0.5 N HNO_3)	1,360	0.514

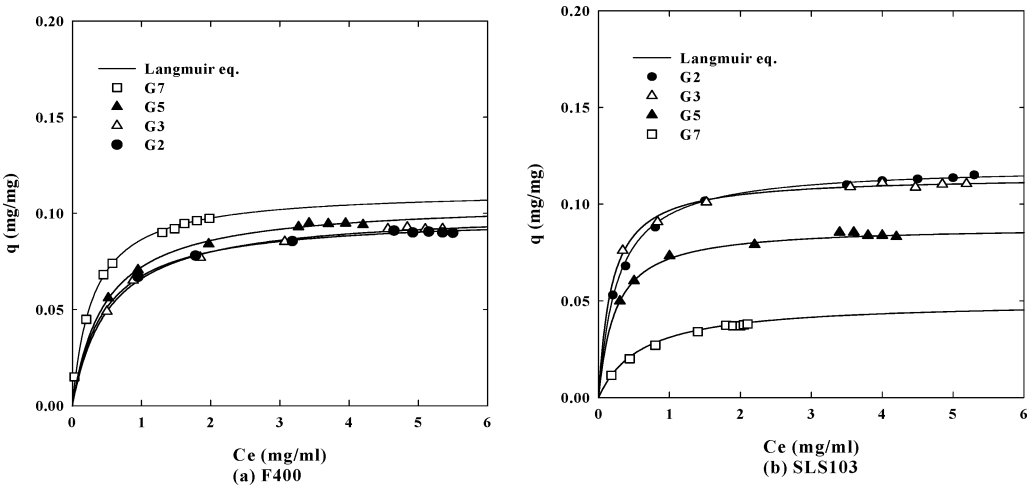

Figure 1. Adsorption isotherm of maltooligosaccharides onto raw activated carbon.

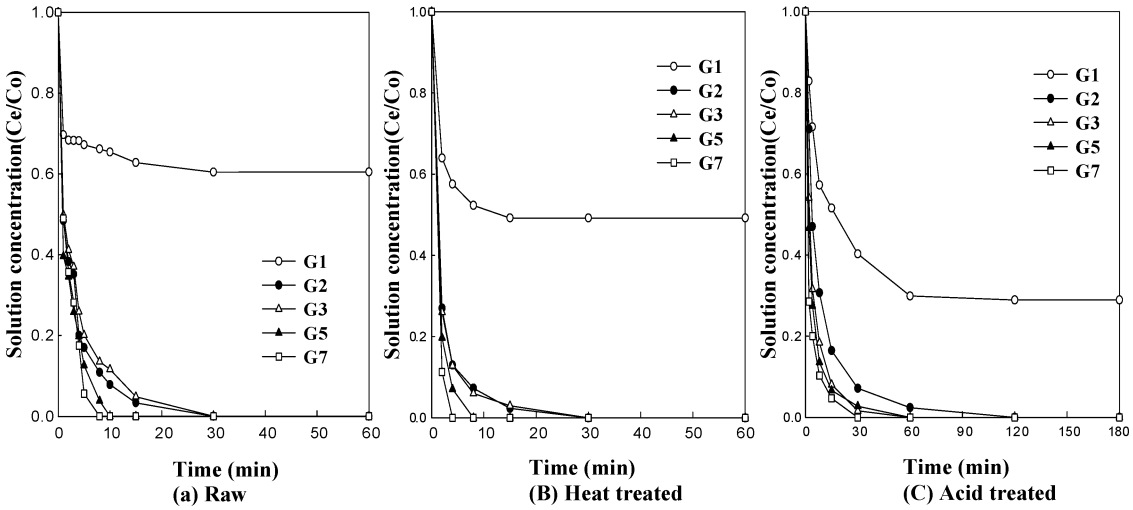

Figure 2. Variation of solution concentration with reaction time. (F400, pH 5.6, adsorbent dosage 15 g/L) (a) Raw, (b) Heat treated and, (c) Acid treated.

coal-based cativated carbon, F400, with a relatively uniform pore size distribution (30–400 Å), were greater than those of smaller molecules. On the other hand, Adsorption amount of smaller molecules, such as maltose and maltotriose, for a coconut shell-based activated carbon, SLS103 which has a smaller pore size, in the range 30–45 Å, were greater than those of larger molecules. Single component isotherm data was correlated by the Langmuir equation. The adsorption of maltooligosaccharide onto GACs was a favorable type and the Langmuir isotherm was used to fit with the experimental equilibrium data.

Figure 2 show the concentration of maltooligosaccharide in the solution phase in a batch reactor. The adsorption time for F400 was not affected much by either heat or acid treatment as shown in Fig. 2. Since the meso-pore volume and meso-pore distribution are not affected much by the heat and acid treatments. But the adsorption time of each sugar for F400 was in the order of G7 (maltoheptaose) < G5 (maltopentaose) < G3 (maltotriose) < G2 (maltose). The amount of G1 adsorbed by F400 much smaller than other sugars.

Figure 3(a) shows the breakthrough curves for SLS103 at pH 7.1. Adsorption experiments were

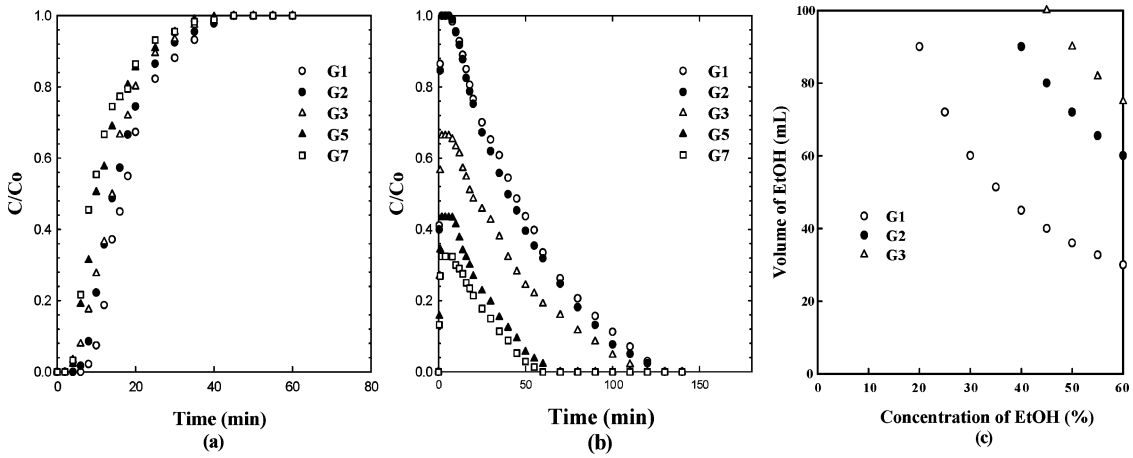

Figure 3. (a) Adsorption breakthrough curves, and (b) Desorption curves of glucose and maltooligosaccharide by 50% ethanol solution in a fixed bed, (c) Relationship between ethanol concentration and volume for 95% desorption onto SLS103.

carried out in a 20 mm ID fixed bed. Twenty grams of dried GAC is packed to the bed of height 120 mm and the maltooligosaccharide solution diluted to 1.35% (w/v) is pumped to the column. The fluid velocity for the adsorption and desorption experiments was kept at 0.36 mm/s, which is approximately equal to 60% of the minimum fluidization velocity.

As shown in this figure, the breakthrough time, defined as the time at $C/C_o = 0.1$, and the exhaustion time, defined as the time at $C/C_o = 0.9$, increase as the molecular weight of the sugar decreases for pH 7.1. At this pH, the breakthrough time for G1 is 25 min which is equivalent to the bed volume of 4.5 and the exhaustion time for G1 is 68.4 min which is equivalent to the bed volume of 12.3. The breakthrough curves of all species, in general, depend on adsorption equilibrium, intraparticle mass transfer, and the hydrodynamic conditions in the column. Intraparticle mass transfer of maltooligosaccharide onto GACs is very small and similar (6.6×10^{-7}–1.86×10^{-8}).

But as shown in Fig. 1, the adsorption amount of each sugar for SLS103 was in order of G7 (maltoheptaose) < G5 (maltopentaose) < G3 (maltotriose) < G2 (maltose). Breakthrough time of maltoheptaose (G7) is shorter than that of other sugars. Desorption curves of the maltooligosaccharide from the saturated beds of SLS103 and F400 using 50% (V/V) ethanol are shown in Fig. 3(b). For the bed of SLS103, the time for desorption and dimensionless concentration decrease with increasing molecular weight of sugar. Recovery yield of small molecules such as G1 and G2 was about 95% but large molecules such as G5 and G7 was about 40%. The large molecular weight sugars, G5 and G7, reach desorption equilibrium at 133 min, which is equivalent to 24 bed volumes of liquid, but the equilibrium desorption times for small molecular weight sugars, G1 and G2, are about two times of that for G7. For F400, contrary to SLS103, the dimensionless concentration increases with molecular weight of sugar but the equilibrium desorption time for each sugar is practically the same. Figure 3(c) shows the relationship between the ethanol concentration and volume for 95% desorption of saccharides, adsorbed at equilibrium on the SLS103, in a batch reactor. This figure shows that more ethanol is required for the desorption of larger saccarides, and the effect of ethanol concentration in the aqueous solution is not important compared to the amount of ethanol in the solution in the concentration range of this study.

4. Conclusions

Adsorption capacity of larger molecules such as maltopentaose and maltoheptaose for a pitch coal base activated carbon, F400, with relatively uniform pore size distribution were greater than those of smaller saccharides. On the other hand, the adsorption amount of smaller molecules such as maltose and maltotriose for a coconut shell base activated carbon, SLS103, with smaller pore size were greater than those of larger saccharides. Acid treatment of the GAC increases the carboxyl group, but did not affect much on the adsorption

rate of saccharides. Heat treatment decreases the adsorption time of F400 due to substantial surface area increase. For the desorption of the adsorbed saccharides with ethanol, the amount of ethanol in the solution was more important than the concentration.

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