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Adsorptive Removal of Organic Acids and Furans from Hydrothermal Treatment Process of Biomass

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Abstract: Hydrothermal treatment of plant biomass using subcritical water is one of the pretreatment methods for producing valuable chemicals such as D-glucose for producing bio-alcohol. However, this treatment causes side reactions and produces by-products such as organic acids and furans which may inhibit the production of alcohols in the following step. In this study, the adsorption process is applied to remove by-products from products solution. As adsorbents, Cellufine A-200, A-800, DIAION WA21J, and activated carbon were used. Among them, Cellufine A-200 selectively adsorbed organic acids and activated carbon showed the best adsorption performance for furans. DIAION WA21J adsorbed both organic acids and furans.

Keywords: Adsorption, biomass, organic acids, separation, subcritical water

INTRODUCTION

Plant biomass is mainly composed of cellulose, hemi-cellulose, and lignin (1–3). Cellulose is forced as a resource of valuable chemicals when its constituent molecule of D-glucose is converted into bio-ethanol (4). The concentration of carbon dioxide in the atmosphere had been rapidly

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increasing over the past one hundred years. These effects are the results of consuming a large amount of fossil fuels. Therefore, the use of renewable biomass origin fuels instead of fossil fuels is one way to prevent global warming. The most commonly used methods to obtain low molecular saccharides from poly-saccharides like cellulose are the use of acid catalysts (5), base catalysts (6), or enzymes (7,8). However, these methods make processes more complicated or time consuming. On the other hand, subcritical water is focused as an environmentally friendly solvent for decomposing poly-saccharides into smaller molecules because of its high reactivity due to the large ion product and small dielectric constant (9,10). Although subcritical water has advantages over the other solvents, it causes side reactions and produces organic acids and furans (11) which are not desired for producing bio-ethanol in the following bio-treatment process. These products are undesired since they behave as enzymatic inhibitors (12–14) in the proceeding processes of producing ethanol from small molecular sugars. Therefore, these undesired products must be removed from the aqueous solution treated by subcritical water. As an example of the production of these materials, some reports mention about the degradation of cellulosic biomass using subcritical water. Sasaki et al. reported that 5-HMF, aldehydes, and acids were produced from cellulose hydrolysis at 320°C, 350°C, and 400°C (15). They also conducted the decomposition of saccharide using a continuous flow reactor and recovered furans and organic acids (16). The separation of these materials from the product aqueous solution is necessary in order to use biomass resources as bio-fuels or as a source of chemical materials. However, the separation of furans and organic acids has not been discussed yet. In this study, four different kinds of adsorbents were used for removing by-products from the aqueous solution. A decomposition experiment of D-glucose was first conducted by using a flow reactor in order to produce a mixture of D-glucose, organic acids, and furans. Then, adsorptions were carried out with pure components and the D-glucose solution of subcritical water treatment.

EXPERIMENTAL

Materials

D(+)-glucose (98%, Wako Pure Chemicals Industries Ltd., Osaka, Japan) was used as a starting material. Reagents used for the product analysis, D(−)-fructose (99%), DL-lactic acid (85–92%), formic acid (99%), and acetic acid (99.9%) were also obtained from Wako. 5-Hydroxymethyl-2-furfural (5-HMF; 99%) and glycolic acid (99%) were

Table 1. Properties of adsorbents

Adsorbent	Types	Functional group	MW exclusion limit (kD)	Particle diameter (μm)	Ion capacity (meq/g dry)
Cellufine A-200	weak anion exchanger	diethylaminoethyl	30	40–130	0.9
Cellufine A-800	weak anion exchanger	diethylaminoethyl	1000	40–130	0.8
DIAION WA21J	weak anion exchanger	polyamine	–	300–1180	5.8
Activated carbon	Coconut shell	–	–	300–600	–

obtained from Sigma-Aldrich Japan. K. K., Tokyo, Japan; 2-furfural (98%), was obtained from Kishida Chemicals Co. Ltd. (Osaka, Japan). For adsorbents, Cellufine A-200 and Cellufine A-800 were purchased from Chisso Corporation (Tokyo, Japan), DIAION WA21J from Mitsubishi Chemical Corporation (Tokyo, Japan), and activated carbon from NACALAI TESQUE, INC. (Kyoto, Japan). The properties of these adsorbents are listed in Table 1.

Adsorptions of Pure Components

Batch methods were used in this experiment. 10 mL of the sample solution was charged into a conical flask with 1 mL of adsorbent and then placed into a thermos tatted water bath which was set at 25°C. Table 2 shows the initial concentrations of the sample solutions. After shaking for 120 minutes the solution was collected by a syringe and filtered using

Table 2. The initial concentrations of the single component solutions

C_0 [mol/L]					
D(+)-glucose	2-furfural	Formic acid	Acetic acid	Glycolic acid	Lactic acid
0.020	0.020	0.0040	0.0040	0.0040	0.0040
0.10	0.10	0.020	0.020	0.020	0.020
0.50	0.50	0.10	0.10	0.10	0.10
2.0		0.50	0.50	0.50	0.50

0.8 μm filter to separate the adsorbent and the solution. These methods were repeated on each adsorbent and sample. Three kinds of adsorptions experiments were conducted; single component adsorption, multi components adsorption, and the adsorption of the treated aqueous solution of D-glucose by subcritical water.

In the adsorption of the single component, formic acid, acetic acid, lactic acid, 2-furfural, and D-glucose were used at various concentrations. Also, these components were mixed with D-glucose for the adsorption of multi-components. The initial concentrations of D-glucose, 2-furfural, and formic acid were prepared at 0.055 mol/L, 0.063 mol/L and 0.068 mol/L, respectively and then combined as a mixture solution.

Adsorptions of Treated D-Glucose Solution

Figure 1 shows the experimental apparatus of the continuous flow reactor which produces an aqueous solution of decomposition products of D-glucose as the sample of adsorption experiment. At first, distilled water was pumped by Pump A into the reactor through a needle valve and then to the rest of the system. The pressure within the whole system was then increased to the reaction pressure using a back-pressure regulator. Once the pressure became stable, the reactor was heated up to the reaction temperature. When the pressure and temperature were stabilized, the flow was switched to D-glucose aqueous solution pumped by Pump B. In order to stop the reaction immediately, the solution was cooled down through the double tube heat exchanger and then sent into the filters. The filtered solution was depressurized to the atmospheric pressure after passing the back pressure regulator. The concentration of D-glucose aqueous solution was prepared for 3.0 wt% with the temperature at 220°C, the pressure at 20 MPa, and the residence time of 90 seconds. 2 mL of the D-glucose aqueous solution treated with subcritical water was also processed using 0.2 g of adsorbents, and then it was compared to the results of adsorptions from pure components.

Analytical Methods

The product components were identified and quantitatively analyzed using high performance liquid chromatography (HPLC) with refraction index (RI-2031 plus; Jasco Corp.) and ultraviolet-visible (870-UV; Jasco Corp.) detectors. Sugar-SH1011 (Showa Denko

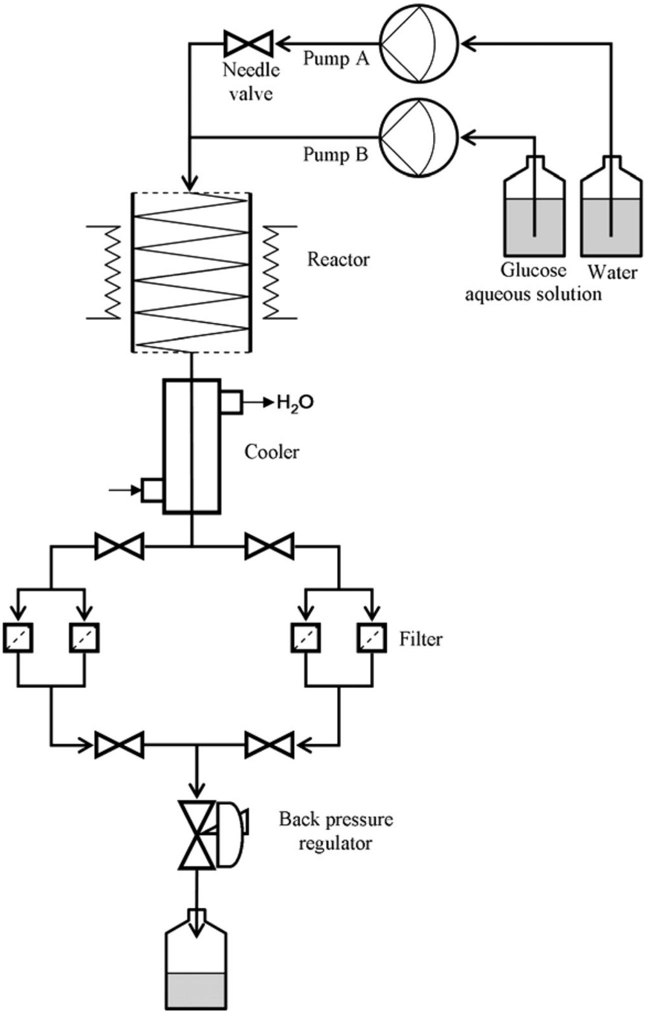


Figure 1. Continuous flow rector.

K.K.) was used as the HPLC column. 3 mmol/L perchloric acid and bromothymol blue (BTB) solution was used as the mobile phase and a coloring reagent, respectively. The coloring reagent was mixed in the immediate aftermath of the column, to detect organic acids. The column temperature was kept at 333 K by the column heater (Sugai U-620; SUGAI CHEMI, INC.). The analyses were performed using product solutions with the injection volume of 20 μl.

RESULTS AND DISCUSSION

Adsorptions of Pure Components

Single component adsorptions were first carried out using four different types of adsorbents; Cellufine A-200, Cellufine A-800, DIAION WA21J, and activated carbon. Figure 2 shows the adsorption isotherms in a log–log plot for the pure component system. Acetic acid, formic acid, and glycolic acid were favorably adsorbed by Cellufine A-200 whereas D-glucose was hardly adsorbed. Overall, Cellufine A-200 is a good adsorbent for adsorbing organic acids. This result represents the property of a weak anion exchanger. However, Cellufine A-800 with the larger molecular weight exclusion limit preferably adsorbed 2-furfural. DIAION WA21J acted as an excellent adsorbent for both formic acid and acetic acid. Since the type of this adsorbent is also the weak anion exchanger, the organic acids were adsorbed. In addition, this adsorbent adsorbed 2-furfural. Although activated carbon behaved as a good adsorbent for 2-furfural and lactic acid, D-glucose was also adsorbed to a certain degree. This tendency is due to the larger pore size of activated carbon compared to the other adsorbents. Additionally, the property of its nonpolar surface cut down the adsorption of the organic acids.

Adsorption isotherms are used to express the relationships between the adsorbates and the adsorbents at constant temperature. The equilibrium adsorption isotherm can be described by using the Freundlich equation.

$$q_e = K_F C_e^{1/n} \tag{3}$$

where q_e is the amount adsorbed at equilibrium, K_F is the Freundlich constant, C_e is the equilibrium concentration, and n is the constant of the adsorption intensity. Equation (3) is rewritten in the logarithmic form as follows

$$\ln q_e = \ln K_F + \frac{1}{n}\ln C_e \tag{4}$$

By plotting Eq. (4), K_F and n can be obtained from the slope and the intercept of the linear line in the plot. Lines in Fig. 2 show the Freundlich isotherm where fitted values of K_F and n are shown in Table 3.

Cellufine A-200 was investigated as a good adsorbent for the organic acids by comparing the values of K_F and n. 2-furfural was adsorbed well by the activated carbon. DIAION WA21J averagely adsorbed the furans and the organic acids. Consequently, D-glucose remained in the liquid as expected since D-glucose is the desired product for bio-ethanol.

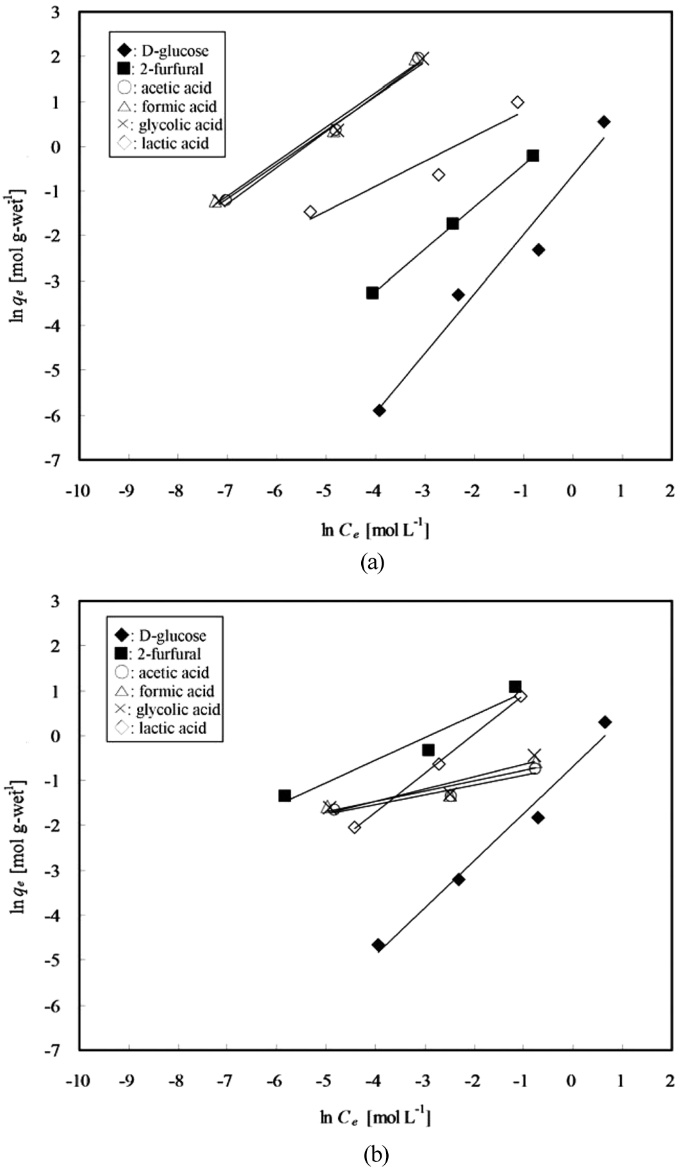
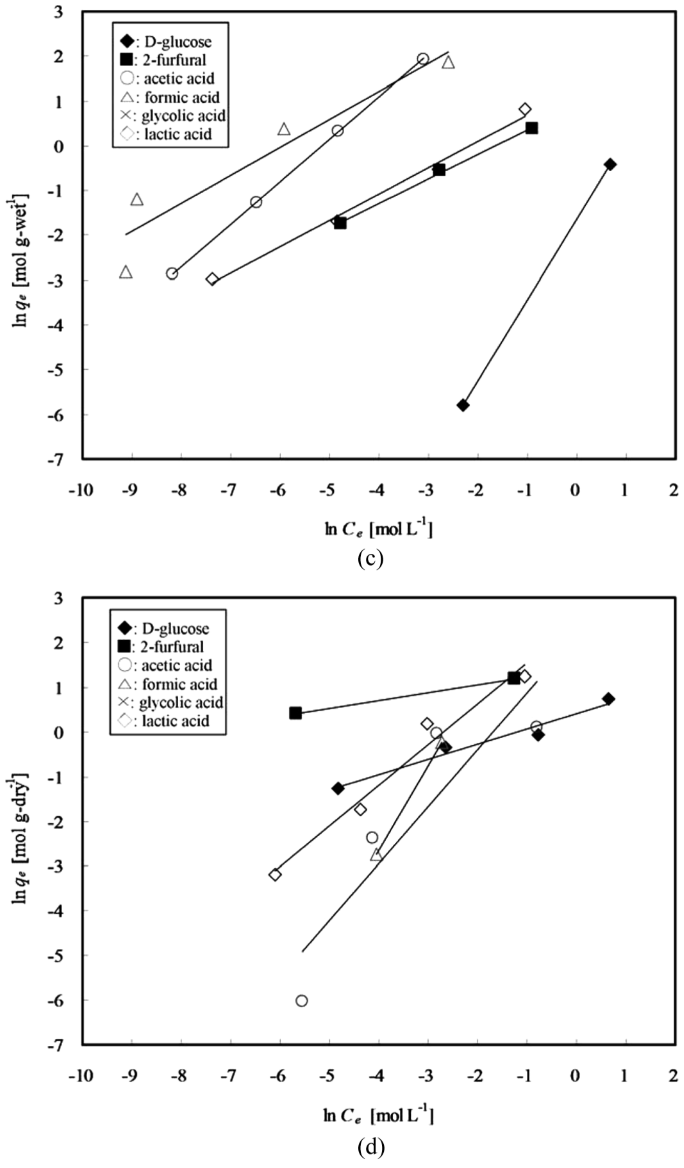


Figure 2. Adsorption isotherms for pure components (a) Cellufine A-200; (b) Cellufine A-800; (c) DIAION WA21J; (d) Activated carbon.



(c)

(d)

Figure 2. Continued.

Adsorption from the multi-components was conducted using activated carbon as a representative adsorbent. As a result, 2-furfural was fully adsorbed even though only about 15% of D-glucose and 28% of formic

Table 3. Parameter in Freundlich isotherms parameters for the adsorption of the single components

	K_F	n	R^2
Cellufine A-200			
D-glucose	0.52	0.76	0.960
2-furfral	1.72	1.06	1.000
formic acid	73.10	1.30	0.987
acetic acid	79.93	1.24	0.992
glycolic acid	64.28	1.31	0.990
lactic acid	3.82	1.79	0.901
Cellufine A-800			
D-glucose	0.51	0.95	0.979
2-furfural	4.31	1.99	0.943
formic acid	0.58	4.41	0.853
acetic acid	0.51	4.59	0.922
glycolic acid	0.69	3.70	0.868
lactic acid	5.85	1.15	0.999
DIAION WA21J			
D-glucose	0.19	0.56	1.000
2-furfral	2.43	1.84	0.998
formic acid	40.46	1.60	0.892
acetic acid	133.29	1.05	1.000
glycolic acid	–	–	–
lactic acid	3.58	1.70	0.991
Activated carbon			
D-glucose	1.51	2.95	0.958
2-furfural	4.04	5.68	1.000
formic acid	126.85	0.54	1.000
acetic acid	8.58	0.79	0.804
glycolic acid	–	–	–
lactic acid	11.56	1.10	0.971

acid were adsorbed. This agrees with the results obtained using pure components. Therefore, it is possible to estimate the adsorption results of the multi components solution by using the isotherms of pure components.

Subcritical Water Treatment of D-Glucose

D-glucose aqueous solution was treated using continuous flow reactor at the conditions of 220°C, 20 MPa, and the reaction time of 90 seconds. Organic acids and furans were produced from D-glucose. Table 4 shows the compositions of the main components produced from the decomposition of

Table 4. Composition and concentration of decomposed D-glucose aqueous solution

Substances	Composition [mol%]	Concentration [mol/L]	Substances	Composition [mol%]	Concentration [mol/L]
Monosaccharide	48.09	8.882×10^{-2}	D-glucose	44.09	8.143×10^{-2}
			D-fructose	4.002	7.392×10^{-3}
Furans & aldehydes	23.99	4.431×10^{-2}	2-furfural	2.528	4.669×10^{-3}
			5-HMF	14.41	2.662×10^{-2}
			glycolaldehyde	4.923	9.092×10^{-3}
			glyceraldehyde	2.126	3.928×10^{-3}
Organic acid	3.277	6.053×10^{-3}	formic acid	1.997	3.688×10^{-3}
			acetic acid	0.4335	8.008×10^{-4}
			lactic acid	0.1981	3.659×10^{-4}
			glycolic acid	0.6485	1.198×10^{-3}

D-glucose. About a half of D-glucose remained in the product solution and 23.99 mol% of furans and aldehydes, 4.00 mol% of D-fructose, and 3.28 mol% of organic acids were produced. Furans and aldehydes consist of 5-HMF, 2-furfural, glycolaldehyde, and glyceraldehyde. Formic acid, glycolic acid, acetic acid, and lactic acid are involved in organic acids. The concentrations of these components are also shown in Table 4.

Finally, the by-products produced in the conversion of D-glucose were separated from the treated D-glucose aqueous solution using different kinds of adsorbents.

The amounts of D-glucose and degradation product adsorbed on each adsorbent are shown in Fig. 3. The activated carbon adsorbed 2-furfural completely. However, the organic acids mostly remained in the solution. On the other hand, the organic acids were successfully removed from the solution with the adsorptions using Cellufine A-200 and DIAION WA21J. For DIAION WA21J, 2-furfural was also removed from the aqueous solution.

The organic acids were adsorbed by Cellufine A-200 and DIAION WA21J as observed for the adsorption of the single pure components. These adsorption behaviors can also be estimated from single component adsorption. From another point of view, Cellufine A-200 and DIAION WA21J are weak anion exchangers and therefore they were able to adsorb organic acids. DIAION WA21J also adsorbed 2-furfural. Activated carbon did not

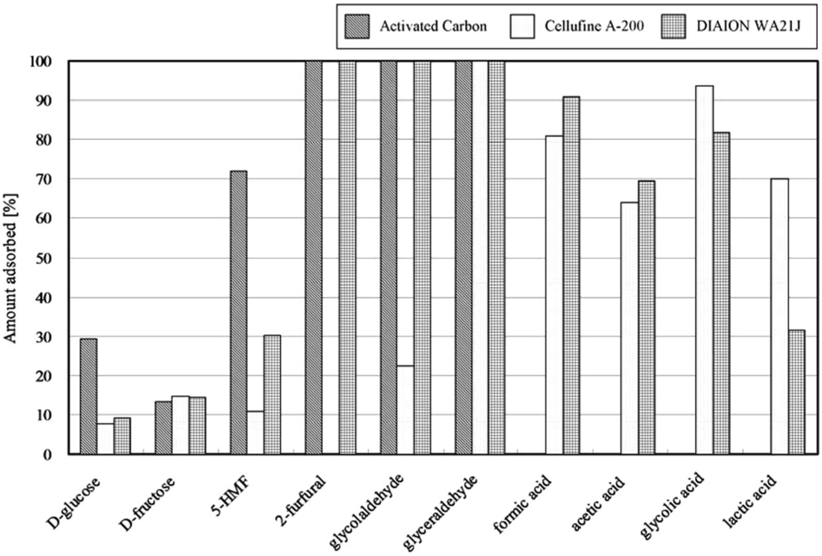


Figure 3. Adsorptions of products from treated D-glucose aqueous solution.

adsorb the organic acids because of its nonpolar surface and its pore size (17,18). The pore size of the activated carbon is relatively large compared to the other adsorbents, and therefore larger molecules such as the furans were preferably adsorbed but not smaller molecules of the organic acids.

CONCLUSIONS

Cellufine A-200, Cellufine A-800, DIAION WA21J, and activated carbon were used as the adsorbents in order to separate organic acids, furans, and aldehydes from the byproducts of D-glucose decomposition. The adsorptions of single molecular aqueous solution were conducted using four different types of adsorbents. These adsorption equilibria were correlated by the isotherm of Freundlich type and evaluated their adsorption behaviors. Formic acid and glycolic acid were well removed from the aqueous solution with Cellufine A-200. Cellufine A-200, Cellufine A-800, and DIAION WA21J hardly adsorbed D-glucose, therefore these adsorbents selectively separate the by-products. Activated carbon behaved as a good adsorbent for 2-furfural which was adsorbed almost entirely. Finally the adsorptions were carried out using treated D-glucose aqueous solution by subcritical water. Activated carbon selectively adsorbed furans without adsorbing the organic acids. On the other hand, Cellufine A-200 adsorbed the organic acids quite well but not furans. DIAION WA21J worked as a favorable adsorbent such that both furans and organic acids were adsorbed. However, a relatively small amount of D-glucose was adsorbed in each adsorbent. Moreover, adsorbent regeneration of the weak anion exchanger is important for scaling up and is relatively easily done using NaOH and NaCl.

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