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Short communication

Sorption of cellooligosaccharides to activated clay in sulfuric acid solution

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ARTICLE INFO

Article history:
Received 22 October 2008
Received in revised form
12 November 2008
Accepted 23 December 2008
Published online 31 January 2009

Keywords:
Activated clay
Cellooligomer
Desorption
Glucose
Hydrolysis
Sorption
Sulfuric acid

ABSTRACT

This paper discusses the sorption of cellooligosaccharides to activated clay in concentrated sulfuric acid solution. Cellobiose was sorbed to the clay in 72% (w/w) sulfuric acid but not in water; the sorption of glucose was not observed in both solutions. Hydrolysate of filter paper cellulose after 72% sulfuric acid treatment was also sorbed to the clay, and the sorbed sugars were partly released by diluting the mixture. The sorbed sugars could also be recovered in the form of D-glucose after hot dilute acid treatment of the sugar-acid-clay suspension.

1. Introduction

Cellulose, a polymer of β-1,4-linked D-glucose residues, is the main component of plant cell wall biomass. Since cellulosic materials represent the most abundant global source of biomass, it has been suggested as an alternative source, to starch/sucrose, of fermentable hexoses, without competing with food/feed industries [1,2]. No facile saccharification systems of cellulose, however, have been established mainly because its tightly-packed crystalline structure hinders efficient hydrolysis by most catalysts [3].

Concentrated sulfuric acid solution is among the exceptional chemical catalysts which can readily break crystalline cellulose structures by disrupting the hydrogen bonding between cellulose chains and efficiently and quantitatively liberate cellulose hydrolysate. In fact, the monosaccharide composition of lignocellulosic biomass is determined by means of the sulfuric acid hydrolysis [4,5]. Presently, extensive research on the sulfuric acid treatment of biomass for bio-fuel production has been reported [6]. Sulfuric acid can be used to hydrolyze the polysaccharides into their monomers for further application (e.g. fermentation) [7,8], or as a catalyst to reduce the recalcitrance of lignocellulosic biomass to enzymatic hydrolysis [9].

However, without a practical means of sugar–acid separation and recovery, the concentrated sulfuric acid hydrolysis

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doi:10.1016/j.biombioe.2008.12.005

process is generally considered costly and uneconomical, and thus not feasible for commercial D-glucose production [10–12]. Although progress has been made in the development of the separation systems such as membrane separation and simulated-moving-bed chromatography systems, further technological breakthroughs are needed in order to reduce the separation cost.

Activated clay is an inorganic particle, generally prepared from smectitic clays or bentonites via treatment with hot sulfuric acid or hydrochloric acid for partial removal of metal ions [13]. It has been used as a catalyst or sorbent in such fields as the petrochemical and food industries. In this paper, the sorption/desorption of cellobiose (CAS 16462-44-5), cellopentaose (CAS 2240-27-9), D-glucose as well as sulfuric acid hydrolysate of cellulose on the activated clay was investigated.

2. Methods

2.1. Binding isotherm

Cellobiose, cellopentaose or D-glucose at various concentrations was dissolved in 0.5 mL of either 72% (w/w) sulfuric acid solution or distilled water at room temperature. The solutions were transferred to 1.5-mL plastic tubes containing 20 mg of activated clay (Wako Pure Chemical Industries Ltd., Osaka, Japan) and mixed with a vortex mixer. After settling for 15 min at room temperature, the mixtures were centrifuged at 23,600 × *g* for 3 min, the supernatants were retrieved and diluted 8-fold with distilled water. The diluted supernatants were hydrolyzed at 100 °C for 1 h and neutralized with 1 mol L^{-1} sodium hydroxide solution. The amount of D-glucose in the solutions was determined using a glucose assay kit (Glucose-C-II, Wako Pure Chemical Industries Ltd. Osaka, Japan). The difference between the amount of free sugar in the solutions and total sugar was regarded as the amount sorbed to the clay.

The binding isotherms were drawn by curve-fitting with a non-linear regression of a one-site binding model using GraphPad Prism version 3.00 for Windows (GraphPad Software, San Diego, CA, USA).

2.2. Sorption of cellulose hydrolysate

Sixty milligrams of filter paper flakes (Cellulose Powder C, Toyo Roshi Co., Ltd., Tokyo, Japan) were mixed with 2 mL of 72% sulfuric acid by grinding with a pestle periodically in a mortar at room temperature. After 1 h hydrolysis, the mixture was transferred to a 15-mL plastic test tube. The mortar and pestle were washed with 10 mL of 72% sulfuric acid, and the wash water was added to the test tube. Aliquots of the solution were diluted with distilled water to sulfuric acid concentrations of 12, 24, 36, 48 and 60%. One milliliter of each dilution was mixed with 50 mg of activated clay in a 1.5-mL plastic tube. The tubes were allowed to settle at room temperature for 1 h and centrifuged at 23,600 × *g* for 3 min; the supernatants were retrieved and diluted with distilled water to a sulfuric acid concentration of 9%. The diluted solutions were further hydrolyzed at 100 °C for 1 h and neutralized with the sodium hydroxide solution. The amount of D-glucose in the solutions was determined using the glucose assay kit. Sugar bound to the clay was calculated by subtracting the amount of free sugar from the total sugar.

2.3. Desorption of cellulose hydrolysate

Twenty-five milligrams of filter paper flakes was hydrolyzed with 1 mL of 72% sulfuric acid under the same conditions stated in Section 2.2. After hydrolysis for 1-h, 0.5 mL of the solution with viscous and transparent hydrolysate of cellulose was transferred to a 15-mL plastic test tube containing 2 mL of 72% sulfuric acid for dilution. In another 15-mL tube, 150 mg of activated clay and 1 mL of the above diluted hydrolysate-acid solution were fully mixed and then settled for 1 h at room temperature. The suspension was further mixed with 7 mL of distilled water and incubated at 90 °C; an aliquot of 0.15 mL from the suspension was sampled to a 1.5-mL tube every 30 min during the incubation. The samples were then centrifuged, and the supernates were hydrolyzed at 100 °C for 1 h; the D-glucose content was determined after neutralization (see Sections 2.1 and 2).

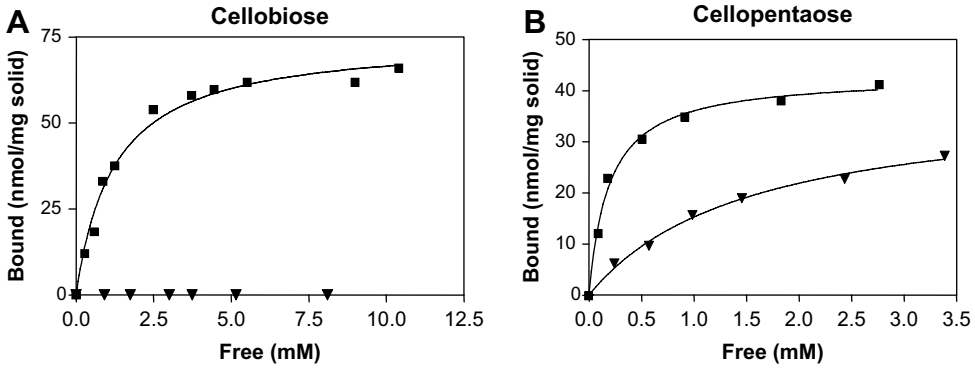

Fig. 1 – Binding isotherm of cellobiose (A) and cellopentaose (B) to active clay. Squares denote cellooligosaccharides in 72% (w/w) sulfuric acid; triangles indicate those in water.