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Physicochemical characterization of novel Schiff bases derived from developed bacterial cellulose 2,3-dialdehyde

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ABSTRACT

The synthesis of two novel Schiff's bases (cellulose-2,3-bis-[(4-methylene-amino)-benzene-sulfonamide] (**5**) & cellulose-2,3-bis-[(4-methylene-amino)-*N*-(thiazol-2-yl)-benzenesulfonamide] (**6**) via condensation reactions of periodate oxidized developed bacterial cellulose ODBC (**2**) with sulfa drugs [sulfanilamide (**3**) & sulfathiazole (**4**)] was reported. The physicochemical characterization of the condensation products was performed using FTIR, ^{1}H NMR, ^{13}C NMR spectral analyses, X-ray diffraction and DTA. The ODBC exhibited the highest degree of oxidation based on the aldehyde group number percentage (82.9%), which confirms the highest reactivity of developed bacterial cellulose [DBC (**1**)]. The X-ray diffractograms indicated an increase in the interplanar distance of the cellulose Schiff base (**6**) compared to ODBC (**2**) due to sulfathiazole (**4**) inclusion between ODBC (**2**) sheets corresponding to the $(1\bar{1}0)$ plane. In addition, the aldehyde content of Schiff base (**6**) was (20.8%) much lower than that of Schiff base (**5**) (41.5%). These results confirmed the high affinity of sulfathiazole (**4**) to the ODBC (**2**) chain, and the substantial changes in the original properties of ODBC were due to these chemical modifications rather than the sulfanilamide (**3**).

1. Introduction

Bacterial cellulose (BC) and its developed form (DBC) have potential application in a wide variety of industrial fields (Keshk, 2014; Keshk & Haijia, 2011; Kucharzewski, Slezak, & Franek, 2003; Klemm, Schumann, Udhardt, & Marsch, 2001; Fontana et al., 1990). DBC has been prepared in denser and less ductile forms with a particle size of 1–5 μm (Keshk & Haijia, 2011). DBC exhibited a lower density value compared to that of commercial cellulose (Avicel PH 101 & 102). Both DBC and Avicel PH 101 exhibited similar behaviour during flow and binding processes. In addition, the weight loss of DBC occurred during a one-step degradation process from approximately 320 °C to 380 °C (Keshk & Haijia, 2011). To improve the functionality of BC without employing any extraneous cross-linking agents, the reactivity of BC must be increased by molecular modifications (Hutchens, Benson, Evans, Rawn, & O'Neill, 2009; Fang, Wan, Tang, Gao, & Dai, 2009; Keshk, 2008; Helenius et al., 2006; Keshk & Nada, 2003; Bielecki, Krystoynowicz, Turkiewicz, & Kalinowska, 2001). Periodate oxidation has been industrially utilized for di-aldehyde production of starch and cellulose (Veelaert, de Wit, Gotlied, & Verhe, 1997; Hutchens et al., 2009). Periodate oxidation is an extremely specific reaction to transform vicinal di-hydroxyl (glycol) groups to paired aldehyde groups without significant side products. In addition, this reaction is extensively used for the structural investigation of carbohydrates (Uraz & Guner, 1997). In the periodate oxidation method, a large number of aldehyde groups are introduced into polysaccharides, which can be further converted to Schiff bases with primary amines (Kim, Kuga, Wada, Okano, & Kondo, 2000). Schiff bases make the di-aldehyde cellulose a valuable intermediate for cellulose-based functional materials, such as adsorbents for heavy metals and drug carriers as well as in the separation and analysis of proteins (Kim & Kuga, 2001). This study describes the synthesis of two novel Schiff's bases via condensation reactions of periodate oxidized developed bacterial cellulose (ODBC) with sulfa drugs (i.e. sulfanilamide and sulfathiazole). The reactivity of ODBC towards sulfa drugs was also investigated via aldehyde content determination. The physicochemical characterization of ODBC and its Schiff bases was performed using FT-IR, ^{1}H and ^{13}C NMR analyses, X-ray diffraction and DTA.

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2. Materials and methods

Sigma-Aldrich supplied all of the chemicals. All of the experiments were conducted at ambient temperature. The *Gluconacetobacter xylinus* ATCC 10245 was supplied by the American Type Culture Collection (ATCC).

2.1. Preparation of developed bacterial cellulose

The developed bacterial cellulose (DBC) was obtained from the hydrolysis of bacterial cellulose using hydrochloric acid according to a protocol reported by Keshk and Haijia (2011).

2.2. Preparation of cellulose 2, 3-dialdhyde

DBC (0.5 g, 0.003 mol) was suspended in 50 ml of distilled water for 1 h, and then, potassium periodate (1.4 g, 0.006 mol) was added gradually. The mixture was heated to 55 °C for 2 h. After heating, the mixture was maintained at room temperature for 48 h. The product (ODBC) was filtered and washed well with distilled water (Scheme 1).

2.3. Preparation of Schiff bases

To a mixture of ODBC (0.35 g, 0.002 mol) in absolute ethanol (20 ml), either sulfanilamide (**3**) (0.68 g, 0.004 mol) or sulfathiazole (**4**) (1.02 g, 0.004 mol) was added. The reaction mixture was heated under reflux for 48 h. The yellow products (i.e., cellulose-2,3-bis-[(4-methylene-amino)-benzenesulfonamide] (**5,** 52% Yield) and cellulose-2,3-bis[(4-methylene-amino)-*N*-(thiazol-2-yl)-benzenesulfonamide] (**6**, 85% Yield) were washed with water and hot ethanol.

2.4. Determination of aldehyde content

The degree of oxidation of DBC was evaluated by determining the aldehyde content (Li, Wu, Mu, & Lin, 2011; Kim et al., 2000; Veelaert et al., 1997). ODBC was converted to the oxime by a Schiff base reaction with hydroxylamine hydrochloride. ODBC (0.15 g) was dissolved in 25 ml of distilled water. The pH was adjusted to a pH value of 5 using 1.0 M sodium hydroxide. Then, 20 ml of 0.72 mol/l hydroxylamine hydrochloride at a pH of 5 was added to the ODBC solution. The mixture was stirred for 12 h in a water bath at 40 °C followed by titration of the released hydrochloric acid with 1.0 M NaOH. The endpoint was determined by matching the colour of the sample solution with that of a blank. Here, the consumption of NaOH solution was recorded as V_C in ml. A DBC solution with the same concentration at a pH of 5 was used as a blank, and its consumption of the alkali solution in ml was recorded as V_b. Therefore, the aldehyde content %(AC) in ODBC was calculated using the following equation:

$$AC\% = \frac{M_{NaOH}(V_C - V_b)160}{m} \times 0.1 \quad (1)$$

where M_{NaOH} = 1.0 mol/l, m is the dry weight (g) of ODBC, and 160 is the molecular weight of ODBC. The aldehyde content in the prepared Schiff bases (**5** and **6**) was determined in a similar way as that in ODBC except that 0.1 mol/l NaOH was used. The blank was treated using the same weight of Schiff base (**5**) or (**6**) in the absence of hydroxylamine hydrochloride to omit any reaction between the sulfonamido group and NaOH under the same conditions.

2.5. FT-IR spectroscopy

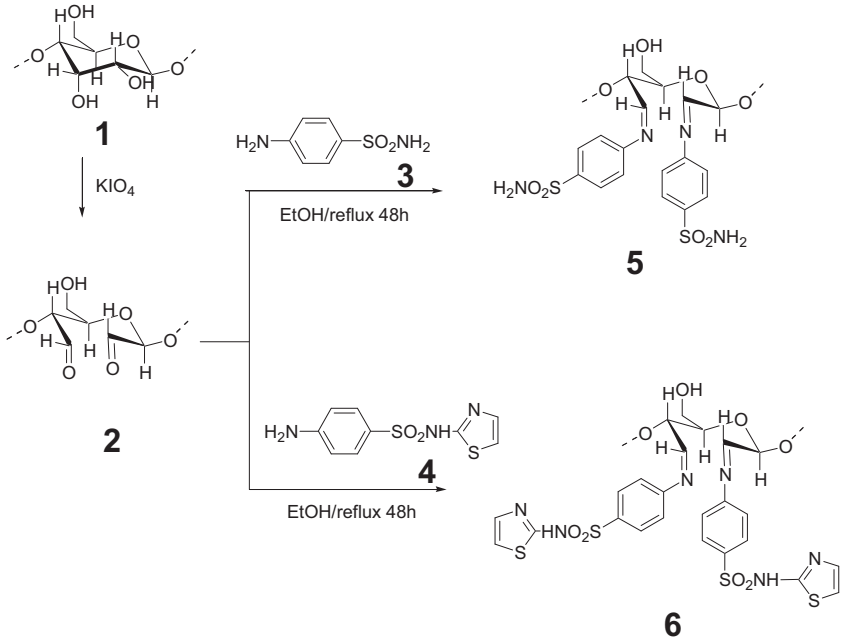
FT-IR spectroscopy (Bruker IFS 66) was performed according to protocols reported by Abbott, Palmer, Gordon and Bagby (1988).

2.6. X-ray diffraction

The X-ray diffraction patterns of DBC, ODBC and their Schiff base derivatives were determined on a Shimadzu-Lab-XRD-6000 diffractometer using Nickel-filtered Cu*K*α radiation at 40 kV and 50 mA.

2.7. Determination of crystallinity index

The crystallinity was calculated from the diffracted intensity data using the method reported by Segal, Creely, Martin, and



Scheme 1. Synthetic route of cellulose Schiff bases **5** and **6**.