



A green approach toward synthesis of large-surface ligands based on cellulose extracted from plant

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Abstract

An original approach for preparing bio-polymer ligands was developed. Two novel bio-polymer ligands were synthesized via oxidation of cellulose extracted (DAC) from safflower plant. Extracted cellulose polymer was crosslinked and periodate oxidized following to preparation of poly-carboxylic acid and Schiff base ligands using sodium chlorite and ethylene diamine, respectively. The physicochemical characterization of the condensation products was performed using Fourier transform infrared (FTIR) spectra. The index bonds of carboxylated and Schiff based cellulose were appeared at about 1731 cm^{-1} and 1649 cm^{-1} , respectively. The cross sectional view of the crosslinked and uncrosslinked products, as absorbed by SEM, showed prous and fibrillose structure for the crosslinked units.

Keywords: bio-polymer cellulose, cellulose dialdehyde, carboxylation, Schiff base, large-surface ligand.

1. Introduction

Cellulose is recognized as the most widespread biomass in nature which has got great attention more because of its carbon-neutral renewability and fascinating physicochemical properties [1, 2]. It can be easily derived from cellulose sources such as water plants, grasses, and other plant substances [3-5] and can be used for hydrogenation [6], reduction [7], oxidation [8] and other catalytic applications. Number of studies on improving mechanical, physical, catalytic and adsorption properties of the cellulose have been reported by blending and incorporating of metal/oxide nanoparticles in cellulose polymer chains [9-11]. Inter-molecular hydrogen bonds and network structure of cellulose usually plays a supporting surface role in composite material and influences the surface structure of composite materials [12]. The aim of the study was to prepare the large-surface bio-polymer ligands the removal applications of heavy metal ions from environmental water samples. Extracted cellulose polymer was crosslinked and periodate oxidized and then poly-carboxylic acid and Schiff base ligands were prepared using sodium chlorite and ethylene diamine, respectively (Figure 1).

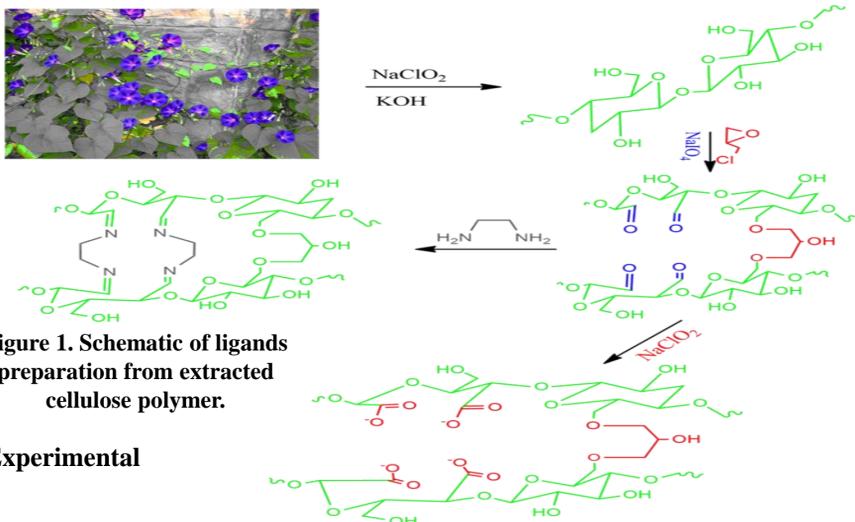


Figure 1. Schematic of ligands preparation from extracted cellulose polymer.

2. Experimental

2.1. Crosslinking of extracted cellulose

Extraction of cellulose from powdered dry stems of *morning glory* (*Ipomoea tricolor*) followed by our previous work [5]. Extracted cellulose (10 g) was first dispersed in water (200 ml) under sonication and continuously stirring (at room temperature for 30 min). The reaction was followed by adding an aqueous solution of NaOH (22%, 50 ml) into the mixture. After mixing of the reaction (at 50 °C for 2.5 h), epichlorohydrin (40 g) and ammonium hydroxide (45 g, 25% solution) were added and the reaction mixture refluxed (at 55 °C for 4.5 h). The product was washed three times with ethanol and water and dried (at 60 °C for 15 h) [13].

2.2. Preparation of crosslinked cellulose Schiff base

The crosslinked cellulose (CC) (8.5 g) immersed into the water (200 ml) and sonicated (for 30 min). The compound was oxidized with NaIO_4 (10 g) in dark area. The reaction mixture was stirred for 24 h (at 45 °C), oxidation was stopped by adding of glycerin (20 g) followed by filtering and washing of the crosslinked aldehyde cellulose (C-AC) with ethanol and water and vacuum dried (at room temperature for 24 h). The C-AC (1.5 g) was refluxed with ethylene diamine (20 ml) overnight. The product was filtrated and washed with toluene and freeze dried (at -50 °C for 24 h) [14].

2.3. Preparation of crosslinked cellulose Schiff base

The crosslinked cellulose (CC) (8.5 g) immersed into the water (200 ml) and sonicated (for 30 min). The compound was oxidized with NaIO_4 (10 g) in dark area. The for 24 h (at 45 °C), oxidation was stopped by adding of glycerin (20 g) followed by filtering reaction mixture was stirred g and washing of the crosslinked aldehyde cellulose (C-AC) with ethanol and water and vacuum dried (at room temperature for 24 h).

The C-AC (1.5 g) was refluxed with ethylene diamine (20 ml) overnight. The product was filtrated and washed with toluene and freeze dried (at -50 °C for 24 h) [14].

2.4. Preparation of crosslinked cellulose carboxylic acid

The dark brown colored of C-AC powder (1.5 g) was dispersed in acetic acid solution (100 ml, 1 M) followed by addition of NaClO_2 (1.5 g) and stirred at room temperature (for overnight). The oxidized product (CC-AC) was centrifuged and freeze dried (at -50 °C for 24 h).

3. Results and Discussion

Figure 2 presents the FTIR spectra of the CC, C-AC, CC-AC and Schiff based product by ethylene diamine (Et-Sch). In comparison to the CC, the characteristic peak of the C-AC at 1727 cm^{-1} appeared due to the carbonyl groups caused by NaIO_4 oxidation. The absorption peak of the Et-Sch at 1593 cm^{-1} indicated that Schiff-base structure (C=N double bond) was formed through the reaction between the aldehyde groups of C-AC and the amino groups of ethylene diamine. For the sample of CC-AC a sharp absorption at 1731 cm^{-1} is attributed to carbonyl groups in the free COOH group, whereas the large and sharp absorption at 1624 cm^{-1} is due to carboxylate groups in their sodium salt forms [15].

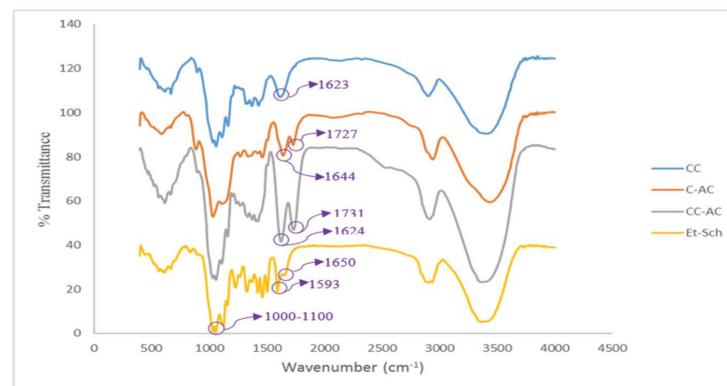


Figure 2. FTIR analysis of the products.

Microstructure and surface morphology of the synthesized products surface was investigated from SEM images. As shown in Figure 3a, cellulose exhibits a rough surface and arranged chains due to the strong intra-molecular hydrogen bonding. CC has a rough surface with sheet-like morphology (Figure 3b). Such surface morphology results from the proximity of different cellulose chains after cross-linking. However, the relatively smooth and porous surface was displayed by CC-AC (Figure 3c) and Et-Sch (Figure 3d), respectively, in comparison with the CC fibers (Figure 3b). A significant change in the morphology of the Et-Sch reveals that greater reactivity of C-AC towards condensation reaction with ethylenediamine forming tetraaza macrocyclic Schiff base crosslinked cellulose ligand [16].

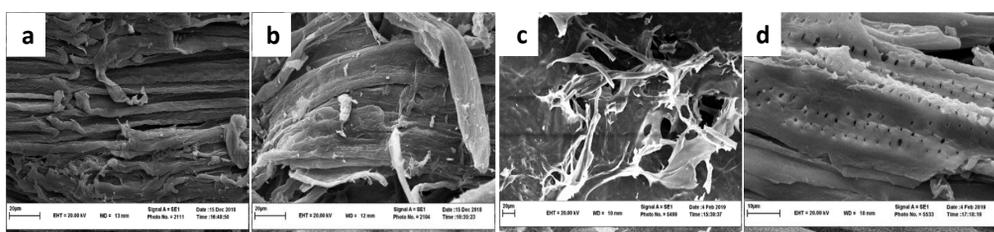


Figure 3. SEM Images of (a) extracted cellulose, (b) CC, (c) CC-AC and (d) Et-Sch.

4. Conclusion

Cellulose polymer (from morning glory) and its ligand derivatives (CC-AC and Et-Sch) were green synthesized by one-step reactions, which included continuous NaIO_4 oxidation, ethylene diamine grafting and further oxidation of C-AC. According to the SEM and FTIR analysis, the ligands have been synthesized successfully. Due to the presence of carboxyl groups, as shown in Figure 2, the CC-AC ligand can be easily dispersible which facilitates aqueous processing for dye and metal absorptions. The formation of tetraaza macrocyclic Schiff base in the polymer sheets (Figure 3d), makes it applicable in metal and dye absorptions.