



## Short Communication

The structure characterization of cellulose xanthogenate derived from the straw of *Eichhornia crassipes*Wenbing Zhou<sup>a</sup>, Duanwei Zhu<sup>a,\*</sup>, Alan Langdon<sup>b</sup>, Lisa Li<sup>b</sup>, Shuijiao Liao<sup>a</sup>, Liangfeng Tan<sup>a</sup><sup>a</sup>Laboratory of Plant Nutrition and Ecological Environment Research, Microelement Research Center of Huazhong Agricultural University, Key Laboratory of Subtropical Agriculture and Environment, Ministry of Agriculture, Wuhan 430070, China<sup>b</sup>Department of Engineering, University of Waikato, Private Bag 3105, Hamilton, New Zealand

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## ABSTRACT

Alkali-treated straw and cellulose xanthogenate were derived from shoot and root biomass of *Eichhornia crassipes* by treatment with NaOH and CS<sub>2</sub>, respectively. The structures of the raw and modified plant materials were characterized by XRD, TGA/DTA, and FTIR. Alkali treatment increased the crystallinity of raw plant material, while the subsequent CS<sub>2</sub> treatment had the reverse effect. The thermal stability of the plant material was diminished by alkali treatment but was restored by subsequent CS<sub>2</sub> treatment. Alkali treatment removed most of the lignin and hemicellulose from the raw plant material, whereas the formation of cellulose xanthogenate introduced new C=S and O-CS-S functional groups.

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## 1. Introduction

The rapid growth rate of the invasive species, *Eichhornia crassipes* (*E. crassipes*), has caused problems in lakes and rivers throughout the world. It is one of the most efficient plant absorbers of nutrients and pollutants from natural and waste waters (Maine et al., 2006; Malik, 2007). It is possible that the harvested biomass of *E. crassipes* might be used to reduce nutrient enrichment and so prevent further invasions. Traditional use of *E. crassipes* biomass has been limited to silage, organic compost, or biogas (Malik, 2007; Zhou et al., 2007). In this study we extended our previous work by focusing on structural characterization of the natural and modified straw of *E. crassipes* and its usefulness as a metal adsorbent (Tan et al., 2008).

In the present study, raw, dried *E. crassipes* material was treated with alkali and converted to cellulose xanthogenate with CS<sub>2</sub>. The effects of these treatments on the crystallinity, thermal stability, and infrared spectroscopic characteristics were then investigated. The results have relevance to large scale harvesting, chemical modification, and utilization of *E. crassipes* biomass as cellulose based adsorbent for water remediation and other purposes.

## 2. Methods

## 2.1. Preparation of raw plant material and composition analysis

Plant samples of *E. crassipes* were collected from Lake Yezihu (E114°23', N30°33') in Wuchang, Wuhan City of China. The shoot and root biomass were separated, using the method of Tan et al. (2008), and kept desiccated at 25 °C.

The benzene and ethanol extracts, cellulose, hemicellulose, lignin, water, and ash were determined according to the National Standard Analysis of China (GB 2677).

## 2.2. Preparation of cellulose xanthogenate

Details of the optimization preparation of cellulose xanthogenate were given in Tan et al. (2008). Plant materials were coded as follows: shoot of *E. crassipes*, 'WH-SL-7'; root of *E. crassipes*, 'WH-R-8'; their corresponding alkali-treated straw, 'WH-SL-14' and 'WH-R-15'; and cellulose xanthogenate, 'WH-SL-21' and 'WH-R-22'.

## 2.3. Characterization of structure of plant materials

## 2.3.1. Pre-treatment of plant materials

Plant materials were oven dried at 100 °C for 24 h, ground to a fine powder in a grinding machine, passed through a 100 mesh sieve and stored in a desiccator.

\* Corresponding author. Tel.: +86 27 87287184; fax: +86 27 87397735.  
E-mail address: [zhudw@mail.hzau.edu.cn](mailto:zhudw@mail.hzau.edu.cn) (D. Zhu).

### 2.3.2. X-ray diffractometry

The diffractograms were recorded at room temperature with a D/max-RA diffractometer using Ni-filtered Cu  $\alpha$  radiation ( $\lambda = 1.54 \text{ \AA}$ ). The operating voltage and current were 40 kV and 40 mA, respectively. The samples were mounted on a carrier for specimen spinning, with a rotational speed of 30 rpm. Data were also collected ( $0.02^\circ 2\theta$  intervals) using a Philips X'PERT System over the scan range of  $12\text{--}26^\circ 2\theta$ .

### 2.3.3. TGA/DTA experiments

Thermal analysis was performed using thermogravimetric analysis (TGA) and differential thermal analysis (DTA) on a simultaneous thermal analyzer (SDT 2960, TA Instrument). The apparatus was continually flushed with air ( $150 \text{ mL min}^{-1}$ ). Samples weighed between 9 and 12 mg and were heated from room temperature to  $600^\circ\text{C}$  at a rate of  $20^\circ\text{C min}^{-1}$ .

### 2.3.4. FTIR spectroscopy

FTIR spectra were obtained with a FTS-40, USA FTIR spectrophotometer using KBr discs containing 2.5% finely ground sample. They were recorded in the absorption mode in the range  $4000\text{--}400 \text{ cm}^{-1}$  with an accumulation of 32 scans and a resolution of  $2 \text{ cm}^{-1}$ .

## 3. Results and discussion

### 3.1. Composition of shoot and root of *E. crassipes*

The compositions of the shoot and root components of *E. crassipes* are summarized in Table 1. Hemicellulose content of shoot is higher than that of the root, whereas the lignin and ash content of root are higher than that of shoot. There were no major differences in the percentages of cellulose and benzene–ethanol extracts of the two components of *E. crassipes*.

### 3.2. Crystallinity

The intensity of the peak between  $22^\circ$  and  $23^\circ$  for native cellulose is considered to represent the crystalline material in cellulose, and the intensity between  $18^\circ$  and  $19^\circ$  represents the background due to amorphous material in cellulose. These two intensities can often be used to calculate a crystallinity index (CrI) of the fiber (Reddy and Yang, 2005). Due to the complexity of the composition of shoot and root of *E. crassipes*, there were no obvious peaks between  $22^\circ$  and  $23^\circ$  for these plant materials (raw material, alkali-treated straw, and cellulose xanthogenate), but the relative intensities of the broad peaks at about  $21^\circ$  gave some information about relative crystallinity after the various treatments.

The results showed that the crystallinity was lowest for the raw shoot and root, intermediate for the cellulose xanthogenates and highest for the alkali-treated straw. Because alkali selectively dissolves or degrades lignin, hemicellulose, pectin, etc., and has little effect on the cellulose, increased relative cellulose content caused by alkali treatment is likely. Alkali treatment may also facilitate restructuring of the amorphous cellulose into crystalline cellulose. With the introduction of  $\text{CS}_2$  groups to form cellulose xanthogenate, plane orientations may be disrupted causing decreased crystallinity.

### 3.3. TGA/DTA analysis

Data for the thermal decomposition of the various materials derived from *E. crassipes* are given in Fig. 1. From Fig. 1A and B, it can be seen that the thermal profile of *E. crassipes* shoot can be divided into 3 stages. The first stage below  $260^\circ\text{C}$ , is the loss of adsorbed water and some dewatering of the cellulose structural units. The second stage between  $260$  and  $400^\circ\text{C}$  is likely to be the thermal decomposition of hemicellulose and cellulose  $\beta$ -(1 $\rightarrow$ 4)-glycosidic linkages. The third stage above  $400^\circ\text{C}$ , is likely to involve the decomposition of remaining cellulose and lignin. The main weight loss took place in the second stage.

In Fig. 1A, the residual weight percentage of 'WH-SL-7' was 19.6%, while those of 'WH-SL-14' and 'WH-SL-21' were 13.4% and 21.9%, respectively. These results indicate that mineral was extracted from shoot material by alkali treatment ('WH-SL-14' low) and replaced by Mg in the xanthogenate ('WH-SL-21').

There are no apparent differences in the weight loss curves of shoot materials below  $260^\circ\text{C}$ , but there may be differences in the differential thermal curves of these materials over the same temperature interval (Fig. 1A and B). The differential temperature value ( $\Delta T$ ) of alkali-treated straw, 'WH-SL-14', is the lowest over the range  $50\text{--}250^\circ\text{C}$  (largest negative value). This is the temperature range over which the endothermic loss of water can be expected. Apparently the water is held more strongly to the alkali-treated material. This is in accordance with the higher crystallinity of 'WH-SL-14' as discussed in Section 3.2.

The exothermic peaks of the shoot samples in the second and the third stages are quite different. The hemicellulose and cellulose exothermic peak of 'WH-SL-7' occurs at about  $320^\circ\text{C}$ , while the residual lignin exothermic peak occurs at about  $472^\circ\text{C}$ . Since alkali treatment selectively dissolves or degrades lignin, hemicellulose, pectin, etc., the content of lignin in 'WH-SL-14' is lower than that of 'WH-SL-7', and thus the residual cellulose of 'WH-SL-14', without the stabilizing lignin, will degrade at a lower temperature (about  $450^\circ\text{C}$ ). In the case of 'WH-SL-21', the incorporation of the  $\text{CS}_2$  appears to have compensated for the loss of lignin in that the decomposition temperatures of the native and  $\text{CS}_2$  modified materials are about the same (Fig. 1B).

The data for the root derived materials, Fig. 1C, indicate similar trends in thermal stability after alkali treatment and subsequent  $\text{CS}_2$  treatment. Because the ash content of root of *E. crassipes* is higher than that of shoot (Table 1), the weight percentages of residual material at  $600^\circ\text{C}$  are higher for root than for shoot materials (Fig. 1A and C). It appears that alkali treatment had little effect on residual ash content, i.e., mineral components of root were not extracted by alkali treatment (whereas they were for the shoot). Chemical treatments of the root material had similar but more destabilizing effects than those observed for the shoot material. The exothermic peaks of 'WH-R-15' and 'WH-R-22' are less well differentiated than those of 'WH-SL-14' and 'WH-SL-21', the second exothermic peak of 'WH-R-15' is lowered by about  $50^\circ\text{C}$  to that of 'WH-SL-14', the second exothermic peak of 'WH-R-22' is also lowered to that of 'WH-SL-21', and there are no apparent differences in the two exothermic peaks of 'WH-R-8' and 'WH-SL-7' (see Fig. 1B and D).

**Table 1**  
Composition of shoot and root of *E. crassipes*.

Material	Water (%)	Benzene and ethanol extract (%)	Cellulose (%)	Lignin (%)	Hemi-cellulose (%)	Ash (%)
Shoot	$4.66 \pm 0.02$	$16.26 \pm 0.17$	$27.40 \pm 0.13$	$11.55 \pm 0.18$	$27.41 \pm 0.43$	$12.72 \pm 0.04$
Root	$5.18 \pm 0.12$	$12.49 \pm 0.06$	$31.34 \pm 0.42$	$16.46 \pm 0.23$	$12.89 \pm 0.11$	$21.65 \pm 0.12$

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