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Functional groups and morphological characteristics of sugarcane bagasse

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Bachelor of Science with Honours
(Chemistry Resource)
2014

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FUNCTIONAL GROUPS AND MORPHOLOGICAL CHARACTERISTIS OF SUGARCANE BAGASSE

HENG CHIE WEI

Project paper is submitted in partial fulfillment of the requirements the Degree of Bachelor of Science with Honours

(Resource Chemistry)

Faculty of Resource Science and Technology

UNIVERSITI MALAYSIA SARAWAK

2014

Acknowledgement

First of all, I would like to express my gratitude to my supervisor, Dr. Sim Siong Fong for guiding and provide a lot information to complete this research. All the experience and the knowledge that I had gained during the research are precious.

I would also to thank postgraduate seniors, Terri Zhuan Ean Lee and Nurul Aida Lu Mohd Irwan Lu giving me extra information about the conducting and working in the laboratory.

Indebt thanks goes to all laboratory assistants especially Encik Wahap and Encik Safri for his help and technical support. Much regard to my course mates for helping me in order to guidance and advice of my final year project.

Lastly, I deepest thanks to my family of their supporting and encouragement me throughout the year.

Declaration

I, Heng Chie Wei hereby declare that this thesis entitled “functional groups and morphological characteristics of sugarcane bagasse” is my own work and effort with the guidance of my supervisor, Dr. Sim Siong Fong, except acknowledge and referenced. No portion of this thesis has previously been submitted for any other university or institution of higher learning.

………………………………..

(Heng Chie Wei)

Program of Resource Chemistry

Faculty of Resource Science and Technology

Universiti Malaysia Sarawak

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List of Abbreviations

Citric Acid	CA
Degree Celcius	^{o}C
Fourier Transform Infrared	FTIR
Scanning Electron Microscopy	SEM
Sugarcane Bagasse	SB

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Abstract

Sugarcane bagasse is a residues of sugarcane and has unique properties that can act as biosorbent. In this project, sugarcane bagasse was modified to serve as biosorbent through chemical modification with citric acid. Sugarcane bagasse was washed and dried at an oven (105^{o}C).The samples was refluxed for one hour before treated with citric acid. The detailed study of functional group and morphology characteristic of raw sugarcane bagasse and the pre-treatments were showing by the Fourier Transform Infrared (FTIR) and Scanning Electron Microscopy (SEM). After treated the sugarcane bagasse it show the significant different of the intensity functional group and the morphology with the untreated sugarcane bagasse.

Keywords: sugarcane bagasse, citric acid, Fourier Transform Infrared, Scanning Electron Microscope

Abstrak

Hampas tebu adalah sisa tebu dan mempunyai ciri-ciri unik yang boleh bertindak sebagai biosorbent. Dalam projek ini, hampas tebu diubahsuai untuk menjadi biosorbent melalui pengubahsuaian kimia dengan asid sitrik. Hampas tebu telah dibasuh dan dikeringkan di dalam ketuhar (105^{o}C). Sampel telah direflukskan selama satu jam sebelum dirawat dengan asid sitrik. Kajian terperinci mengenai kumpulan berfungsi dan ciri morfologi hampas tebu mentah dan pra-rawatan telah ditunjukkan dengan FTIR dan SEM. Selepas ubahsuai hampas tebu menunjukkan perbezaan dengan sebelum diubahsuai.

Kata Kunci: hampas tebu, asid sitrik, Fourier Transform Infrared, Mikroskop Elektron Imbasan

Chapter 1: Introduction

Sugarcane bagasse is a natural lignocellulosic biomass composed primary of cellulose, hemicellulose and lignin. A huge amount of sugarcane residues are generated from alcohol and sugar industry. It has been widely used for variety application for example, sugarcane residues are burn to generate energy and it can be converted into biogas. Other applications of sugarcane bagasse are as sources of feed, pulp, cloth, paper and board. Recycling and reusing of sugarcane bagasse would reduce the issues of waste disposal and environmental pollution.

Sugarcane bagasse can be potentially used as biosorbent due to the presence of numerous phenolic and hydroxyl functional groups (Yeneneh *et al.*, 2011; Mandal & Chakrabarty, 2011; Pehlivan *et al.*, 2012). It has been widely used to removal heavy metals from waste water (Alomá *et al.*, 2012; Basso *et al.*, 2002; Garg *et al.*, 2007; Hoces *et al.*, 2011; Khoramzadeh *et al.*, 2013; Krishnani *et al.*, 2004; Lara *et al.*, 2010; Liu *et al.*, 2012; Pehlivan *et al.*, 2013; Pereira *et al.*, 2010; Santos *et al.*, 2010; Santos *et al.*, 2011; Sud *et al.*, 2008; Vinodhini & Das, 2009; Xing *et al.*, 2010), dye (Fiorentin *et al.*, 2010; Jiang *et al.*, 2012; Ong *et al.*, 2010; Ong *et al.*, 2013; Saad *et al.*, 2010; Silva *et al.*, 2011; Yu *et al.*, 2011; Yu *et al.*, 2012a; Yu *et al.*, 2012b) and gasoline (Brandão *et al.*, 2010). As a matter of fact, biomass has been known as potential biosorbent; various biomasses have been examined such as banana peel (Annadurai *et al.*, 2002), cattail root (Hu *et al.*, 2010), coriandrum sativum (Karunasagar *et al.*, 2005), grape stalk wastes (Villaescusa *et al.*, 2004), jute stick powder (Panda *et al.*, 2009), lalang (Imperata cylindrica) leaf powder (Hanafiah *et al.*, 2007), leaf powder (Ngah & Hanafiah, 2008a), neem bark (Bhattacharya *et al.*, 2006), neem leaf (Bhattacharyya & Sharma, 2004), maize leaf (Babarinde *et al.*, 2006), orange peel (Namasivayam *et al*., 1996; Annadurai *et al*., 2002), papaya wood (Saeed *et al*., 2005), peanut hull pellets (Johnson *et al*., 2002), rice husk (Han *et al*., 2008), rice husk ash (Bhattacharya *et al*., 2006), sago waste (Quek *et al*., 1998), saltbush (*Atriplex canescens*) leaves (Sawalha *et al*., 2006; Sawalha *et al*., 2007), sunflower stalk (Sun & Xu, 1997), teak leaf powder (King *et al*., 2006), tree fern (Ho & Wang, 2004; Ho *et al*., 2004; Ho, 2003) and other agricultural by-products. The major advantages of using the biomass as biosorbent are that they are cheap, renewable and available in abundance (Vaughan *et al*., 2001; Ngah & Hanafiah, 2008b).

The objectives of this study are to determine the functional group and morphological characteristics of citric acid treated and untreated of sugarcane bagasse to evaluate their potential as biosorbent.

Chapter 2: Literature Review

2.1 Sugarcane Bagasse

Sugarcane bagasse contains low density of fiber. Sugarcane bagasse, as other typical biomasses, contains cellulose and hemicellulose that are embedded within the lignin matrix as shown in Figure 2.1 (Ratanakhanokchai *et al*., 2013). Averagely, sugarcane bagasse contains 50 % of cellulose (polymer of six-carbon sugars), 27 % of polyose and 23 % of lignin with 3.5% fat, 2.4 % ash, 3.5 wax (Corrales *et al*., 2012; Karnitz *et al*., 2007; Sun *et al*., 2004).

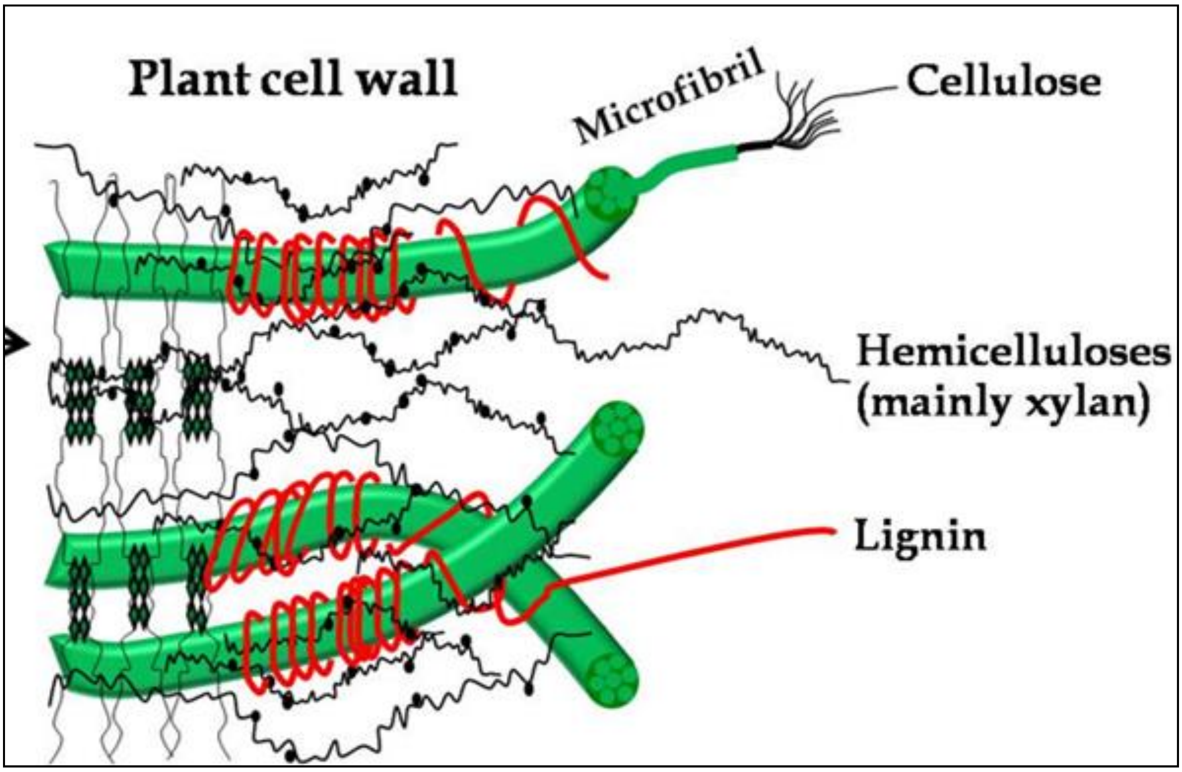

Figure 2.1: Structure of lignocellulose biomass (Ratanakhanokchai *et al*., 2013)

2.1.1 Cellulose

Cellulose is linear homopolysaccharide composed of β-D-glucopyranose units linked together with (1→4)-glycosidic bonds (Balat *et al*., 2008; Chen *et al*., 2011; Liu *et al*., 2008). According to Júnior *et al*. (2009), the cellulose molecular chains, formed by anhydroglucopyranose units, are joined through the β-(1→4) - glycosidic bonds. It also contains primary and secondary hydroxyl group (Júnior *et al*., 2009). According to Klemm *et al*. (2005), the intramolecular hydrogen bond between cellulose microfibril determines the straightness of the chain whereas the inter chain may influence the formation of crystalline or amorphous structure of cellulose.

The properties of cellulose are semi-crystalline, insoluble in water and organic solvent (Kumar *et al*., 2013), has low density, good mechanical properties and biodegradable (Zimmermann & Schwaller, 2005). Mosier *et al*. (2005) stated that, most of the cellulose are insoluble in water and cannot depolymerize due to the highly oriented crystalline structure. However, the cellulose can undergo hydrolysis broken into small units using sulfuric acid (Mosier *et al*., 2005). The hydrolysis will not remove lignin and hemicellulose completely so sodium chloride process is employed in addition to result in cellulose degradation (Saheb & Jog, 1999).

Anhydro-glucose unit of cellulose can undergo chemical reaction such as nitration, oxidation, acetylation and other (Orlando *et al*., 2002; Sun *et al*., 2004).

2.1.2 Polyose

The homopolymer such as xylan and heteropolymer such as glucomannans are the main chain of polyose (Júnior *et al*., 2009). Same with cellulose, it contains primary and secondary hydroxyl groups (Júnior *et al*., 2009). The elimination of xylan will cause the cellulose structure to be exposed (Guo *et al*., 2009).

2.1.3 Hemicellulose

The second abundant components of renewable biomass is the non-cellulosic heteropolysaccharides- hemicellulose. The basic units of carbohydrates such as arabinose, galactose, glucose, mannose and xylose formed the amorphous polymerized hemicellulose (Sun *et al*., 2003) and generally it is made up of compound of C5 and C6 (Corrales *et al*., 2012). Hemicellulose contains furfural, acetic acids, arabinose, glucuronic and xylose (Rezende *et al*., 2011). It contains reactive free hydroxyl groups in the basic units of carbohydrates (Gröndahl *et al*., 2003). Hemicellulose is linked to cellulose microfibril by hydrogen bonds (Mosier *et al*., 2005).

Pretreatment using dilute acid could convert hemicellulose into soluble sugar and to facilitate the enzymatic hydrolysis of cellulose (Balat *et al*., 2008; Keshwani & Cheng, 2009).

2.1.4 Lignin

Lignin is the highly branched and phenolic macromolecules, embedding cellulose and hemicellulose. It is formed from aromatic polymer of phenylpropane unit with β-*O*-4 aryl ether linkages (Liu *et al*., 2008). It is more persistent to enzyme degradation and its distribution determine the cell wall resistance to hydrolysis (Laser *et al*., 2002; Zhang & Lynd, 2004; Himmel *et al*., 2007).

Dehydrogenative polymerization of monolignols or phenylpropanoid units such as coniferyl alcohol, *p*- coumaryl alcohol and sinapyl alcohol form lignin (Ralph *et al.*, 1992; Sun *et al.*, 2003). The phenylpropanoid unit and hydroxyl phenolic group can be found in the lignin as complex polymer (Fengel & Wegener, 1983; Júnior *et al*., 2009).

The rate of delignification is influenced by the structure of lignin such as the ratio of guaocyl nuclei to syringyl nuclei and the number of ring conjugated carbonyl group (Gierer & Noren, 1982).

Karnitz *et al.* (2010) states that cellulose and polyses contains primary and secondary hydroxyl groups. Sugarcane bagasse contains hydroxyl group that can react with chemicals resulting in the surface modification. According to Karnitz *et al.* (2010), hydroxyl and phenolic group of lignin are more selective for Ca^{2+} and Mg^{2+} ion.

2.2 Biosorption

According to Santos *et al.* (2012), biosorption is the process where adsorbate example heavy metal are adsorbed using the agro-industry waste. Ngah and Hanafiah (2008b) states that, physical and chemical treatment could improve the adsorption ability of the adsorbent in removing heavy metals from the aqueous solution. Crini (2006) states that, this is also a method to remove suspended solids oil in solution, organic matter and odor. The biomasses are safe to use and eco-friendly (Arief *et al.*, 2008).

During adsorption, the complex formation and electrostatic interaction are formed between the metal ion and the functional groups present in the biomass (Alam & Ahmad, 2011). In removals of dye, Van der Waals force and electrostatic interaction are found via physical mechanisms. The chemical binding involving covalent and ionic interactions are generated between dye and sorbent (Won *et al.*, 2008). Other mechanisms of removal include ion exchange, complexation, covalent binding, and micro-precipitation (Rahmati *et al.*, 2011; Witek-Krowiak, 2012).

The functional groups for example phosphate, amino and carboxylate group of biomass are important for adsorption of metal ions (Santos *et al.*, 2010; Sen *et al.*, 2010). The biosorption efficiency can be enhanced by chemical modification of the biomass (Santos *et al.*, 2012).

Sugarcane bagasse has been employed to remove chromium in aqueous solution through the ion exchange and adsorption processes (Krishnani *et al.*, 2004; Sharma & Forster, 1994). Sugarcane bagasse has also been applied to remove nitrate via anion exchange mechanism (Orlando *et al*., 2002). More commonly, agricultural by-products is effective in removing heavy metals from the contaminated effluent (Reddad *et al*., 2003; Selvi *et al*., 2001).

2.3 Functional group properties of sugarcane bagasse

The main functional group that influences the adsorption of heavy metals are carboxyl, carboxylic anhydrides, phenols, lactones, lactols, carbonyls, quinones, and quinone-like structures (Boehm, 1994). The functional groups properties reported for sugarcane bagasse is summarized in Table 2.1.

For raw sugarcane bagasse, the carboxyl groups present are weak acid (Santos *et al*., 2012). In the moderately acid medium, carboxyl groups of raw bagasse generate negative charged sites (Santos *et al*., 2012). This cause interaction with positive charge.

Absorption band at 1600 cm^{-1}, 1509cm^{-1}, 1464cm^{-1} and 1422cm^{-1} are indicative of lignin (Sun *et al*., 2003). At 895 cm^{-1}, the band assigned to β-glycosidic linkages of cellulose after treatment of temperature 130 and 160 ^{o}C (Chen *et al*., 2011). According to Chen *et al*. (2011), the band is missing in raw sugarcane bagasse due to lignin and hemicellulose coverage. The functional groups observed after chemical treatment of sugarcane bagasse is shown in Table 2.2.

Table 2.1: The general functional group of raw sugarcane bagasse.

Wavenumber (cm^{-1})	**Functional group**
3600-3100	Free and intermolecular bonded hydroxyl group of cellulose (Mandal & Chakrabarty, 2011; Mothé & Miranda, 2009; Sadaf *et al.*, 2014; Sharma & Nandi 2013).
2921	C-H bond (Mothé & Miranda, 2009; Sadaf *et al.*, 2014; Sharma & Nandi 2013).
1721	Carbonyl group of hemicellulose (Mothé & Miranda, 2009)
1700	C=O stretching vibration (Sadaf *et al.*, 2014)
1631	C=C bond (Sharma & Nandi 2013)
1423	CH_3 (Sharma & Nandi 2013); Symmetric deformation of CH_2 group of cellulose (Mothé, & Miranda, 2009)
1243	C-O-C of cellulose (Mothé & Miranda, 2009)
1160	C- N bond(Sharma & Nandi 2013)
1155	C-O-C asymmetric deformation of hemicellulose and cellulose (Mothé & Miranda, 2009)
1048	C- O bond due to alcohols and carboxylic acids (Sharma & Nandi 2013)
1704	carboxylic groups of galactouronic acid (Sharma & Nandi 2013)

Table 2.2: Functional group change treated and untreated sugarcane bagasse

Wavenumber (cm^{-1})	**Functional group**	**Type of treatment and description**
3600-3100	OH stretching of cellulose (Gua *et al*., 2009; Mandal & Chakrabarty, 2011; Mothé & Miranda, 2009; Mulinari *et al*., 2009; Santos *et al*., 2012; Singh *et al*., 2005; Soliman *et al*., 2011; Zhang *et al*.,2011)	
2970-2860	Aliphatic CH stretching of CH_2 and CH_3 groups in polysaccharides (Sharma & Kaur, 2011; Soliman *et al*., 2011; Sun *et al*., 2004)	
2916	C-H group (Santos *et al*., 2012)	
2950	Methoxy group ($-OCH_3$) present in lignin (Gua *et al*., 2009; Xiao *et al*., 2001b)	It reduce band after treated with dilute acid due to the hydrolysis process occur (Gua *et al*., 2009)
2925	CH_2 asymmetric stretching (Gurgel *et al*., 2008)	The intensity increase due to introduction of succinyl group of treatment with succinic anhydride(Gurgel *et al*., 2008)
2916.66	CH stretching of CH_2 and CH_3 in polysaccharides (Soliman *et al*., 2011)	
2900	$–CH_2$ group of cellulose (Rungrodnimitchai, 2014)	
2893	$–CH_2$ symmetric and asymmetric stretching (Zhang *et al*.,2011)	
2888	Axial deformation of C-H group (Mothé & Miranda, 2009; Mulinari *et al*., 2009)	Band occur in sugarcane bagasse cellulose (Mulinari *et al*., 2009)
2835	Methoxy group ($-OCH_3$) present in lignin (Gua *et al*., 2009; Xiao *et al*., 2001b)	It reduce band after treated with dilute acid due to the hydrolysis process occur (Gua *et al*., 2009)
1765-1700	C=O stretching of acetyl or carboxylic acid from xylans, pectin, hemicellulose (Mandal & Chakrabarty, 2011; Sain & Panthapulakkal, 2006; Sun *et al*., 2005; Zhang *et al*., 2011)	
1750	Free and esterified carboxyl group (Santos *et al*., 2012)	
1740	Represent hemicellulosic fraction of water soluble include ferulic group ester, uronic and acetyl group (Sun *et al*., 2004).	The band disappear after treatment with 0.5M of NaOH due to ester bond cleavage(Sun *et al*., 2004)
1730	Present of carboxyl group (Santos *et al*., 2012); C=O stretching vibration	Disappeared during treated with $NaClO_2$,

	of acetyl and uronic ester group from pectin, hemicellulose or the ester linkage of carboxylic group of ferulic and p-caumaric acid of lignin or hemicellulose (Sain & Panthapulakkal, 2006; Sun *et al*., 2005; Mandal & Chakrabarty, 2011)	sulfuric acid and alkali (Mandal & Chakrabarty, 2011) After treated with citric acid it cause he band increase (Santos *et al*., 2012)
1734	ester groups C–O symmetric and asymmetric stretching (Gurgel *et al*., 2008)	
1732	stretching of unconjugated C=O groups present in polysaccharides and xylan (Mulinari *et al*., 2009)	sugarcane bagasse cellulose (Mulinari *et al*., 2009)
1721	Carbonyl band (C=O) of the hemicellulose (Mothé & Miranda, 2009)	
1720	aldehyde group absorption peak due to acetyl groups in the lignin or hemicellulose (Gua *et al*., 2009; Sun *et al*., 2003)	The band will absence during treated with alkali and alkaline peroxide and not oxidize the glycosidic band and hydroxyl group of hemicellulose (Sun *et al*., 2004)
1696-1705	C=O unconjugated of ester, ketones in carbohydrates (Singh *et al*., 2005)	
1604.86	C=C stretching of aromatic ring in lignin (Zhang *et al*.,2011)	
1650	ketone group absorption peak involving intramolecular hydrogen bonds (Gua *et al*., 2009) Free and esterified carboxyl group (Santos *et al*., 2012)	
1650-1630	OH of water (Mandal & Chakrabarty, 2011; Mulinari *et al*., 2009)	Band occur of sugarcane bagasse cellulose (Mulinari *et al*., 2009)
1649–1641	O–H bending of the adsorbed water (Sun *et al*., 2004; Troedec *et al*., 2008)	Appear during alkali treatment (Mandal, & Chakrabarty, 2011)
1639	Due to CO stretching vibration of carboxylic acid (Santos *et al*., 2012)	
1620–1595	C=C stretching of aromatic ring of lignin (Mandal & Chakrabarty, 2011; Zhang *et al*.,2011)	
1602 and weal 1050	Aromatic C=C in plane symmetrical stretching vibration of aromatic ring of lignin (Gua *et al*., 2009)	Disappeared during treated with $NaClO_2$, sulfuric acid and alkali (Mandal & Chakrabarty, 2011)
1600	Vibration aromatic ring of lignin (Singh *et al*., 2005; Zhang *et al*., 2011; Sun *et al*., 2003)	
1600–1590	skeletal vibrations of benzene ring (Sharma, & Kaur, 2011)	
1514	Aromatic skeletal vibration and C=O stretch of lignin (Zhang *et al*.,2011)	