Extraction, modification, characterization and metal adsorption properties of cellulose obtained from banana stem and bamboo stem

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Abstract: Banana stem and bamboo stem can be known as few of the agricultural residues in the agricultural sector, which are inexpensive, readily available, environmentally friendly, and recyclability. Cellulose was extracted from the banana stem and bamboo stem by using the following chemical processes: Soxhlet extraction, alkali treatment and bleaching process respectively. The cellulose obtained after the above processes was treated with glycine (10 %, 20 %, and 30 %, 40 % and 50 % w/v) in NaOH solution to synthesize cellulose-glycine hydrogel series. The synthesized hydrogels were treated with mono, di and trivalent cation solutions to study the metal adsorption capacities with different compositions of hydrogel prepared. Then the two samples and untreated cellulose obtained from both banana and bamboo stems were characterized using FTIR spectroscopy.

Keywords: Cellulose, Hemicellulose, Lignin, H*ydrogel*, G*lycine*, Metal adsorption

1. INTRODUCTION

The banana can be identified as one of the most well-known and useful plants in the world. Almost all the parts of a banana plant: fruit, leaves, flower bud, trunk, and pseudo-stem, can be utilized. (Subagya & Chafidz, 2018).

The bamboo plant has rapid growth and has a high dry matter yield per hectare (Guimaraes, *et al*., 2015). In recent years, a lot of research work has been done on the use of cellulose fibers as a reinforcing material for composites. This is mainly due to their high strength and stiffness combined with low weight and biodegradability. (Liew, *et al*., 2015).

Plant fibers are mainly composed of cellulose, hemicellulose and lignin (Moran, *et al*., 2007). Cellulose is the most abundant natural polymer on earth and exhibits many attractive properties such as thermal and chemical stability, nontoxicity, biodegradability, ecofriendly and biocompatibility (Jayaramudu, *et al*., 2017). Cellulose was extracted from banana and bamboo stems using dewaxing, alkali treatment and bleaching process (Erdogan, *et al*., 2016).
During the past decade, there has been a high increase of cellulose-based research due to significant importance in cellulosic modification (Shanmugam, *et al*., 2015). Cellulose and cellulose derivatives play an important role in producing green hydrogels for improving the absorption performance of many adsorbent materials (Jayaramudu, *et al*., 2017). Hydrogels are polymeric substances and capable of holding large amounts of aqueous solutions compared to their body mass because of hydrophilic functional groups in their structure. Crosslinking is one of the simplest reactions used to improve the physic-chemical properties of cellulose and cellulose derivatives (Haque & Monda, 2016).

Modified cellulose hydrogels were used to adsorb some heavy metallic ions in water (Mohadi, *et al*., 2019). Cellulose is insoluble in common solvents due to the formation of strong inter or intra molecular hydrogen bonds and its long chain structure (Jayaramudu, *et al*., 2017). The crystalline structure of cellulose is a closely packed chain with Van der Waals interactions and numerous forms of intra- and intermolecular hydrogen bonding (Rehman, *et al*., 2018).

Finding affordable and environment-friendly options to decontaminate wastewater generated with heavy metals and dyes to prevent the depletion of accessible freshwater resources is one of the indispensable challenges of the 21st century (Akter, *et al*., 2021). Due to industrialization processes such as mining activities, fossil fuels, automobile emissions the effect of heavy metal ions becomes a threat to environment and to the living organism is a particular concern worldwide (Zhou, *et al*., 2012).

In this research study, an attempt has been made to demonstrate the effect of cellulose glycine hydrogel on heavy metal absorption, na mely Na^{+}, Cd^{2+} and Cr^{3+}. At the same time, hydrogels are characterized using FTIR spectrum for further analysis.

2. METHODOLOGY

2.1. Materials and Equipment

Banana stems were obtained from the C Wing Women's Hostel Garden at Eastern University, Sri Lanka and Bamboo stems were obtained from Kirimetiyana, Lunuwila, Sri Lanka. All the methods mentioned below were carried out for the banana stem and bamboo stem separately.

2.2. Sample Preparation

The banana stem and bamboo stem were washed with distilled water several times to remove ash, dust and other residues and air-dried for 48 hours. Then the banana stem and bamboo stem were cut into 1-5 cm small pieces and the banana stem pieces were oven dried at 75 ºC for 3 days and the bamboo stem pieces were oven dried at 105 ºC for five days. Then the dried pieces were ground using a grinder and sieved (0 -50 µm).

2.3. Pretreatment of Samples

The dried stem sample (10 g) was weighed by electric balance and purified with hexane at 70 ºC using Soxhlet extraction apparatus for the ratio (1:20) solid to liquid for 6 hours to remove chlorophyll and waxes. Then the Soxhlet purified pieces were dried in a desiccator for 24 hours. Finally, the obtained compound is weighed.

2.4. Alkali Treatment

The purified samples obtained after Soxhlet extraction were treated with 1.5 % Sodium hydroxide according to solid to solvent ratio 1:20 at 80 ºC for 6 hours to remove hemicellulose in the stem samples. Then they were filtered using a Buchner funnel and washed with distilled water. Moreover, the sample was stirred using a magnetic stirrer several times. The samples were tested until pH value became neutral. In addition, the obtained sample was kept in a desiccator for 24 hours.

2.5. Bleaching Treatment

The sample obtained from alkali treatment was subjected to bleaching treatment with Hydrogen peroxide and 99.9 % Acetic acid (1:1) in order to solid to liquid (1:20) ratio to remove lignin in the stem samples. This was heated up to 70 ºC for four hours. Then the solid materials were washed with distilled water several times until the pH value of the sample was neutral. Then the sample was dried at a desiccator. Then the sample (cellulose) can be taken for identification, modification and metal absorption procedures.

2.6. Identification of Cellulose

2.6.1. Fehling's test

Cellulose is a reducing sugar, which is made by combining glucose monomers via β-(1, 4) linkage. Therefore, it has free aldehyde groups in it. 2 g of cellulose sample was taken to a test tube and 3 ml of Fehling's reagent was added. Then it was gently heated in a water bath until the blue-colored solution turned into brick red.

2.6.2. Tollen's test

Another test was carried out using Tollen's reagent. 1 g of sample was taken into a test tube and 2 ml of Tollen's reagent was added. In addition, the test tube was observed until a silver mirror appeared in the test tube wall.

2.7. Modification of Cellulose

A 0.5 g of extracted cellulose was dissolved in 10 ml of two $moldm^{-3}$ Sodium hydroxide and stirred by keeping in an ice bath for an hour. Additionally, an alkali solution of glycine (10 % w/v) was prepared by dissolving glycine in two $moldm^{-3}$ Sodium hydroxide. Likewise, glycine (20 %, 30 %, 40 %, and 50 %) series were prepared for further steps. Then 25 ml of glycine solutions were poured into the mixture of cellulose respectively. Different types of glycine cellulose hydrogels were prepared and labeled them as CEL5GLY0, CEL5GLY10, CEL5GLY20, CEL5GLY30, CEL5GLY40 and CEL5GLY50, which denotes the 0.5 g cellulose from CEL5 and 10 % of glycine from GLY 10. The cellulose glycine hydrogel mixture was stirred in an ice bath for another one hour and kept at room temperature overnight. Then the hydrogels were washed with 5 % acetic acid for neutralization until pH became 7.0. Then the obtained hydrogel samples were kept in the freezer for 48 hours.

2.8. Characterization of Cellulose hydrogels

The hydrogels were characterized using FT-IR spectrum ranging from 4000-400 cm^{-1} at resolution 4 cm^{-1}. An untreated cellulose sample and a cellulose glycine hydrogel sample from both banana and bamboo stem were analyzed for comparison purpose.

2.9. Metal adsorption capacity of Cellulose hydrogels

To study the metal ion concentration effect of monovalent ions, divalent ions and trivalent ions were carried out at room temperature. The hydrogel samples were initially treated with Sodium chloride and then washed with one $moldm^{-3}$ HCl. Then it was washed with distilled water until the pH value became neutral using litmus paper. 20 mg of hydrogel samples were measured into conical flasks and 20 ml of Na^+, Cd^{2+}, and Cr^{3+} solutions were added respectively to the prepared hydrogel series. They were stirred continuously for 6 hours and the absorptions were observed using atomic absorption spectroscopy). The heavy metal ion adsorption is measured using the following equation.

$$Qe = (Ce - Ci)\, V / m$$

Where Qe is the adsorption capacity at equilibrium, Ce is the concentration of the sample at equilibrium and Ci is the initial concentration. V is the volume of ionic solution and m is the dried cellulose sample.

2.9.1 Preparation of Na^+ solution

Na+ solutions (50 mgL^{-1}) were prepared by dissolving 0.13 g solid NaCl in 1000 ml with distilled water. The other solutions (10 mgL^{-1}, 20 mgL-1, 30 mgL^{-1}, 40 mgL^{-1}) of different concentrations were adjusted by serial dilution.

2.9.2 Preparation of Cd^{2+} solution

Cd^{2+} solutions (50 mgL^{-1}) were prepared by dissolving 0.10 g solid $CdCl_2.H_2O$ in 1000 ml with distilled water. The other solutions (10 mgL-1, 20 mgL^{-1}, 30 mgL^{-1}, 40 mgL^{-1}) of different concentrations were adjusted by serial dilution.

2.9.3 Preparation of Cr^{3+} solution

Cr^{3+} solutions (50 mgL^{-1}) were prepared by dissolving 0.48 g solid $CrK(SO_4)_2.12H_2O$ in 1000 ml with distilled water. The other solutions (10 mgL^{-1}, 20 mgL^{-1}, 30 mgL^{-1}, 40 mgL^{-1}) of different concentrations were adjusted by serial dilution.

3. RESULTS AND DISCUSSION

3.1 Chemical Composition

The chemical composition of the banana stem and bamboo stem after hexane treatment, alkali treatment and bleaching treatment are shown in the Table 1 and Figure 1.

Figure 1: Cellulose obtained from banana stem and bamboo stem respectively

Table 1: Chemical composition of banana stem and bamboo stem

Sample	Dry amount (g)/ Ash (%)	After hexane treatment (g) / Hemicellulose (%)	After alkali treatment (g) / Lignin (%)	After bleaching process (g)/ Cellulose (%)
Banana	8/5.25	7.58 /33.50	4.90 /12.37	3.91/48.8
Bamboo	10 /4.6	9.54 /26.2	6.92/25	4.42 /44.2

Table 2: The metal adsorption capacity of monovalent cation Na+ on untreated and treated banana stem cellulose glycine hydrogel

Type of CelGly	Metal adsorption capacity of Na^+ cation(mg/g)				
	10 mgL^{-1}	20 mgL^{-1}	30 mgL^{-1}	40 mgL^{-1}	50 mgL^{-1}
Cel5Gly0	0.3479	0.4673	0.4871	0.5975	0.6307
Cel5Gly10	0.3724	0.3909	0.5195	0.6054	0.7145
Cel5Gly20	0.4993	0.5044	0.6163	0.6792	0.7327
Cel5Gly30	0.5744	0.6189	0.6535	0.7128	0.7956
Cel5Gly40	0.5035	0.5898	0.6230	0.6901	0.7748
Cel5Gly50	0.4792	0.5433	0.6127	0.7043	0.7502

Table 3: The metal adsorption capacity of monovalent cation Na^+ on untreated and treated bamboo stem cellulose glycine hydrogel.

Type of CelGly	Metal adsorption capacity of Na^+ cation(mg/g)				
	10 mgL^{-1}	20 mgL^{-1}	30 mgL^{-1}	40 mgL^{-1}	50 mgL^{-1}
Cel5Gly0	0.1234	0.1348	0.1589	0.1864	0.1958
Cel5Gly10	0.0876	0.1563	0.1798	0.1930	0.2130
Cel5Gly20	0.1249	0.1462	0.1843	0.2176	0.2293
Cel5Gly30	0.1943	0.1986	0.2006	0.2187	0.2354
Cel5Gly40	0.1657	0.1704	0.1907	0.2064	0.2271
Cel5Gly50	0.1721	0.1863	0.2012	0.2107	0.2184

Table 4: The metal adsorption capacity of trivalent cation Cr^{3+} on treated and untreated banana stem cellulose glycine hydrogel

Type of CelGly	Metal adsorption capacity of Cr^{3+} cation(mg/g)				
	10 mgL^{-1}	20 mgL^{-1}	30 mgL^{-1}	40 mgL^{-1}	50 mgL^{-1}
Cel5Gly0	0.4995	0.4619	0.6213	0.7480	0.8934
Cel5Gly10	0.5322	0.6513	0.6801	0.7115	0.9636
Cel5Gly20	0.5900	0.7318	0.7483	0.8534	1.0621
Cel5Gly30	0.7364	0.8567	0.8714	0.9546	1.2294
Cel5Gly40	0.6913	0.7456	0.9324	0.8801	1.1116
Cel5Gly50	0.7063	0.7312	0.7731	0.8692	1.0874

Table 5: The metal adsorption capacity of trivalent cation Cr^{3+} on treated and untreated bamboo stem cellulose glycine hydrogel

Type of CelGly	Metal adsorption capacity of Cr^{3+} cation(mg/g)				
	10 mgL^{-1}	20 mgL^{-1}	30 mgL^{-1}	40 mgL^{-1}	50 mgL^{-1}
Cel5Gly0	0.1356	0.1562	0.1506	0.1569	0.1634
Cel5Gly10	0.1556	0.1587	0.1573	0.1607	0.1659
Cel5Gly20	0.1577	0.1599	0.1680	0.1723	0.1965
Cel5Gly30	0.1761	0.1657	0.1704	0.1831	0.2013
Cel5Gly40	0.1654	0.1682	0.1651	0.1709	0.1765
Cel5Gly50	0.1643	0.1611	0.1690	0.1743	0.2003

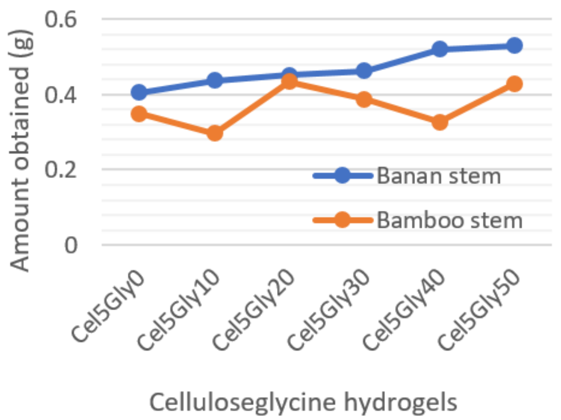

Figure 2: The amount of cellulose-glycine hydrogel from Banana and bamboo stem with different composition

The amount of cellulose–glycine hydrogel obtained from 0.5 g of cellulose from Banana and bamboo stem are shown in Figure 2.

3.2 Metal adsorption capacity

The behavior of monovalent, divalent and trivalent metal adsorption properties of cellulose glycine hydrogels from banana and bamboo stems are studied in the following tables 2-3 given below. 20 mg of each hydrogel samples were subjected to ion solutions with10 mgL^{-1},20 mgL^{-1}, 30 mgL^{-1}, 40 mgL^{-1} and 50 mgL^{-1} respectively. The data represents the metal adsorption property of the hydrogels. The Cel5Gly30 hydrogel series shows a higher adsorption value than the other hydrogels. All the ion solutions show lower concentration values than the initial concentric values after they are treated with cellulose glycine hydrogel. So, hydrogels can be used in wastewater treatment with heavy metal dilution.

The data from the AAS spectroscopy are shown in Figures 3-4 and it represents a clear image about the mono and di-valent adsorption behaviors of the hydrogel samples. It shows the divalent behavior of cellulose glycine hydrogel by banana stem and bamboo stem.

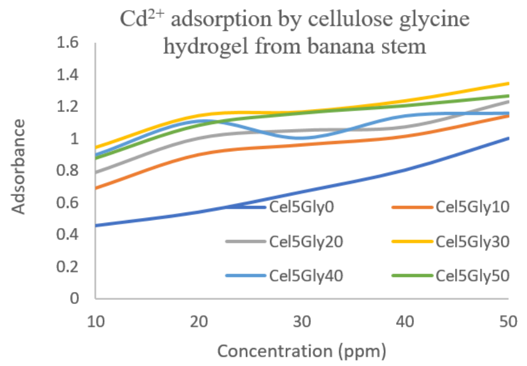

Figure 3: Cd^{2+} adsorption by cellulose glycine hydrogel by banana stem

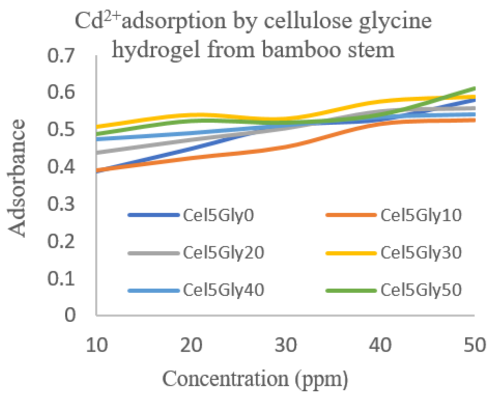

Figure 4: Cd^{2+} adsorption by cellulose glycine hydrogel by bamboo stem

Tables 4 and 5 show the trivalent behavior of cellulose glycine hydrogel by banana stem and bamboo stem.

Hydrogels prepared from banana stem show more affinity towards metal adsorption than the bamboo stem hydrogels. It may be because of fewer adsorbent sites present in the bamboo stem hydrogels. In addition, hydrogels adsorb divalent cation rather than the monovalent and trivalent cation solutions. Normally, hydrogel adsorption increases with the radius of the metal cation. Then the affinity of metal adsorption can be identified as trivalent> divalent> monovalent. However, this order differs with the pH value of the solute,

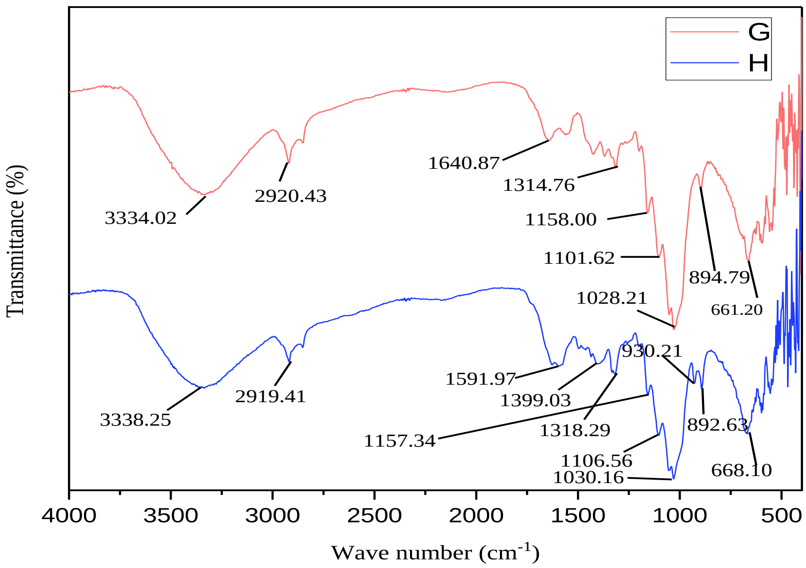

Figure 5: FTIR analysis of cellulose and cellulose glycine hydrogel from banana stem (G; The spectrum of cellulose, H: The spectrum of cellulose glycine hydrogel)

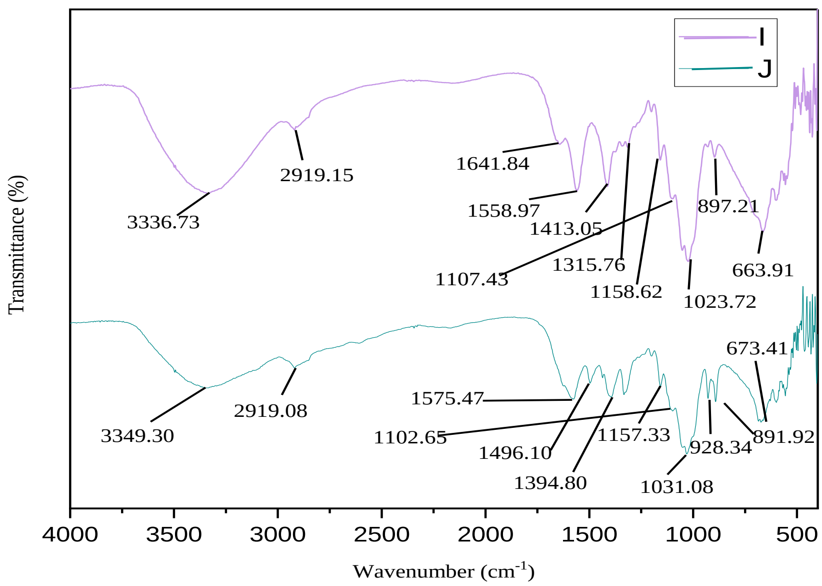

Figure 6: FTIR analysis of cellulose and cellulose glycine hydrogel from bamboo stem (*I: The spectrum of cellulose, J: The spectrum of cellulose glycine hydrogel*)

initial concentration, amount of adsorbate and the temperature inside the cation solution. According to the results, hydrogels show more affinity for adsorbing divalent cation. Moreover, Cel5Gly30 hydrogel is in forward of adsorbing metal ions in solutions than Cel5Gly40 and Cel5Gly50. The metal adsorption property of the hydrogels can be varied due to the temperature, pH value, and dosage of adsorbent used, contact time and initial concentration of the ion solution. Hydrogels are more popular in modern times to purify water bodies because of effectiveness, reusability, low cost, easy operation, biodegradable, recyclability and environment friendly.

3.3 FTIR analysis

The following FTIR shift values for cellulose and cellulose glycine hydrogel from banana stem (Figures 5-6). Normally the FTIR spectrum revealed C=O bond in FTIR at around $1700cm^{-1}$ .As per the results it is not appeared any band in that range in both banana stem and bamboo stem spectrums. Absence of the adsorption band around 1680 cm^{-1} associated with the amide or ester group stretching vibrations. This indicates that the cellulose glycine hydrogel does not occur a chemical crosslinking, as the band is absent. Therefore, the glycine hydrogel is cross-linked with the cellulose molecule via a physical crosslinking.

4. CONCLUSION

Both banana and bamboo stems contain a rich amount of cellulose compared to lignin and hemicellulose in the cell structure on both stems. The hexane treatment, alkali treatment and bleaching process eventually discard the ash, hemicellulose and lignin and other bio residues in plant cell walls respectively. A banana stem enriches more cellulose content compared to the cellulose amount in a bamboo stem. In the banana stem, it contains 5.25 % ash, 33.50 % of hemicellulose, 12.37 % of lignin and 48.8 % of cellulose. In addition, in the bamboo stem it contains 4.6 % of ash, 26.2 % of hemicellulose, 25 % of lignin and 44.2 % of cellulose. All the cellulose hydrogel series adsorb metal ions in the ionic solution. According to the results obtained, the Cel5Gly30 cellulose glycine hydrogel shows more heavy metal adsorption capacity. Moreover, the hydrogel series adsorb heavy metals according to the order divalent>trivalent>monovalent. In addition, the hydrogel samples prepared on banana stems show a high affinity for adsorbing heavy metals compared with hydrogel samples prepared with bamboo stem fibers.

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