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Novel Method of Lignin Separation from Almond Shells Applying Multiple Contacts

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Abstract - *Almond shell is the name given to the ligneous material forming the thick endocarp or husk of the almond tree fruit. Lignin is the second most abundant natural polymer next to cellulose. Its complex structure helps it to function like adhesive that binds cellulose and hemicelluloses. The present work addresses to the isolation of lignin from almond shells. A novel method that includes different solvents in combination of multiple stage contacting in a reflux setup has been used. The solvents included ethanol-water (60:40 v/v) and 3% NaOH. The FTIR analysis of the samples L1, L21, L22 and L32 have been carried out. The spectrogram of these samples is compared with that of lignin isolated from almond shells and reported in literature. From the comparison, it can be observed that the wavenumbers are in agreement with each other and with that reported in literature. The percentage yield of lignin isolated is observed to be 5.89%, 16.54%, 28.33% respectively for single stage contacting using EtOH-H2O, two stage contacting with EtOH-H2O at 1st stage & 3% NaOH solution at 2nd stage and two stage contacting using 3% NaOH solution at both stages respectively. Thus, it can be concluded that of the various combinations tried in the present work, two stage extraction employing 3% NaOH solution in each stage using reflux setup resulted in better yield.*

Key Words: Novel lignin isolation technique, lignin isolation, almond shells, multistage contacting, 3%NaoH solution

1. INTRODUCTION

Almond fruit consists of three or correctly four portions: kernel or meat, middle shell, outer green shell cover or almond hull and a thin leathery layer known as brown skin of meat or seed coat. The nutritional importance of almond fruit is related to its kernel. Other parts of fruit such as shells and hulls were used as livestock feed and burned as fuel. In the past decades, different phenolic compounds were characterised and identified in almond seed extract and its skin, shell and hull as almond by-products. In addition, poly-phenols are abundant micronutrients in the human diet, and evidence for their role in the prevention of degenerative diseases such as cancer and cardiovascular diseases is emerging. The health effects of poly-phenols depend on the amount consumed and on their bioavailability. [1]

Almond shell is the name given to the ligneous material forming the thick endocarp or husk of the almond tree fruit. When the fruit is processed to obtain the edible seeds, big ligneous fragments are separated. These materials remain available as a waste product for which no important industrial use has been developed, so they are normally incinerated or dumped without control. Almond shells can be ground up and used as bedding for garden planters and landscape material similar to wood chips. Almond shells are most commonly sold to co-generation plants to be used as a fuel source. They are robust and rigid in nature. This nature of shells indicates presence of lignin and cellulose.

2. LITERATURE SURVEY

Pure cellulose crystals had been successfully extracted by Najeh Maaloul, Rim Ben Arfi, Manuel Rendueles, Achraf Ghorbal, Mario Diaz from Tunisian almond shells using a combination of chemical treatments, such as alkaline treatment, bleaching, and sulphuric acid hydrolysis. The hydrolysis products of cellulose crystals without further dialysis had been thoroughly characterized. In this work, the chemical analysis of the raw materials revealed interesting levels of α-Cellulose (29.9 wt%) and lignin content (30.1 wt%). Before the extraction of cellulose, dried almond shell was milled and screened to select the fraction of the particles that were below 60 mesh. The crushed plants fibers were dewaxed with a mixture of chloroform and absolute ethanol (2:1 ratio, v/v) under a mechanical stirring for 24h. Then, the fibers were washed with distilled water until filtrate pH was neutral and dried. Dried product was treated in 4 wt% NaOH solutions at 80-90℃ for 2h to remove hemicelluloses with residual starch and pectin. This alkali treatment was conducted two times, and after each treatment, the fibers were filtered and washed with distilled water to remove the alkali-soluble components. Lignin in the fibers plants was removed by a sodium hypochlorite solution 2.5 wt% at 70℃ for 1h under mechanical stirring and was repeating two times. The bleached fibers were subsequently filtered, washed with distilled water, and air dried. Bleaching treatment was used to facilitate the removal of the majority of the residual lignin content. [2]

Almond shell was treated by different methods to extract lignin by Ane Sequeiros, Darci Alberto Gatto, Jalel Labidi and Luis Serrano. Alkaline, organosolv-ethanol, formosolv and acetosolv-formosolv processes were studied. The results showed that the best delignification process was achieved with formic acid (formic acid/water 80:20, v/v; 0.2% of HCl as catalyst; solid/liquid ratio 1:10; 130°C 90 min; constant stiring) with a total lignin content 83.60% and only 1.89% of total sugar content. [3]
Five pulping methods using different reagents were used for the delignification of almond shells: sodium hydroxide 7.5 % v/v for 24 h at 60°C, potassium hydroxide 7.5 % v/v for 24 h at 60°C, formic acid/water 90/10 v/v, organosolv with ethanol/ water 60/40 v/v and sodium hydroxide 15 % v/v in an autoclave for 90 min at 120°C. Nanopaper sheets were produced and the properties were compared to conventional micropaper. The different treatments influenced the amount of lignin eliminated, which had a direct relationship on the subsequent bleaching treatments to obtain pure cellulose. Hence, the different chemical methods influenced the crystallinity of the fibers which also influenced the yield of cellulose nanofibers and different nanopapers. It was found that the lignin content was significantly reduced after all treatments. Using the organosolv process, the lignin content decreased by 10 %; this decline was lower than that obtained with other treatments, but a higher purity lignin can be obtained. The other treatments resulted in more delignification, but the most effective chemical treatment in order to remove lignin was formic acid with a 30 % reduction.[4]

3. PRESENT WORK

3.1 Objective

The present work addresses to the isolation of lignin from almond shells. A novel method that includes different solvents in combination of multiple stage contacting in a reflux setup has been used. The solvents studied include ethanol-water (60:40 v/v) and 3% NaOH solution in combination for two stage contacting.

3.2 Methodology

The schematic representation of methodology followed in the present work in lignin extraction using different solvents is shown in Figure 1.

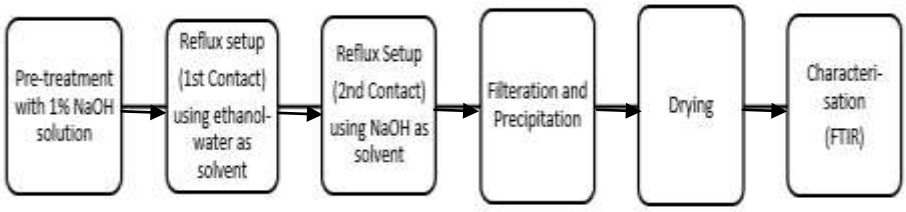

Fig -1: Methodology of present work

3.2.1 Materials and Experimental Procedure

Almond shells obtained from local grocery shop, NaOH pallets, ethanol, concentrated HCl solution, reflux setup, concentrated H_2SO_4 etc**.**

3.2.2 Size Reduction

The almond shells were separated from kernel. Dust and other unwanted impurities were removed. Almond shells were ground to obtain particle size in micro meters. The procedure followed in isolation of lignin is elaborated in the Figure 2.

3.2.3 Pre-treatment of almond shells

20gm of ground almond shell was kept in 1% NaOH solution for 96 hours. The solution was filtered to separate treated almond shells.

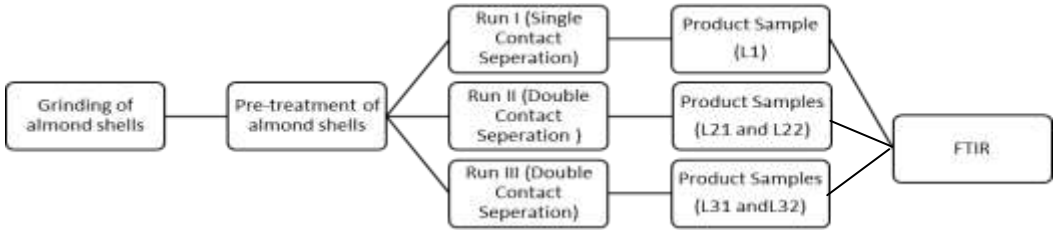

Fig -2: Sequence of process steps followed

3.2.4 Process Details

Run 1**:** After pre-treatment, almond shells were heated at 80°C in ethanol/water solution (60/40 v/v) using reflux setup for 2 hours. The solution was filtered to give 1st supernatant solution and solid almond shell particles as residue. 1st supernatant solution was treated with concentrated H_2SO_4 to precipitate out brown coloured powder. This precipitate was separated by filtration and stored as sample L1.

Run 2**:** The steps in run 1 were followed to obtain 1st supernatant solution, which was treated with concentrated HCl to precipitate out brown coloured powder. This precipitate was separated by filtration and stored as Sample L21. The residual almond shell particles exhibited hard and rigid structure which indicated presence of lignin. These particles were again treated for second contact at 90°C in 3% NaOH solution using reflux setup for 2 hours. The solution was filtered to give 2nd supernatant and solid almond shell particles. 2nd supernatant solution was treated with concentrated HCl to give dense brown precipitate. The solution was filtered and the solids obtained were stored as sample L22. This sample was dried at 65°C.
Run 3: Here NaOH solution was used as solvent for both contacts. H_2SO_4 was used for precipitation. The samples obtained after 1st and 2nd contact were stored as Sample L31 and L32 respectively.

The details of process parameters are as given in the Table 1. The actual photographs of process carried out are shown in Figure 3.

Fig-3: Actual photographs of process steps

Quantity of raw material	Experimental run	Solvent	Temp (°C)	Time (min)	Product code	Quantity of lignin in product	Quantity of cellulosic material
20 grams	Run 1	Ethanol-water 60:40 (v/v)	80	120	L1	0.62	18.42
	Run 2	Ethanol-water 60:40 (v/v)	80	120	L21	0.66	15.03
		3% NaOH solution	80	120	L22	1.08	
	Run 3	3% NaOH solution	80	120	L31	1.96	14.78
		3% NaOH solution	80	120	L32	1.02	

Table 1: Process parameters

3.3 Results and discussions

The FTIR analysis of the samples L1, L21, L22 and L32 have been carried out. The spectrogram of these samples is compared with that of lignin isolated from almond shells and reported in literature [3]. The details of wavenumber and comparison with interpretations are mentioned in the Table 2. Similarly, the spectrograms are given in figure 5,6,7 and 8 respectively.
From the comparison, it can be observed that the wavenumbers are in agreement with each other and with that reported in literature.

Thus, it can be interpreted that lignin has been successfully extracted from almond shells using the combinations of solvents studied in multiple contacting.

However, based on overall interpretations it can be said that double contact separation using 3% NaOH gives better results in terms of yield and is more effective in isolation of lignin from almond shells.

Fig -4: Actual photographs of sample

Table 2: Comparison of FTIR spectrogram

Sr No.	Functional group	Wavenumber				Wavenumber from literature [3]
		L1	L21	L22	L32	
1	Vibration caused by stretching of O-H group	3368	3352	3393	3387	3350-3400
2	Aliphatic C-H stretching vibration of methyl group	2940	2938	2936	2938	2935-2940

3	Aliphatic C-H stretching vibration of methylene group	2868	2839	2875	2890	2838-2896
4	Aromatic carbonyl/carboxyl and in unconjugated ketone C=O group	1714	1718	1715	1719	1711-1720
5	Aromatic C=C stretching C=O in conjugated ketone	1629	1645	1632	1640	1650-1595
6	Aromatic C=C ring stretching and aromatic ring vibration of phenylpropane groups	1427	1423	1424	1420	1425
7	Aliphatic C-H stretch in CH_3	1373	1377	1371	1379	1374
8	Breathing of syringyl (S) ring with C-O stretching	1320	1324	1329	1328	1326
9	Breathing of guaiacyl (G) ring with C-O stretching	1169	1164	1204	1180	1168-1218
10	Vibration by deformation of C-H bond in the syringyl (S) substrate	1114	1114	1113	1118	1111-1117
11	Characteristic band of hemicellulose	1031	1029	1030	1035	1027-1034
12	Breathing of the guaiacyl (G) ring with C-O stretching	905	912	908	915	902-917
13	Xylose constituting polysaccharide	895	894	900	896	897

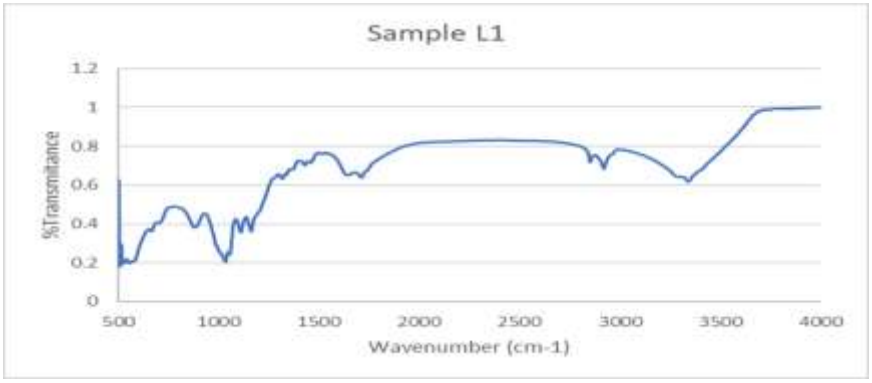

Fig-5: FTIR spectrogram of L1

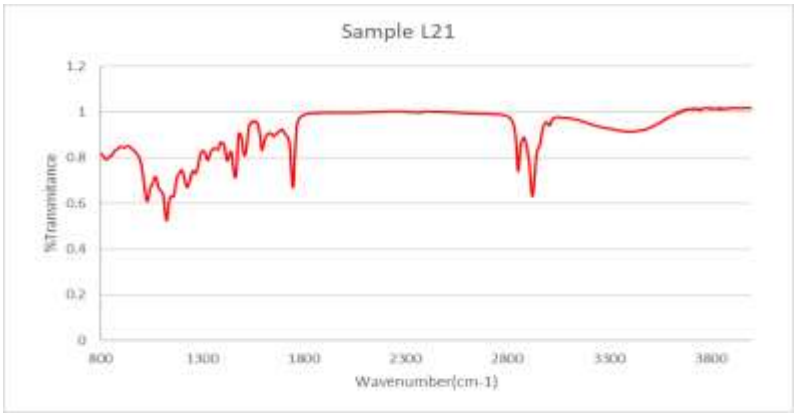

Fig-6: FTIR spectrogram of L21

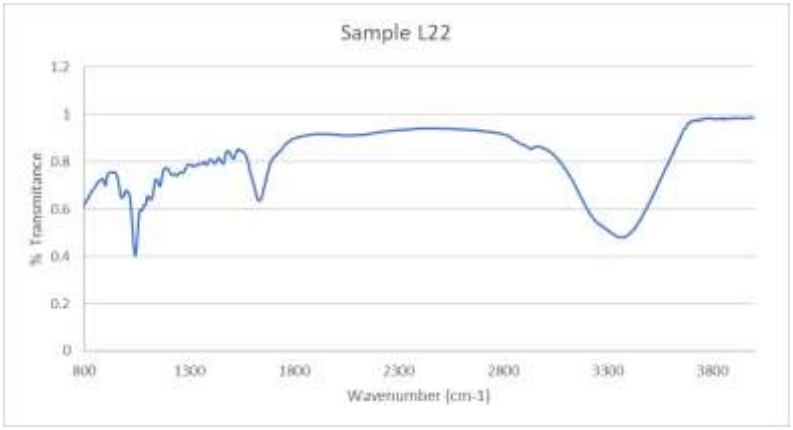

Fig-7: FTIR spectrogram of L22

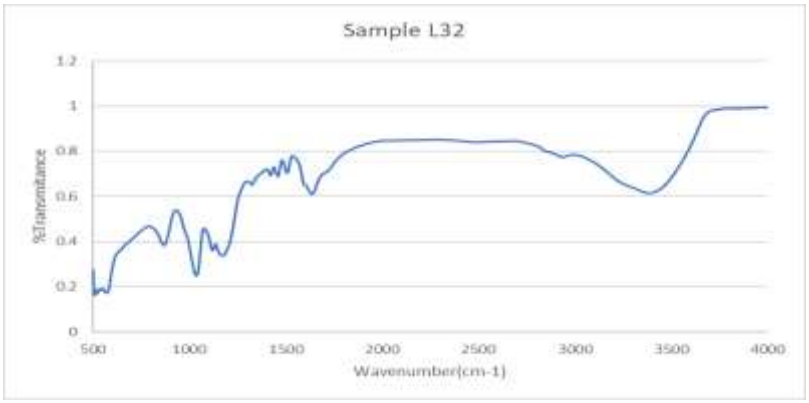

Fig-8: FTIR spectrogram of L32

4. CONCLUSIONS

A large quantity of waste generated is posing various problems such as disposal issues, land, water and air pollution apart from loss of valuable ingredients present in the waste material. All over the world many initiatives have been taking place in this regard.

The present work addresses to utilisation of one such waste material, almond shells. Experimental runs have been conducted for isolation of lignin from almond shells using novel technique of solvent extraction at ambient pressure condition under reflux. Combination of solvents for multistage contacting have been studied. The solvents include ethanol-water and 3% NaOH solution. Samples of lignin isolated have been analysed for functional group presence of lignin using FTIR technique. The comparison of the spectrogram of some of the samples with that reported in the literature has indicated the successful isolation of lignin from almond shells. The percentage yield of lignin isolated is observed to be 5.89%, 16.54%, 28.33% respectively for single stage contacting using EtOH-H_2O, two stage contacting with EtOH-H_2O at 1st stage & 3% NaOH solution at 2nd stage and two stage contacting using 3% NaOH solution at both stages respectively. Thus, it can be concluded, of the various combinations tried in the present work, two stage extraction employing 3% NaOH solution in each stage using reflux setup resulted in better yield.

The work is demonstrative and it is felt necessary to conduct a greater number of experimental runs with more stages to increase the percent of lignin isolated.

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