



Stepwise removal of Lignin sulfonate hydroxyl ion to reduce its solubility in an aqueous environment: As a Coating in slow-release systems or absorbent base

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ABSTRACT

The presence of functional groups in the structure of lignin increases its ability to make changes and carry out chemical reactions, and this work strengthens its commercial applications. The main goal of this research is to reduce the solubility of lignin-sulfonate using the acetylation process, especially multi-stage acetylation, to improve its ability. For this purpose, reducing or removing the hydroxyl groups is necessary. In this research, Lignin sulfonate was extracted from the wastewater of Mazandaran wood and paper factory. Then, the decrease in the solubility of Lignin sulfonate was studied by performing the acetylation reaction of Lignin sulfonate in a multi-stage manner. From FT-IR, GC-MS, SEM, XRD, and Contact Angle analyses, the effect of stepwise acetylation on the structure of Lignin sulfonate bio-polymer was studied. The results showed that the hydroxyl groups were significantly reduced in the multi-stage acetylation process of Lignin sulfonate, which significantly reduced the solubility and hydrophilicity of the product compared to the raw material. The solubility, weight of the product, GC-MS analysis, and FT-IR analysis of the solution showed the necessity of choosing the ethanol solvent in the purification of the product. Thus, by improving the crystallization process of the product, the amount of acetylated Lignin sulfonate produced increased significantly. This research tried to provide a suitable analysis for the severe exothermic reaction of ethanol to purify impurities and improve the quality and quantity of acetylated lignin sulfonate products.

1. Introduction

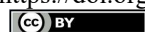
Lignin is the second biopolymer in the world after cellulose, constituting 15-40% by weight of wood [1, 2]. Also, lignin is the largest natural source of aromatic compounds and has excellent potential for use in many industrial applications [3, 4]. Pulp and paper industries produce between 50 and 70 million tons of lignin annually. However, only 2% of it is used to create value-added products. This material is underused [1, 2, 5-7]. Today, lignin is mainly used to generate energy through combustion in pulping processes. In this way, it is very beneficial to identify value-added products based on lignin and develop processes for their production [2, 8-11]. However, the complex structure of lignin has limited the possibility of its proper understanding and use in

value-added industrial applications [12]. To produce value-added products based on lignin, in addition to extracting lignin from biomass, modifying its structure is a suitable solution for using this renewable product [2, 13, 14].

Lignin obtained from sulfite pulping processes is characterized as lignosulfonate [1, 15]. Currently, lignosulfonate accounts for 90% of the total commercial lignin market, and the total annual production of lignosulfonates worldwide is approximately 1.8 million tons [15-18]. In general, lignosulfonate contains significant amounts of sulfur in the form of sulfonate groups, and due to the presence of these sulfonate groups, it has a negative surface charge. Therefore, it can remove the cations in the solution. Another feature of sulfonate groups is the increase in solubility in water [2, 19]. Due

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to its unique properties, Lignin sulfonate has wide industrial applications such as use in animal feed, pesticides, surfactants, as a lubricant in drilling mud and concrete, and as a stabilizer in colloidal suspensions [15, 19-22].

Due to the existence of multiple functional groups in the structure of lignin, by changing the functional groups, various properties can be created for the modified lignin [23]. Among the important functional groups in lignin structure, hydroxyl groups are among the most reactive functional groups; by changing the hydroxyl group, the solubility of lignin changes considerably [6].

Among all the reactions involving lignin hydroxyl groups, esterification is the simplest method according to the reaction parameters and reagents. Therefore, chemical modification of hydroxyl groups through esterification or acetylation process is a promising approach to functionalize lignin. Because this reaction is widely used to modify lignocellulosic sources [6, 24-26]. Improved resistance to oxidation, decreased solubility in water, decreased dissolution in non-polar solvents, and increased thermal stability are all results of acetylating lignin [27-29].

As esterification agents and catalysts, Acetic anhydride ($C_4H_6O_3$) and pyridine (C_5H_5N) are often used in the liquid phase of the acetylation procedure [28, 30, 31]. Recently, several approaches have studied lignin acetylation, including parameters affecting Lignin sulfonate acetylation using acetic anhydride and its optimization [32]. Research also shows that in the case of nano lignin sulfonate production, the acetylation process occurs at a lower temperature and time [31, 33].

Therefore, this article extracts lignin sulfonate from the wastewater of the Mazandaran wood and paper factory (Chokam). Subsequently, the structural alterations of lignin sulfonate are examined by a gradual execution of the acetylation reaction. Therefore, structural changes of lignin are studied with the help of FT-IR, GC-MS, SEM, XRD, and contact angle analyses. The main goal of this research is to reduce the solubility of Lignin sulfonate. Due to the use of this biopolymer as a coating in slow-release systems for fertilizer or drug delivery [34-39], it is necessary to reduce the solubility of the biopolymer in water.

2. Materials and methods

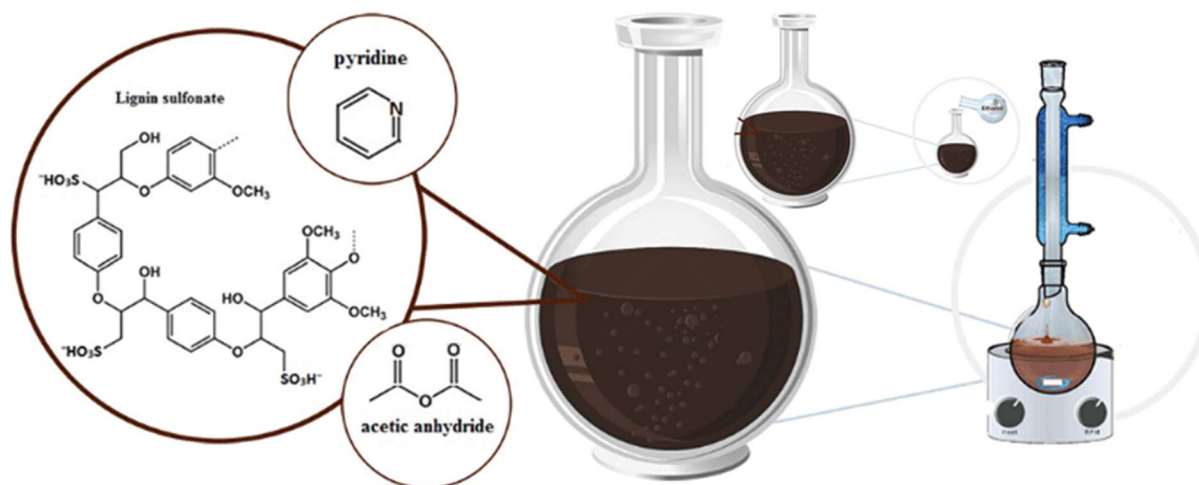
2.1. Materials

In this research, Industrial chemicals such as black liquor (prepared from Mazandaran wood and paper factory effluent), calcium oxide (Ghatran Chimi Co. Iran), sulfuric acid (Dr. Mojallali Industrial Chemical Complex Co. Iran), acetic anhydride (Pars Chemical Co. Iran), pyridine (Merck Co. Germany)) and 96% ethanol (Hamon Teb Central Iran Co.) were used.

2.2. Extraction and acetylation of lignin sulfonate (Acetylated lignin sulfonate)

This research prepared Lignin sulfonate from black liquor (wastewater from a wood and paper factory in northern Iran). Then, Lignin sulfonate was extracted using the precipitation method in two steps: adding calcium oxide and sulfuric acid and reducing the pH.

Acetic anhydride and pyridine were also used to perform the Lignin sulfonate acetylation reaction (Scheme. 1). The acetylation method was as follows: one gram of dry Lignin sulfonate was mixed with an equal volume percentage of acetic anhydride and pyridine (20 ml), and then the reaction was carried out at $100^\circ C$ for 48 hours. Then, ethanol solvent was used to purify the product. For this purpose, after the reaction is finished and its temperature is cooled down to room temperature, ethanol (equal to the volume of the solution) is slowly added into the container of the reaction solution with stirring (the reason for the slow addition of ethanol to the reaction solution is to avoid a sudden increase in the initial temperature. It is almost three times the room temperature in a few minutes due to the exothermic nature of the solution). Next, the solution is centrifugated after stirring for 0.5 to 1 hour; then, its temperature is reduced to room temperature. Finally, the product was separated with the help of a centrifuge and dried in an oven for 12 hours at a temperature of $60^\circ C$ [32, 40]. Modified Lignin sulfonate's structure was examined using a stepwise acetylation procedure. This article carries out acetylation until the lignin sulfonate that has been acetylated is hardly soluble in water.



Scheme 1. An illustration of the lignin sulfonate acetylation process and the ethanol-based purification of acetylated lignin sulfonate

3. Results and Discussion

3.1. Investigation of product purification and study of exothermic reaction

This research used ethanol solvent to purify the product after the acetylation process. In addition to producing the main product (Acetylated lignin sulfonate), side reactions also occur in the reaction vessel. By GC-MS analysis of the reaction solution before purifying impurities with ethanol, the solution contains about 73% methyl acetate, 10% ethyl acetate, and 4% acetic acid (Table 1).

Due to the acetylation process, acetic anhydride and pyridine are usually used to increase the acetylation reaction's efficiency. One of the side reactions that happens in the container is the hydrolysis reaction of

excess acetic anhydride. The product of this reaction is acetic acid. Methyl acetate is probably produced through the combination of acetic acid with aryl-methoxy groups in the structure of Lignin sulfonate (reaction 1). After adding ethanol and purifying the product, the results of GC-MS analysis showed that methyl acetate was lost, and its ethyl ester compound was produced.

Ethanol reacts with excess acetic anhydride, which leads to the formation of ethyl acetate. This process is highly exothermic so that in less than 5 minutes, the temperature of the test container reaches from room temperature to more than 82 °C (Scheme. 2). Acetic acid is also produced as a result of this reaction. Chemical reaction 2 shows the side reaction of acetic anhydride with ethanol. Acetic acid can also react with excess ethanol and produce ethyl acetate (reaction 3) [41].

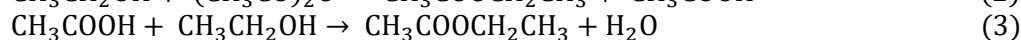
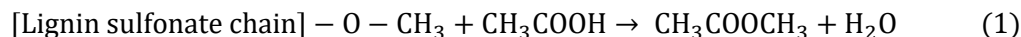
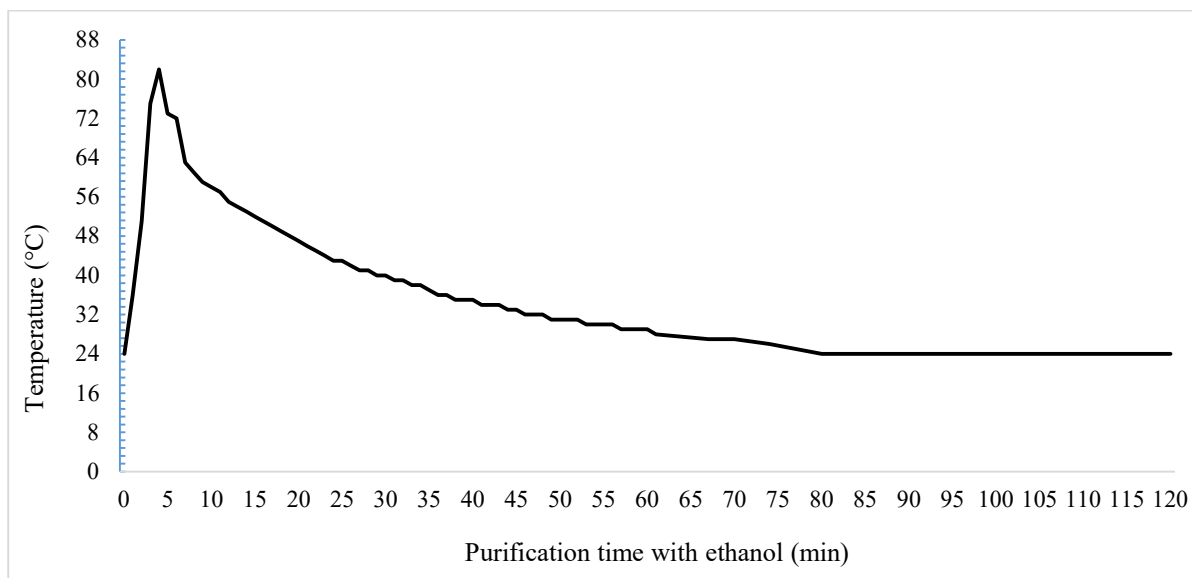


Table 1. Results of GC-MS analysis of the sample before and after using ethanol solvent

Process	Peak No	Material	Molecular Weight (g/mol)	Retention time (min)	Area (%)
Before Purification	1	Methyl acetate	74.08	1.681	73.07
	2	Acetic acid	60.05	2.132	4.43
	3	pyridine	79.1	3.024	22.50
After Purification	1	Ethanol	46.07	1.571	75.30
	2	Ethyl acetate	88.11	1.972	10.61
	3	pyridine	79.1	3.034	14.08



Scheme. 2. Severe temperature changes in the process of decontamination of the product with ethanol

3.2. The effect of ethanol on obtaining more Acetylated lignin sulfonate

By checking the solubility of the product in Table 2, it can be seen that the solubility of Lignin sulfonate in ethanol is negligible. Also, the weight of Acetylated lignin sulfonate increases almost 2.5 times after decontamination with ethanol compared to before

decontamination. This can be attributed to the possibility of more sedimentation of suspended particles of Acetylated lignin sulfonate in the solution after adding ethanol. In other words, with the presence of ethanol solvent, the process of crystallization and product formation is close to completion [42]. In another study, the use of ethanol to obtain Acetylated lignin sulfonate was confirmed [3].

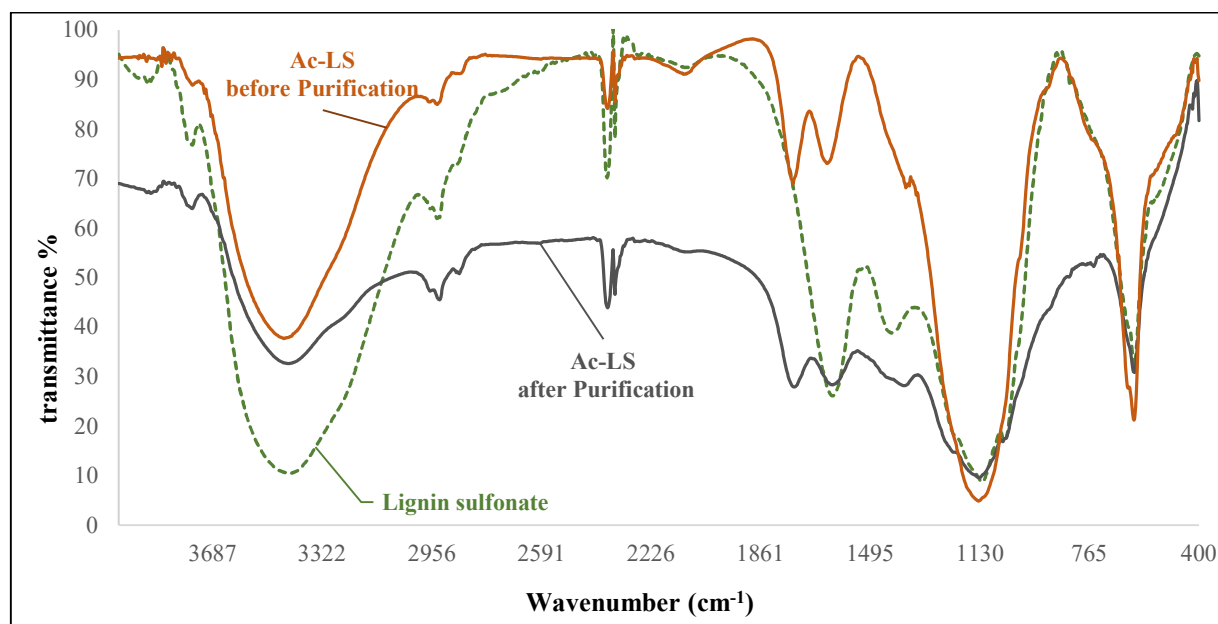
Table 2. Solubility of lignin sulfonate and acetylated lignin sulfonate (first step of acetylation) in ethanol

Purification time (hour)	Temperature (°C)	Solubility in ethanol (g/100ml)		Acetylated lignin sulfonate weight (g)	
		Lignin sulfonate	Acetylated lignin sulfonate	Before purification	After purification
24	Room temperature	0.09	0.11	390	950
2	80	0.1	0.13		

3.3. Examining the FT-IR spectrum of the product (before and after decontamination with ethanol)

Functional groups, especially hydroxyl, carbonyl, and sulfonate groups, are essential structural characteristics of lignin, and their quantitative and qualitative determination is an integral part of studying lignin structure [43]. No profound differences are observed in the absorption areas of peaks from 1370 to 3420 cm^{-1} , especially in the carbonyl functional group's (C=O) absorption peak, which indicates the presence of both

acetylated and lignin sulfonate. So that in the FT-IR spectrum of the product before and after neutralizing with ethanol, the reduction of the hydroxyl functional group (-OH) and the creation of the C=O coincide, which indicates the acetylation reaction (Scheme. 3). The slight differences in the product spectra before and after decontamination with ethanol can be caused by the reduction or removal of products such as carboxyl groups such as acetic acid and acetic anhydride as well as acetates such as methyl and ethyl acetate in the decontamination process with ethanol.



Scheme 3. FT-IR spectrum; Acetylated lignin sulfonate (Ac-LS) before and after decontamination with ethanol

3.4. Investigating the solubility and color change of Lignin sulfonate in the multi-stage acetylation process

One of the significant disadvantages of using lignin sulfonate in some applications is its solubility in water. On the other hand, lignin sulfonate gives more hydrophilic properties to composites due to the presence of water-soluble sulfonate groups in its structure [12]. Also, the main factor of the ability of Lignin sulfonate complex compounds is derived from hydroxyl groups

The comparison of FT-IR spectra of Lignin sulfonate and product in a multi-step acetylation process (three steps) is shown in Scheme. 4 and Table 3. By examining the spectrum of the product in all three stages of the acetylation process, the peak related to $-OH$ s has been significantly reduced. This decreasing trend of $-OH$ s is more observed in the 2nd and 3rd steps of acetylation, and it can be concluded that the solubility of Acetylated lignin sulfonate decreases by performing multi-step acetylation and confirms the success of the multi-step acetylation process. Also, the broad peak that appears in

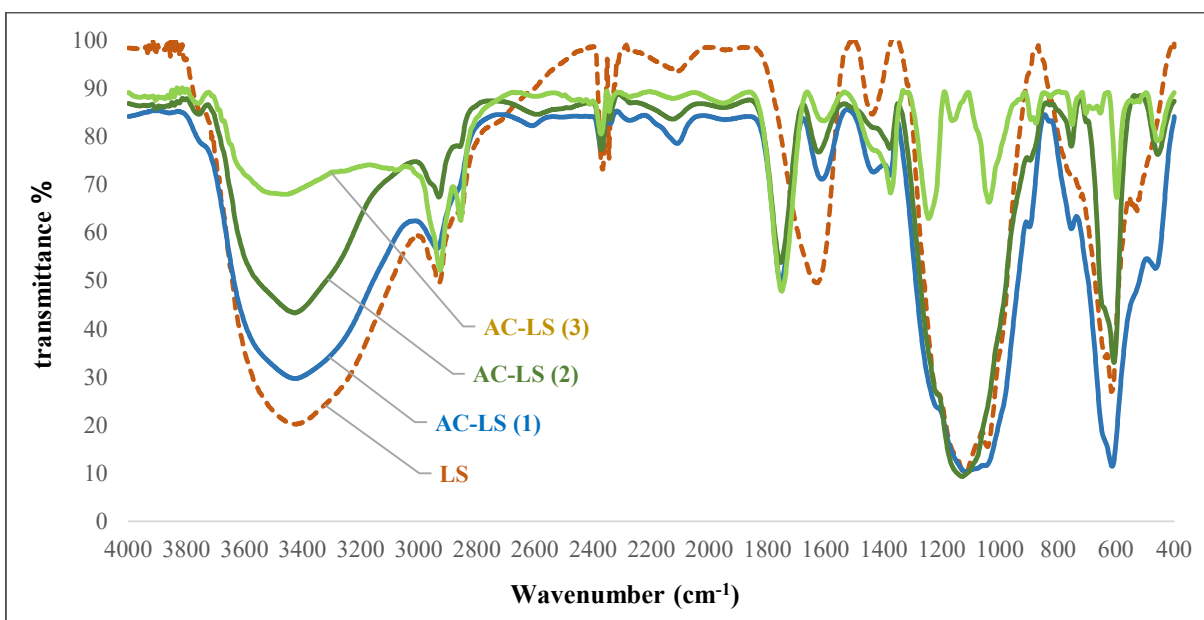
[19, 44]. Therefore, the chemical modification of hydroxyl groups is done through the acetylation process to reduce the polarity and solubility of lignin [25, 26]. Lignin sulfonate is more soluble in water because it contains significant sulfonate groups [19]. Consequently, the solubility of lignin sulfonate or acetylated lignin sulfonate (after each acetylation step) in water was investigated in this study by FT-IR analysis, contact angle measurement, and solubility determination [32, 45, 46].

3200-3500 Cm^{-1} for Lignin sulfonate represents the spectrum related to the stretching vibrations of the $-OH$, which shows that the structure of lignin sulfonate has many phenolic and alcoholic hydroxyl groups.

Also, in addition to reducing the $-OH$, a $C=O$ absorption peak can be seen in all three stages of the acetylation process. An interesting point to note in stepwise acetylation is the significant change in the 600-1600 Cm^{-1} peaks. A drastic decrease in the sulfonate functional group is also happening.

Table 3. Changes in the absorption of $-OH$ and $C=O$ during multi-level acetylation of Lignin sulfonate

Acetylated lignin sulfonate	Acetylation levels	$-OH$		$C=O$	
		Bond (cm^{-1})	absorption	Bond (cm^{-1})	absorption
lignin sulfonate	First level	3426	29	1754	49
	Second level	3428	43	1756	53
	Third level	3457	68	1752	47
Lignin sulfonate (Standard)		3446	10	-	-



Scheme. 4. FTIR spectrum; acetylated lignin sulfonate (AC-LS) & Lignin sulfonate in all three steps of acetylation

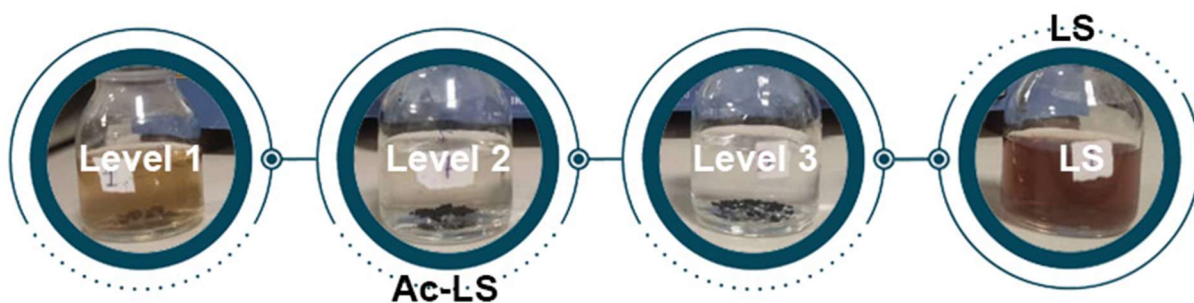
It is also based on Table 4 and Scheme. 5, the solubility of the samples in water shows a decreasing trend with increasing acetylation steps, while Lignin sulfonate is very hydrophilic, and the solubility of Lignin sulfonate in water is higher. The reason for increasing the solubility of Lignin sulfonate in water can be related to the presence of hydroxyl and sulfonate factors in the structure of Lignin sulfonate. Therefore, the solubility decreases by performing the acetylation steps, so the solubility of Lignin sulfonate reaches about 17% of its initial value after three times acetylation. Considering the brown color of Lignin sulfonate, if Lignin sulfonate is dissolved in water, the water will turn brown. Due to the completion of Lignin sulfonate's second and third acetylation steps, its brown color (the possibility of removing chromophoric groups [47] from the structure of

Lignin sulfonate) is no longer observed. Therefore, triple Acetylated lignin sulfonate can be used as an absorbent or base in various industries, including water and wastewater treatment. In a report, Lignin sulfonate was used as an iron corrosion inhibitor in aqueous environments [44].

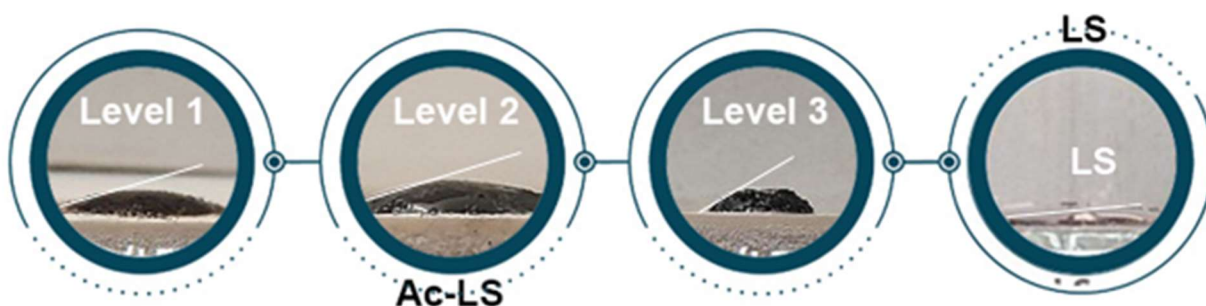
The change in the contact angle of Lignin sulfonate and the product in all three stages of the acetylation process is presented in Scheme. 6. The results show that lignin sulfonate has created the highest level of hydrophilicity. The increase in the contact angle of the product indicates that the multi-stage acetylation process has positively affected the product's hydrophobicity. In other words, by performing the stepwise acetylation process, the contact angle concerning the horizon increases as the number of steps increases.

Table 4. Acetylated lignin sulfonate solubility at all three acetylation levels in water (at room temperature for 24 hours)

Acetylation Levels	Solubility in water (g/100 ml)		Solubility in water (%)	
	Acetylated lignin sulfonate		Acetylated lignin sulfonate	
1	0.5965		59.5	
2	0.354		35.4	
3	0.177		17.7	



Scheme. 5. Color change and solubility trend of Lignin sulfonate and Acetylated lignin sulfonate in all three stages of the acetylation process

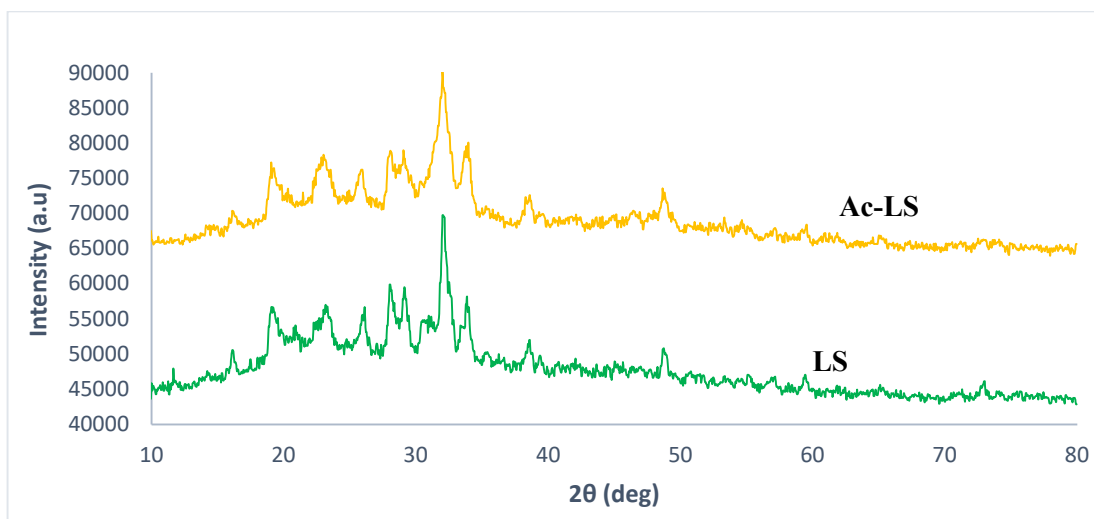


Scheme. 6. Change of contact angle of Lignin sulfonate and Acetylated lignin sulfonate in all three stages of the acetylation process

3.5. Characterization by XRD

In general, the supramolecular structure of lignin is considered amorphous. It has an irregular spherical structure, and lignin sulfonate is in the form of unstable particles due to its polyelectrolyte properties [48]. XRD analysis was performed to evaluate the crystal structure of Lignin sulfonate samples and the product of the acetylation process (Acetylated lignin sulfonate) in Scheme. 7. In the obtained patterns, two relatively sharp

peaks are observed at the distance of 20.3 degrees and 32.4 degrees, which are related to crystalline regions, and small peaks on the broad curve are related to amorphous regions. As can be seen, the intensity of the peaks and the structure of the crystals are maintained during the acetylation process. However, less broad peaks appear in the curve of Acetylated lignin sulfonate. This can probably be attributed to the increased distance between the crystal layers [49].

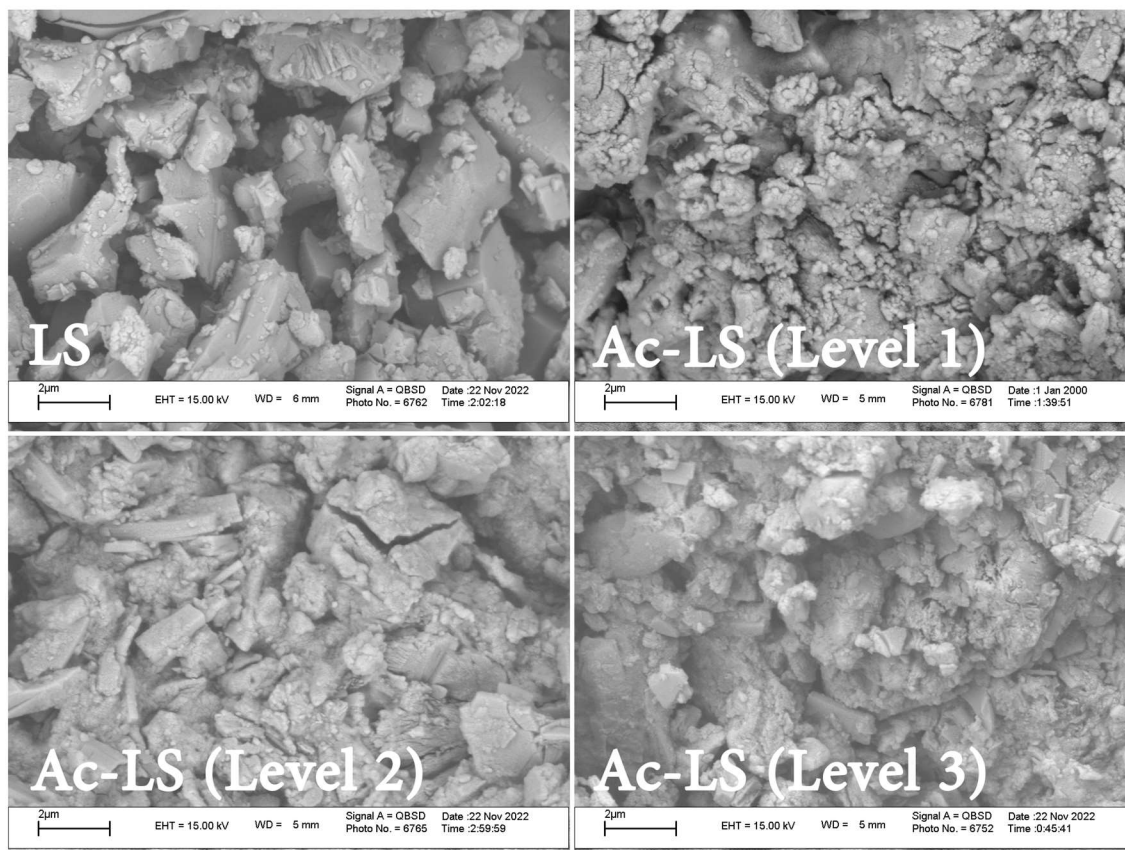


Scheme. 7. X-ray diffraction (XRD) curves: Lignin sulfonate (LS) and acetylated lignin sulfonate (Ac-LS) in the first stage of the acetylation process

3.6. Characterization by SEM

SEM images of Lignin sulfonate and the product in all three stages of the acetylation process are shown in Scheme. 8. The structure of Lignin sulfonate is observed

in the form of large irregular blocks and smooth surfaces, which shows the main characteristic of its structure. While other images related to the acetylation process of Lignin sulfonate (steps 1 to 3) show an uneven surface. This unfairness is observed more in stages 2 and 3.



Scheme. 8. SEM images of lignin sulfonate and product in all three stages of the acetylation process

4. Conclusion

The complex structure of lignin makes it difficult to use in commercial applications; therefore, the best way to use this renewable product is to modify its chemical structure. The functional groups in the structure of lignin cause its changes and reactivity. One of the properties of lignin is its solubility and hydrophilicity. By reducing hydroxyl and sulfonate functional groups, the solubility of lignin, especially Lignin sulfonate, can be reduced.

The acetylation process is a suitable solution for reducing $-OH$ s. This research extracted Lignin sulfonate from the wastewater of a wood and paper factory in Iran. Then, its solubility was significantly reduced by carrying out the multi-stage acetylation process of Lignin sulfonate. Also, due to Lignin sulfonate's second and third stages of acetylation, its brown color was no longer observed in the aqueous medium. This article studied

structural changes of lignin using FT-IR, GC-MS, SEM, XRD, and contact angle analyses. From the comparison of FT-IR spectra of Lignin sulfonate and Acetylated lignin sulfonate in the broad areas of $3200-3500\text{ cm}^{-1}$, a severe decrease in the peak of the hydroxyl group was observed by performing stepwise acetylation. Also, in addition to reducing the $-OH$, the absorption peak of the $C=O$ can be seen in all three stages of the acetylation process. Also, the contact angle method proved that by doing more steps of acetylation, the contact angle increases concerning the horizon surface. In other words, increasing the contact angle means decreasing the solubility and hydrophobicity of the substance. SEM images showed the appearance of modified Lignin sulfonate and Lignin sulfonate. The stepwise operation could not have a profound change on the external structure of lignin. Also, XRD confirmed the amorphous

nature of Lignin sulfonate and Acetylated lignin sulfonate.

One of the essential results of this research is the analysis of the extreme exothermicity of the acetylation reaction. The reaction between ethanol and excess acetic

anhydride is highly exothermic, so the balloon temperature reaches 82 °C in less than 5 minutes. Also, from the results of GC-MS analysis, it can be seen that methyl acetate, ethyl acetate, and acetic acid are intermediate products of acetylation reaction.

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