

## 이온교환체로서 리그닌의 이용과 평가

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## Use and Evaluation of Lignin as Ion Exchangers

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**요 약.** 수산화나트륨과 과산화 무기산을 사용하여 흑색 액체로부터 수산화 리그닌과 과산화 리그닌을 얻었다. 과산화 리그닌을 10% HCl을 사용하여 가수분해하여 가수분해 리그닌을 얻었다. 카르복실화와 인산화과정을 거쳐 카르복시 리그닌과 인산화 리그닌을 얻었다. 에피클로르히드린을 사용하여 가교 리그닌도 얻었다. 이들 얻어진 리그닌들을 적외선분광법, 열량분석, 시차열분석법으로 분석 하였다. 이들 얻어진 리그닌의 금속이온 흡착효과를 조사하였다. 과산화 리그닌이 수산화된 리그닌 보다 흡착 능력이 우수하였다.

**주제어:** 가수분해 리그닌, 인산화 리그닌, 가교된 리그닌, 과산화 리그닌, 염기성 리그닌

**ABSTRACT.** Modified lignins were prepared. Soda and peroxy lignins were precipitated from black liquor produced from bagasse pulping with soda and peroxyacid pulping process. The precipitated lignins were hydrolyzed using 10% HCl. Different functional groups were also incorporated into lignin by carboxylation and phosphorylation reactions. Moreover crosslinking of these lignins were carried out using epichlorohydrin. Characterization of the modified lignins and lignins derivative were carried out using Infrared spectroscopy. Thermal analysis of these compounds were also carried out using TGA and DTA techniques. Efficiency of sorption of metal ions by the modified lignin was also investigated. It was found that, the peroxy lignin and its derivatives show higher efficiency toward metal ions uptake than the soda lignin.

**Keywords:** Hydrolyzed lignin, Phosphorylated lignin, Crosslinked lignin, Peroxy lignin, Soda lignin

## INTRODUCTION

Fibrous raw materials such as wood or agricultural residues consist of three dominating polymers: cellulose, hemicelluloses and lignin. These polymers are known as lignocellulosic material. Lignin is the third most naturally abundant carbon substrate and is more important than hemicellulose in woody substrates. It is most resistant to microbial decomposition due to its random linkages among aromatic rings. Structurally, lignin is a complex polymer of phenyl-propane units. More than 50% of the phenylpropane units in lignin are linked by ether bonds and the rest by carbon-to-carbon bonds.<sup>1,2</sup> Lignin mainly holds the fibers together in the wood. During the chemical treatment, the linkages between lig-

nin and the other carbohydrates are broken; the lignin is degraded and the degradation products are dissolved. Because lignin is constituted basically from phenylpropane units, it is viewed as an interesting alternative source for aromatic compounds. Also, Lignins can be used in dispersant, emulsifiers, metals sequester, adhesives, ion exchangers<sup>3</sup> and phenolic resins.<sup>4-6</sup> The present study focused on the preprecipitated lignins from produced waste black liquors of soda and peroxyacid pulping. Characterization of lignin is highly affected by the pulping process. So, during pulping process, lignin is demethylated and degraded causing an increase of the phenolic hydroxyl groups.<sup>7</sup> Unmodified lignins are often poorly soluble and resist flow when heated while modified lignin differs in its solubility.<sup>8</sup>

### Characterization of different kinds of lignin (With regard to methods of isolation of lignin)

A common factor to all lignins, is that their structures consist mainly of phenyl propane units. Spectroscopic methods e.g. IR, UV and NMR can be used to get information about the structure of lignin.<sup>9</sup> Phenolic acid carboxylic groups of organosolved lignin are higher than kraft lignin. The hydroxyl groups in kraft lignin are more than in organosolved lignin.<sup>10</sup> Agricultural wastes represent a cheap source and environmentally safe raw material for preparation of ion exchangers to uptake metal ions from water.<sup>11-12</sup> The lignocellulosic materials have low ion exchange adsorption capacity as well as physical stability. Incorporation of certain groups onto the lignocellulosic materials such as phosphate, sulphate and carboxylic groups,<sup>13-14</sup> increase their sorption/adsorption efficiency toward cation exchangers. Also, it is possible to produce anion exchangers by incorporating certain groups onto agricultural residues. Epichlorohydrin is commercially used as crosslinker for preparation of acid cation exchanger.<sup>15</sup> Thermal analyses of the lignin and its derivatives are studied to give an idea of the effect of these incorporated functional groups on their molecular structure and thermal properties. Thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) reveal some analogies and difference in thermal behavior of lignin and its derivatives. It is found that, incorporation of certain functional groups, e.g. phosphate, carboxyl and cyano groups onto lignocellulosic materials increases their thermal stability.

The aim of this work is to study the molecular structure and characterization of precipitated lignin from black liquors produced by soda and peroxyacid pulping of bagasse. Also, the thermal degradation as well as the ion exchange properties of these preprecipitated lignin and its derivatives as carboxylated and phosphorylated lignins are also investigated. The crosslinking of lignin by epichlorohydrin is also studied.

## EXPERIMENTAL

### Material

The raw materials used in this study were depithed bagasse delivered from Edfo Sugar and Paper Pulp Mills, Edfo, Egypt (during depithing, bagasse lost 20% of its weight as pith); Lignin was precipitated by dilution of waste black liquor produced from bagasse peroxyacid pulping, by distilled water and dilution of waste black liquor produced from bagasse soda pulping by 50% sulfuric acid. All Reagents used for this study were obtained

from Merk-schudardt (analytical grade). Metal ions of (Cd, Mn, Zn, Mg.), all these metals are atomic absorption standard solutions (Merk).

### Methods

**Prehydrolysis:** of raw material was carried out before soda pulping process using 1.5% H<sub>2</sub>SO<sub>4</sub> for 2hr. at 110 °C in autoclave.

**Pulping of bagasse:** (a) Soda pulping: Raw material was cooked by using 20% NaOH solution using (6:1) liquor ratio, at 160 °C under pressure in autoclave for 2 hours. (b) Peroxyacid pulping method: Raw material was cooked in polyvinyl acetate bag using 16% peroxyacid and 7:1 liquor ratio at 85 °C for 2hr.

**Bleaching:** It was carried out by using sodium hypochlorite, H<sub>2</sub>O<sub>2</sub> and ClO<sub>2</sub>.

**Chemical analysis:** Lignin,  $\alpha$ -cellulose, hemicelluloses, and ash content was estimated by Tappi standard method (T13 wd-74), (T203 OS-61), (T19 wd-71) as mentioned elsewhere.<sup>16</sup>

**Degree of polymerization:** (D.P) of the produced bleached pulp was determined by dissolving the cellulose sample in a copper ammonium hydroxide, Cu concentration 13 g/l and ammonia concentration 200 g/l. By determining the viscosity of this solution, the average degree of polymerization can be easily found by applying Schulz and Blaschke, (1941) expanded Staudinger equation.<sup>17</sup>

**Lignin precipitation:** Soda lignin was precipitated from the produced waste black liquor of soda pulping using 10% H<sub>2</sub>SO<sub>4</sub>. The peroxy lignin was precipitated from the peroxy acid waste black liquor using water. After precipitation, the precipitated lignins were filtered, washed with distilled water till neutrality and then air dried.

**Hydrolysis of lignin:** Lignin was hydrolysed with 5-15% H<sub>2</sub>SO<sub>4</sub> acid under reflux for different times.

**Cellulose derivative:** (a) Carboxylated lignin: It was prepared by oxidation of lignin with sodium chlorite at 70 °C for 2hr. (b) Phosphorylated lignin: It was prepared according to the method of Lehrfeld.<sup>18</sup> (c) Crosslinking: Lignin was cross linked by epichlorohydrin.<sup>19</sup>

**Phosphorous determination:** It was determined by dissolving 0.2 g of lignin in conc. HNO<sub>3</sub> (10 ml). After complete dissolving the volume was adjusted to 25 ml in measuring flask using deionized water. The phosphorus was determined using ICP-AES Jobin Yvon J4/85 spectrometer.

**Sorption of metal ions:** 0.2 g of sample was stirred in 25 ml solution containing differ metal ions (20 ppm for every metal ion), for 30 min. filter, and the remain metal

ions in the filtrate was determined using ICP analyzer.

**Infrared spectroscopy measurement:** It was carried out by using (Jasco FTIR 8000C) Spectrometer. The sample was determined by KBr disc technique. The scanning of the FTIR spectrophotometer was carried out from 4000 to 500  $\text{cm}^{-1}$ .

**Thermal analysis:** The TGA of samples was measured using Thermogravimetric Analyzer TGA-7. All experiments were carried out under  $\text{N}_2$  atmosphere where heating ratio 10  $^\circ\text{C}/\text{minute}$ .

## RESULTS AND DISCUSSION

Table 1 show results of the ability of lignin and its derivative of the absorption of different metal ions, (Cd, Mn, Zn, Mg), results in Table 1 could be summarized as follows (a) Comparison of the ability of peroxy lignin to absorb metal ions with soda lignin shows that the peroxy lignin is more efficient than soda lignin. (b) Incorporation of different functional groups into lignin increases its sorption properties to metal ions uptake so, the metal ions uptake by the hydrolyzed lignin is higher than that in case of unhydrolyzed soda lignin. (c) Uptake ability are improved as a results of lignin modification

### Comparison between different kinds of lignin soda and peroxy acid lignin to metal ions

Table 1 show the results of Metal ion absorbed by soda compared to peroxyacid lignin, generally peroxy lignin show higher efficiency to absorb metal ions from their solution than soda lignin, in fact, even efficiency of the

**Table 1.** Ion exchange properties of incorporated lignin with different functional groups

Kind of lignin	Metal ions uptake microgram $\mu$ mole/g			
	Cd	Mn	Zn	Mg
Soda lignin	0.77	85.8	6.2	3.9
peroxy lignin	1.50	90.10	10.90	5.60
Hydrolyzed soda lignin	1.20	90.5	8.3	4.8
Crosslinked soda lignin	0.98	90.4	8.1	5.2
Carboxylated lignin	1.10	96.4	9.6	8.2
Phosphorylated lignin	1.95	104.2	24.3	11.6
Phosphorylated peroxy lignin	2.00	125.3	30.2	16.4

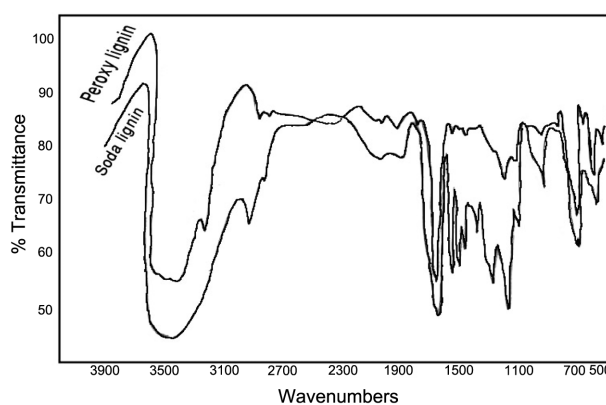
**Table 2.** Relative absorbance of some characteristic bands of hydrolyzed and Unhydrolyzed soda lignin and peroxyacid lignins

Kind of lignin	CH (2830 $\text{cm}^{-1}$ )	OH (3420 $\text{cm}^{-1}$ )	OH Phenolic (1375 $\text{cm}^{-1}$ )	COOH (1715 $\text{cm}^{-1}$ )	$\beta$ -o-4lignin (1112 $\text{cm}^{-1}$ )
Soda lignin	0.53	1.80	0.11	0.11	1.95
Peroxyacid lignin	----	2.10	0.98	0.86	1.15
Hydrolyzed soda lignin	0.41	----	0.43	0.24	1.80

metal uptake is improved when peroxy lignin is used but it seem that absorption improvement is metal dependant; efficiency was improved by 94.8%, 5%, 75.8% and 43.6%) for Cd, Mn, Zn and Mg, respectively), efficiency improvement could be attributed to the increase of carboxyl groups formation in peroxy lignin and increase of degradation of  $\beta$ -O-4 linkage between the units of lignin molecule (phenyl propane unites) during peroxyacid pulping process. This degradation increases the formation of OH phenolic groups in lignin molecule (Table 2). This was confirmed by the higher relative absorbance (ratio of intensity of any band/band intensity at 1325  $\text{cm}^{-1}$ ) of C=O of carboxyl groups at 1715  $\text{cm}^{-1}$  and the lower relative absorbance of the band which is characteristic of  $\beta$ -O-4 of peroxyacid lignin over the soda lignin. As shown in Table 2 and Fig. 1 the relative absorbance of OH phenolic groups 375  $\text{cm}^{-1}$  in case of peroxyacid lignin, is higher than that of the soda lignin. All these reasons cause an increase of the efficiency of peroxyacid lignin toward metal ion uptake than soda lignin.

On the other hand, variation of the ability of soda and peroxyacid lignin to absorb different metal could be attributed to steric and electronic effects of metal ions and lignin. Also, ionic radius of metal ions has a highly effect on the binding of metal ions with lignin. Boyed<sup>20</sup> stated that, the ion exchange sorption affinities are determined chiefly by the magnitude of the charge and hydrated radius of ions in solution.

Thermal analysis measurements of the precipitated lig-



**Fig. 1.** Infrared spectroscopy of Soda and Peroxyacid Lignin.

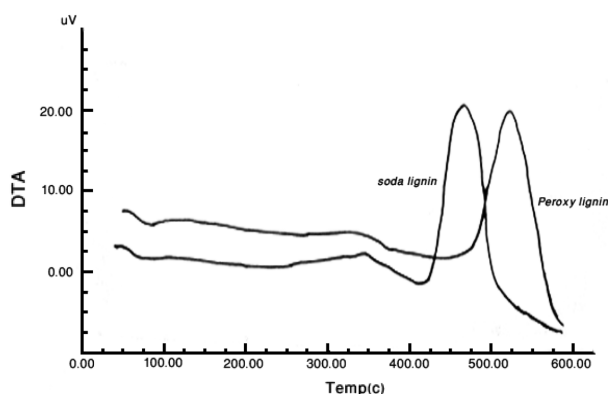


Fig. 2. Differential thermal analysis of Soda and Peroxy Lignin.

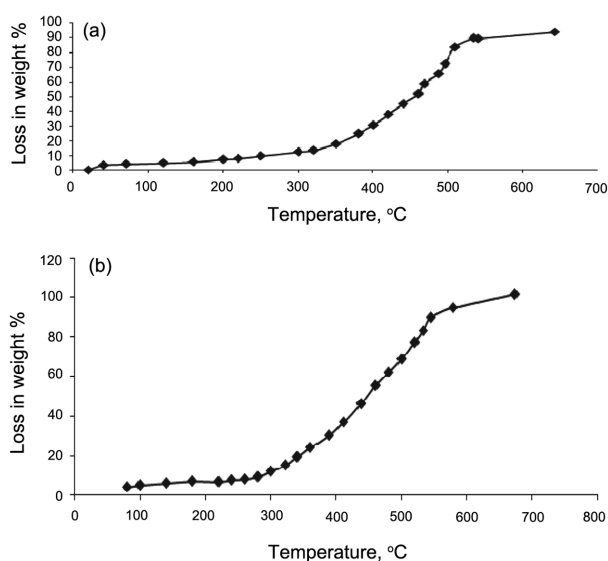


Fig. 3. TGA of (a) soda lignin and (b) peroxyacid lignin.

nin were also studied to draw a picture about the stability of different lignin against thermal treatment.

Fig. 2 show the thermal analysis curve of soda and peroxyacid lignins Fig. 2, as we can deduce from the curve, there are two exothermic bands at about 485 and 540 °C for soda and peroxyacid lignin, respectively which reflect the higher thermal stability of peroxy lignin against soda, which may be attributed to the higher carboxyl content of peroxyacid lignin compared to soda lignin. Thermal gravimetric analysis curve, TGA of soda and peroxy acid lignins Fig. 3 Show that minor and major decomposition temperature of peroxy lignin is higher than that of the soda lig-

nin. Results were calculated and tabulated in Table 3.

From the Table 3, the minor decomposition temperature of lignin started from 180 °C with decrease in weight. This can be due to the pyrolysis of the lignin to different gases by increasing the temperature. The major decomposition temperature was due to the increase of the combustion of the material and change to carbon dioxide.

Although the minor and major decomposition temperature of peroxy lignin was higher than soda lignin, the loss in weight in case of peroxy lignin is nearly lower than soda lignin if they calculated at the same temperature. The higher stability of peroxy lignin against thermal effect, than soda lignin can be attributed to the increase of the formation of carboxyl groups in peroxy lignin as well as dissolving of low molecular weight of lignin during pulping process.

#### Effect of hydrolysis on the affinity of lignin toward metal ion absorption:

Table 1 show results of the metal absorption of different metal by the hydrolyzed and unhydrolyzed soda lignin, from Table 1 it is clear that the metal ions uptake by the hydrolyzed lignin is higher than unhydrolyzed soda lignin, The absorption of metal ions uptake improvement is metal dependant; efficiency was improved by 55.8%, 5.2%, 33.9% and 23.1%) for Cd, Mn, Zn and Mg, respectively) This can be attributed to the increased degradation of lignin polymer. This degradation increases the end groups of the lignin which in turn increases the formation of carboxylic and hydroxyl groups that enhance their efficiency toward metal ions absorption. This can be confirmed by the lower relative absorbance of band at 1112  $\text{cm}^{-1}$  (which characteristic to the  $\beta$ -O-4 linkage between lignin molecule) of hydrolyzed lignin than unhydrolyzed one. Table 2.

From Table 2 relative absorbance of the C-O band band at 1375  $\text{cm}^{-1}$  charactrstic to C-O of phenolic OH group is increased by hydrolysis, which also affect the affinity of the hydrolyzed lignin toward metal ions uptake (i.e., it increase the affinity of hydrolyzed lignin toward metal ions uptake) above finding is confirmed by the decrease of the relative absorbance of -CH band of -CH<sub>3</sub> of methoxyl group of the hydrolyzed lignin due to the hydrlysis of -OCH<sub>3</sub> with increases of the relative absorbance of -OH of hydrolyzed lignin.

Table 3. Thermal gravimetric analysis of soda and peroxyacid lignin

Kind of lignin	Minor decomp. (Temp.)	Wt. Loss (%)	Major decomp. (Temp.)	Wt.Loss (%)
Soda lignin	180	8	540	88
Peroxy lignin	240	11	570	90

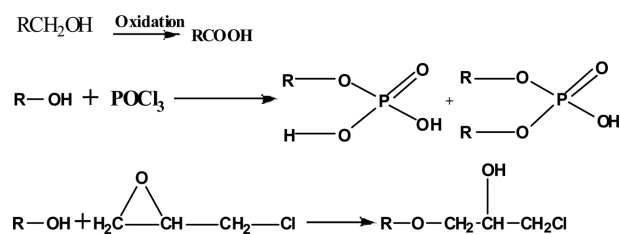
### Ion exchange properties of incorporated lignin with different functional groups

Ion exchange and infrared properties of incorporated lignin with different functional groups e.g. carboxylic, crosslinked and phosphorylated lignin were also studied; results are summarized in *Table 1*.

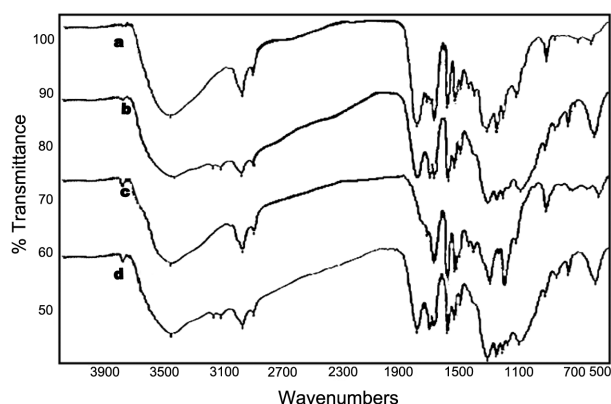
It is clear that the incorporated functional group in lignin has a high effect on the efficiency of lignin in metal ion uptake, moreover, lignin with incorporated phosphate group has a higher effect on efficiency of lignin in metal ions uptake. (i.e., generally phosphorylated lignin more than Carboxylated more than crosslinked one), *Table 1*. This can be attributed to the fact that the phosphate group incorporated by the lignin, has two anions beside one anion but the carboxyl or crosslinking formed has one anion, as shown in *Scheme 1*.

Crosslinking of lignin with epichlorohydrine increases its affinity to absorb metal ions. This can be attributed to the increase of chains which attached to lignin and consequently this increase the contact between metal ions and lignin. So, the absorption of metal ions increases.

Phosphorylated peroxy lignin has a higher efficiency toward metal ions uptake compared to the phosphorylated soda lignin. This is attributed to the phosphorylated peroxy lignin which has two kinds of functional groups which is able to absorb metal ions. These groups are  $\text{—}\overset{\text{O}}{\text{C}}\text{—OH}$  and



*Scheme 1.*



**Fig. 4.** IR spectra of (a) peroxy lignin, (b) phosphorylated peroxy lignin, (c) Soda lignin, and (d) phosphorylated soda lignin.

$\text{—}\overset{\text{O}}{\text{P}}(\text{OH})_2$  groups. This also due to the higher phosphate groups (72 ppm) in peroxy lignin than soda lignin (63 ppm). So for these reasons, the phosphorylated peroxy lignin has a higher efficiency toward metal ions uptake than phosphorylated soda lignin. This was confirmed by infrared spectra in which the relative absorbance of C-O-P band at  $1200\text{ cm}^{-1}$  (which characteristic to phosphate group) of peroxy lignin phosphate is (1.4) while it was (1.16) in the soda lignin phosphate. *Fig. 4*.

## CONCLUSION

The increase of carboxyl groups of peroxy lignin which is formed during the peroxyacid pulping process, as well as, the increase of degradation of  $\beta$ -O-4 linkage between the units of lignin molecule. This degradation increases the formation of -OH phenolic groups in peroxy acetic acid lignin molecule leading to higher efficiency of peroxy lignin to absorb metal ions, from their solution, than soda lignin. Peroxy lignin has a higher stability for thermal treatments than the soda lignin.

Incorporation of different functional groups into lignin increases its sorption properties to metal ions uptake so, the metal ions uptake by the hydrolyzed lignin is higher than that in case of unhydrolyzed soda lignin. The lignin with incorporated phosphate group has a higher effect on efficiency of lignin toward metal ions uptake than carboxyl or crosslinking one. The sorption of metal ions depends on the structure of ions exchanger electronegativity, steric and radius of metal ions.

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