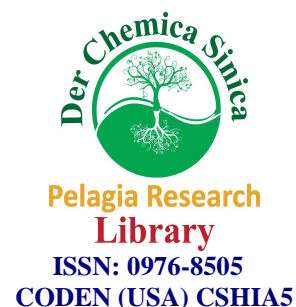




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Preparation of lignin from waste black liquors as ion exchangers

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ABSTRACT

Soda and peroxyacid lignins are precipitated from produced black liquor from cotton stalks pulping with soda and peroxyacid pulping process. These precipitated peroxyacid lignins are hydrolyzed using 10% HCl. Different functional groups are incorporated into lignin by carboxylation and phosphorylation reactions. Also, cross linking of these lignins was carried out by using epichlorohydrine. Infrared spectroscopy of these lignins and their derivatives were studied. On the other hand, the efficiency of sorption of metal ions by this modified lignin was investigated. It has been seen that, the peroxyacid lignin has higher efficiency toward metal ions uptake than the soda lignin. Thermal analysis of these lignins was also studied using TGA and DTA techniques.

Keywords: lignin, peroxyacid lignin, soda pulping, peroxyacid pulping, cotton stalks, ion exchanger.

INTRODUCTION

The largest renewable resource of carbohydrates in nature is lignocellulosic biomaterials. Lignocellulosic biomass is less expensive and more abundant than starch or sucrose containing Feedstocks [1]. Lignocellulosic biomaterials are grouped into different categories according to source, such as forest biomass (hard wood, soft wood, saw dust), agricultural residues (corn stover, cob, wheat straw, rice straw, oat hull, sugar bagasse, cotton stalk), herbaceous grass (switch grass, bermuda grass, alfalfa fiber, rye grass) and municipal waste (waste paper, waste food, paper mill sludge) [2,3,4]. Besides these lignocellulosic materials some free-floating aquatic plants like water hyacinth, water lettuce have also been reported for good carbohydrate content [5,6]. Lignocellulosic biomass is composed of majorly carbohydrate polymers (cellulose and hemicellulose), relatively much lesser quantity of lignin and a small fraction of other compounds like extractives, acids, salts and minerals. The cellulose and hemicellulose, which typically comprise two thirds of the dry mass, are polysaccharides that can be hydrolysed to sugars and eventually be converted to valuable products mainly via fermentation [7]. The main products obtained from this route include enzymes, furfural, amino acids, organic acids (e.g. lactic acid, succinic acid), biohydrogen, methane and bioethanol [8]. Bioethanol produced from various lignocellulosic materials is a renewable fuel, is becoming increasingly important today as a consequence of greater concern for the increasing greenhouse effect, depleting oil reserves, and rising oil prices [9- 11].

The present study is focused on the precipitated 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 [12]. Because lignin is constituted basically from phenylpropane unites, it is a source for aromatic compounds. It can be used as a source of dispersant, emulsifiers, adhesives and ion exchangers [13-17] and phenolic resins.

A common factor to all lignins is that their structures are mainly consisting of phenyl propane units [18]. Spectroscopic methods e.g IR, UV and NMR can be used to give information about the structure of lignin [19].

Phenolic acid carboxylic groups of organosolve lignin are higher than in case of kraft lignin. The hydroxyl groups in kraft lignin are higher than that in organosolve lignin [20, 21]. Agricultural wastes represent of cheap and environmentally safe as a material for preparation of ion exchangers for metal ions uptake from water [22, 23]. The lignocellulosic materials have low ion exchange adsorption capacity as well as physical stability. So, chemical modification, copolymerization [24] or cross-linking [25] of these agricultural wastes allow for the development of efficient ion exchangers [26] to the agricultural residues increase their efficiency toward cation exchange. Incorporation of certain groups onto the lignocellulosic materials such as phosphate, sulfate and carboxylic groups [27- 29] increased their sorption efficiency toward cation exchangers. Also, it can be possible to produce anion exchangers by incorporation of certain groups onto agricultural residues. Epichlorohydrine is a commercially used as cross linker for preparation of acid cation exchanger [30]. Thermal analyses of the lignin and its derivatives are studied to give an idea on 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.

In this study, the structure and characterization of precipitated lignin from produced black liquors wastes from soda and peroxyacid pulping of cotton stalks provided from the field was carried out. On the other hand, the thermal degradation as well as the ion exchange properties of these precipitated lignin and its derivatives as carboxylated and phosphate lignins were also investigated. The cross linking of lignin by epichlorohydrine was also studied.

MATERIALS AND METHODS

Raw material

The raw material used in this work was debarked cotton stalks raw material delivered from the field, Egypt.

Preparation of pulp

Soda pulping method

Soda pulping of raw material was carried out using 20 % NaOH solution using (10:1) liquor ratio, at 150°C under pressure in autoclave for 2 hours.

Peroxyacid pulping method

Peroxyacid pulping of cotton stalks raw material was carried out by cooking in polyvinyl acetate bag using 16 % peroxyacid and 10:1 liquor ratio at 80°C for 2hr.

The percentage of lignin, α -cellulose, hemicelluloses [31], and ash content was determined according to [32]. The produced pulp bleached by using sodium hypochlorite, H₂O₂ and ClO₂.

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 [33] expanded Staudinger equation:

Lignin precipitation

Precipitation of lignin from waste black liquor produced from soda pulping of cotton stalks was carried out using 10 % H₂SO₄. The peroxyacid lignin was precipitated from the peroxyacid acid waste black liquor using water. After precipitation, the precipitated lignins were filtered, washed with distilled water till neutrality and then air dried. Lignin was hydrolyzed with 5-15 % H₂SO₄ acid under reflux for different times.

Carboxylation

Carboxylated lignin was prepared by oxidation of lignin with sodium chlorite at 70°C for 2hr.

Phosphorylation

Phosphorylated lignin was prepared according to the method of [29, 34]. Lignin has been reacted with phosphorous oxychloride (POCl₃) in the presence of pyridine under reflux at 115°C for 2 hrs.

Crosslinking

Lignin was cross linked by epichlorohydrine [35].

determination of incorporated Phosphate groups onto lignin

0.1g of phosphorylated lignin was boiled in conc. HNO_3 (10ml) until dissolution, and cooled. 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.

Ion Exchanger

0.2g of phosphorylated lignin was stirred in 25 ml solution containing mixture of metal ions (Fe, Cu, Cr, and Pb) of 20 ppm concentration for every metal ion), for 30 min. The reaction product was filtered, and the remaining metal ions in the filtrate were determined using ICP spectrometer.

Infrared spectroscopy of precipitated lignin was carried out by (Jasco FTER 8000C) Spectrometer. The sample was determined by KBr disc technique.

The TGA of samples was measured using Thermogravimetric Analyzer TGA-7. All experiments were carried out under N_2 atmosphere where heating ratio $10^\circ\text{C}/\text{minute}$.

RESULTS AND DISCUSSION**Characterization of different kinds of lignin (soda and peroxyacid lignin)****Ion exchange properties**

It is found that the peroxyacid lignin has a higher efficiency to absorb metal ion from their solution than soda lignin Table (1). This can be due to the increase of formation carboxyl groups in peroxyacid lignin and. Increase of degradation of $\beta\text{-O-4}$ 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 (1). This confirmed by the higher relative absorbance (ratio of intensity of any band /band intensity at 1325cm^{-1}), of C=O of carboxyl groups at 1715 cm^{-1} and the lower relative absorbance of the band which characteristic of $\beta\text{-O-4}$ of peroxyacid lignin than the soda lignin. . From the table it is seen also, that the relative absorbance of OH phenolic groups at 1375 cm^{-1} in case of peroxyacid lignin is higher than that in soda lignin. All these reasons cause an increase of the efficiency of peroxyacid lignin toward metal ion uptake than soda lignin.

From table (2), it is clear that the amount of the absorbed different metal ions by soda or peroxyacid lignin is not the same. This is probably due to both 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. [35] stated that, the ion exchange sorption affinities are determined chiefly by the magnitude of the charge and hydrated radius of ions in solution.

The thermal analysis of the precipitated lignin was investigated to give an idea of the stability of different lignin against thermal treatment.

From differential thermal analysis curve of soda and peroxyacid lignins Fig. (2), it is seen two exothermic band at about 485 and 540°C for soda and peroxyacid lignin respectively. This means that the peroxyacid lignin is higher stability for thermal treatments than the soda lignin. This may be due to the higher carboxyl content of peroxyacid lignin than soda lignin.

From TGA curve of soda and peroxyacid lignins Fig. (3), it is seen that the minor and major decomposition temperature of peroxyacid lignin is higher than that in case of soda lignin. The results were calculated and tabulated in Table (3).

From the table, the minor decomposition temperature of lignin is begun 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 formed due to the increase of the combustion of the material and change to carbon dioxide.

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

From table (4) it is clear that the metal ions uptake by the hydrolyzed lignin is higher than that in case of unhydrolyzed soda lignin. This can be due to the increase in the degradation of lignin polymer. This degradation increase the end groups of the lignin which increase of the formation of carboxylic and hydroxyl groups which

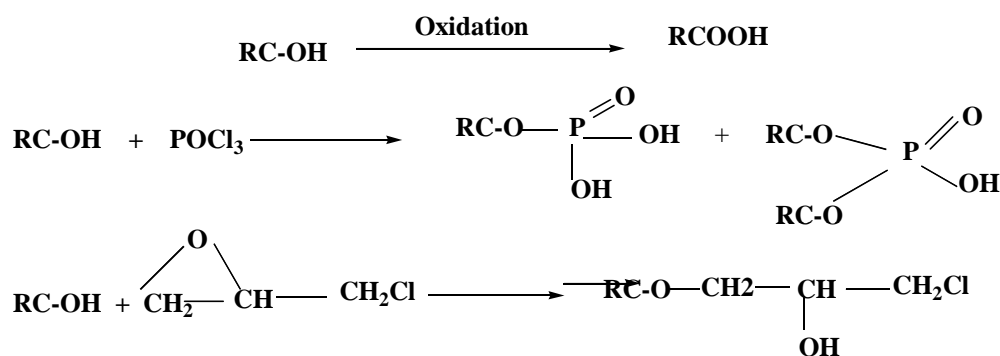
enhancing its efficiency toward metal ions absorption. This can be confirmed by the lower relative absorbance of band at 1112cm^{-1} (which characteristic to the $\beta\text{-O-4}$ linkage between lignin molecule) of hydrolyzed lignin than unhydrolyzed one Table (5).

Also from the table, it is seen that the relative absorbance of band at 1375cm^{-1} characteristic to C-O of phenolic OH group is increase by hydrolysis. This may be also increase the affinity of hydrolyzed lignin toward metal ions uptake. These can be confirmed by decrease the relative absorbance of $-\text{CH}$ band of $-\text{CH}_3$ of methoxy group of the hydrolyzed lignin due to the hydrolysis of $-\text{OCH}_3$ with increase the relative absorbance of $-\text{OH}$ of hydrolyzed lignin.

Ion exchange properties of incorporated lignin with different functional groups

In another trial the ion exchange and infrared properties of incorporated lignin with different functional groups e.g. carboxylic, cross linked and phosphorylated lignin are examined, Table (6).

From Table (6), it is clear that the incorporated functional group in lignin has a high effect on the efficiency of lignin toward metal ion uptake. It is seen from table that the lignin with incorporated phosphate group has a higher effect on efficiency of lignin toward metal ions uptake. This can be due to that the phosphate group incorporated the lignin has two anion beside one anion but the carboxyl or crosslinking formed has one anion as shown in the following scheme:



Cross linking of lignin with epichlorohydrine increases its affinity to absorb metal ions. This can be attributed to the increase of chains which attached with lignin and consequently this increase the contact between metal ions and lignin. So, the absorption of metal ions increases. From table (6) it is clear that the phosphorylated peroxyacid lignin has a higher efficiency toward metal ions uptake than the phosphorylated soda lignin. This is attributed to that the phosphorylated peroxyacid lignin has two kinds of functional which has affinity to absorb metal ions. These groups are COOH and PO_4H_2 groups. This also due to the higher phosphate groups (72 ppm) in peroxyacid lignin than soda lignin (63 ppm). So for these reasons, the phosphorylated peroxyacid lignin has a higher efficiency toward metal ions uptake than phosphorylated soda lignin. This can be proved from infrared spectra in which the relative absorbance of C-O-P band at 1200cm^{-1} (which characteristic to phosphate group) of peroxyacid lignin phosphate is (1.4) while it was (1.16) in the soda lignin phosphate.

Metal ion uptake by phosphorylated bleached cotton stalks pulp and lignin

The comparison between lignin and the produced bleached pulp was investigated. From Table (7), it is clear that the bleached pulp has higher affinity toward sorption of metal ions than the soda lignin. This can be explained by the higher OH groups incorporated in cellulose as well as higher porosity of bleached pulp (due to its formation of chains) than lignin. This cellulosic chain increases the pulp porosity and consequently the contact between cellulose chains and metal ions enhances. This increases the sorption of metal ion by cellulose.

From table (8), it is clear that the decomposition temperature of lignin is higher than bleached pulp with low weight loss% Fig. (4). This is attributed to that the nature of lignin was molecules bonded with each other with $\beta\text{-O-4}$ linkage, but in case of bleached pulp it consists of chain arranged on each other. This means that lignin has high resistance against thermal treatment more than cellulose.

Table (1): Relative absorbance of some characteristic bands in precipitated soda and peroxyacid lignins.

Kinds of lignin	OH (3420cm^{-1})	OH Phenolic (1375cm^{-1})	COOH (1715cm^{-1})	$\beta\text{-O-4}$ lignin (1112cm^{-1})
Soda lignin	1.81	0.12	0.12	1.96
Peroxyacid lignin	2.11	0.99	0.87	1.16

Table (2): Metal ions absorbed by soda and peroxyacid lignin:

Kinds of lignin	Cd (μ mole/g)	Mn (μ mole/g)	Zn (μ mole/g)	Mg (μ mole/g)
Soda lignin	0.78	85.21	6.21	3.92
Peroxyacid lignin	1.51	90.11	10.91	5.62

Table (3): Thermal gravimetric analysis of soda and kraft lignin:

Kind of lignin	Minor decomp. (temp.)	Wt. Loss (%)	Major decomp (temp.)	Wt. Loss (%)
Soda lignin	180	7	541	87
Peroxyacid lignin	240	10	571	90

Table (4): Effect of hydrolysis of the affinity of lignin toward metal ion absorption:

Kind of lignin	Cd (μ mole/g)	Mn (μ mole/g)	Zn (μ mole/g)	Mg (μ mole/g)
Soda lignin	0.77	85.8	6.2	3.9
Hydrolyzed soda lignin	1.20	90.5	8.3	4.8

Table (5): relative absorbance of characteristic bands of hydrolyzed and unhydrolysed soda lignin.

Kind of lignin	CH (2830 cm^{-1})	OH plane (1375 cm^{-1})	COOH (1715 cm^{-1})	B-O-4 (1112 cm^{-1})
Soda lignin	0.53	0.11	0.09	1.95
Hydrolyzed soda lignin	0.41	0.43	0.24	1.80

Table (6): Ion exchange properties of lignin derivative of different function groups:

Kinds of lignin	Metal ions uptake microgram μ mole/g			
	Cd	Mn	Zn	Mg
Soda lignin	0.77	85.8	6.2	3.9
Cross linked 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 (7): The metal ions uptake by lignin and bleached pulp.

Material	Metal ions uptake microgram (μ mole/g)			
	Cd	Mn	Zn	Mg
Bleached pulp	2.64	89.4	16.2	4.8
Soda lignin	0.77	85.2	6.2	3.9

Table (8): Thermogravimetry analysis of bleached pulp and lignin.

Material	Minor decomp. (temp.)	Wt. Loss (%)	Major decomp. (temp.)	Wt. Loss (%)
Bleached pulp	280	8	450	92
Soda lignin	180	8	500	86

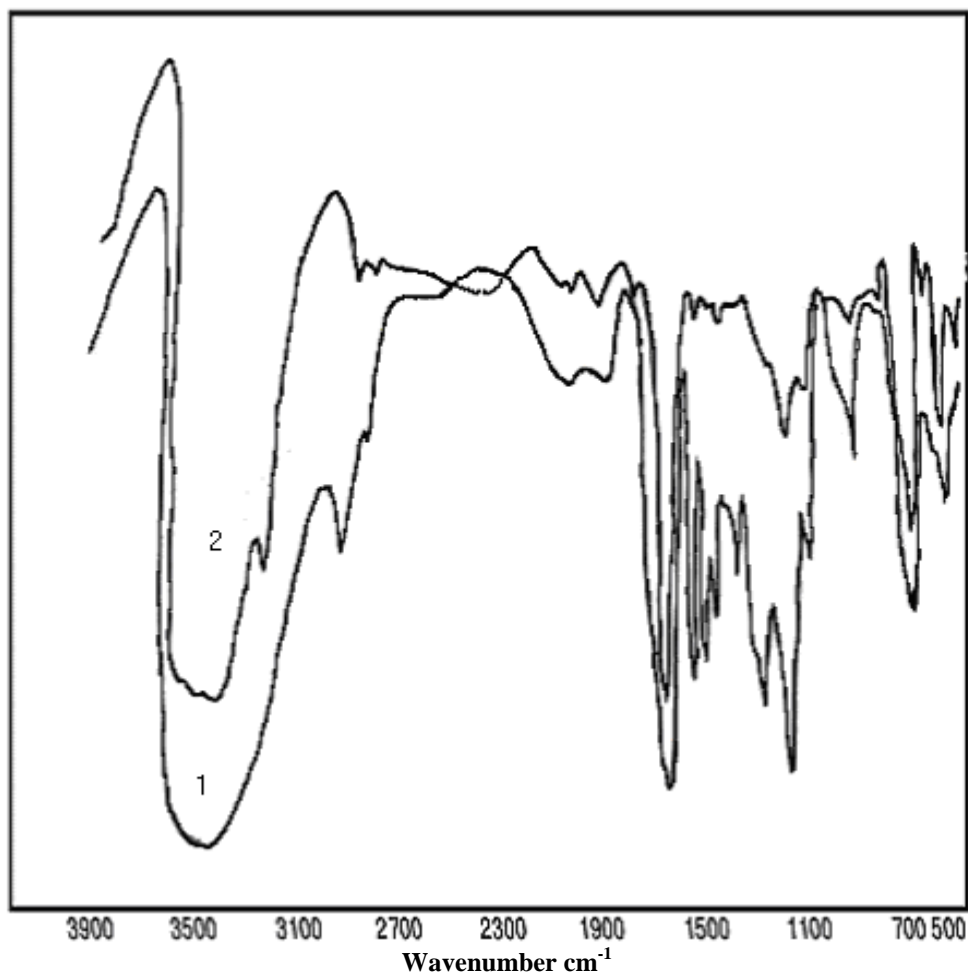


Fig (1): Infrared spectroscopy of (1) soda and (2) peroxyacid lignin.

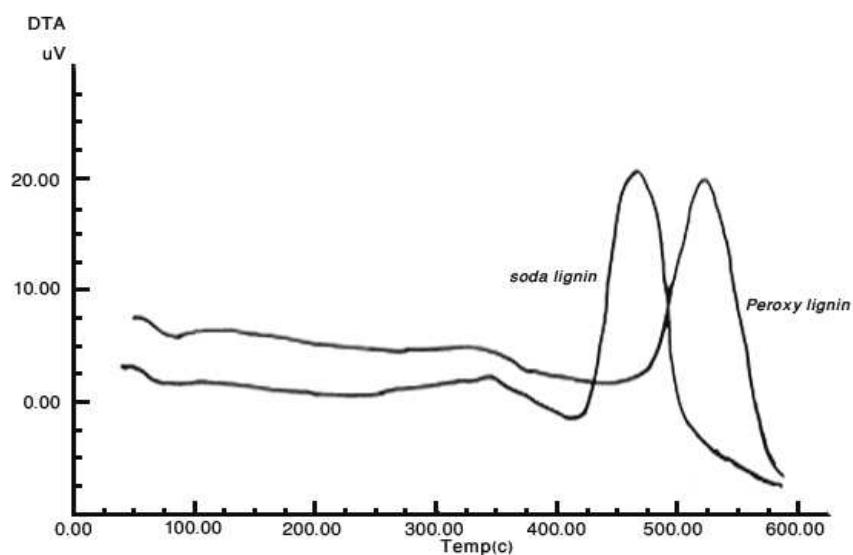


Fig (2): Differential thermal analysis of soda and peroxyacid lignin

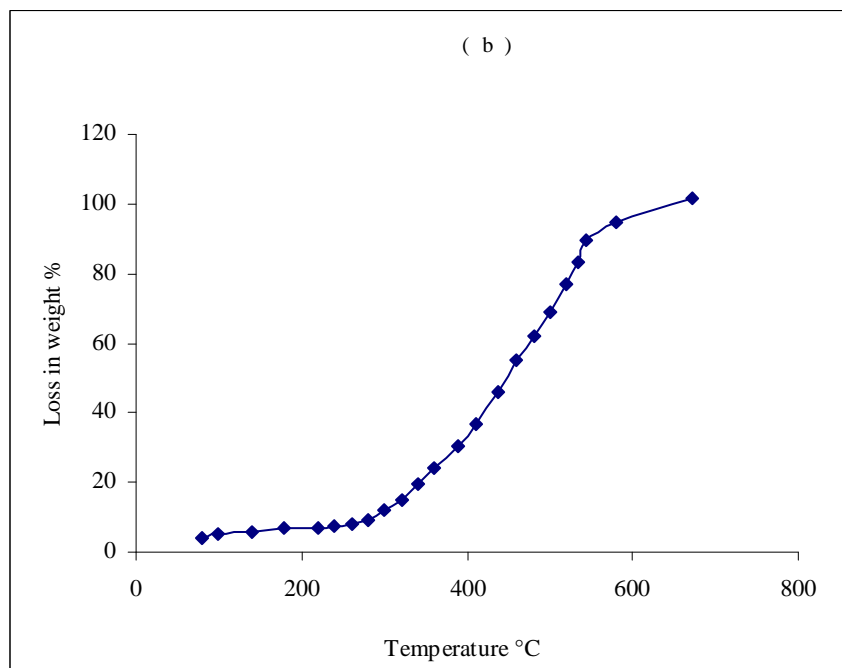
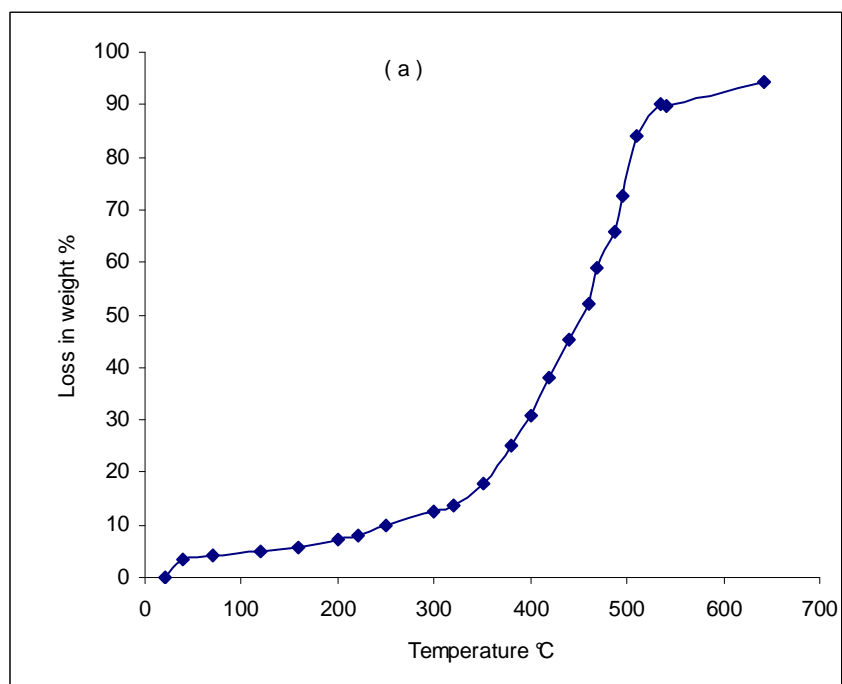


Fig (3): TGA of (a) soda lignin and (b) peroxyacid lignin

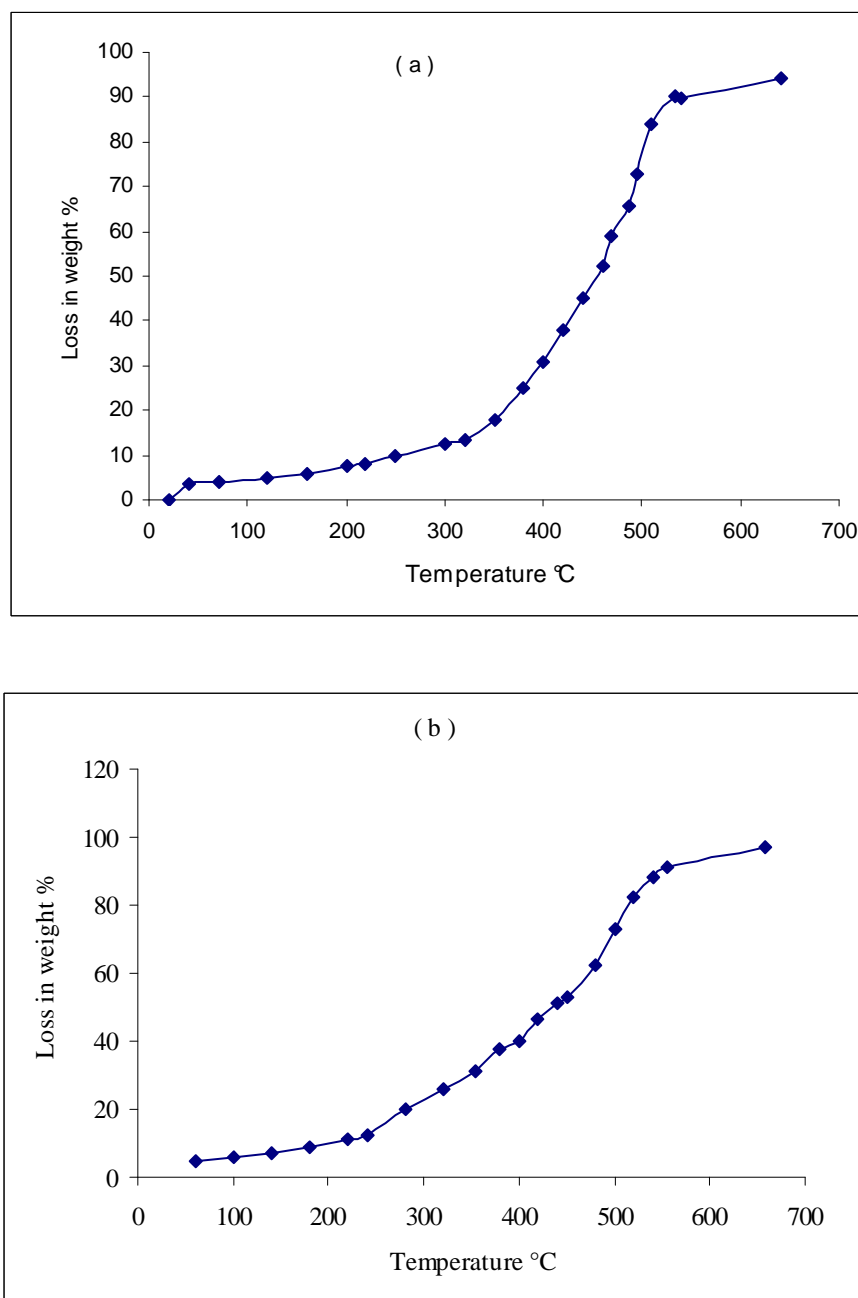


Fig (4): TGA of (a) Soda lignin and (b) bleached soda cotton stalks pulp.

CONCLUSION

Peroxyacid lignin has a higher affinity toward metal ions uptake than soda lignin. The thermal stability of peroxyacid lignin is higher than soda lignin. Incorporation of different functional groups into lignin increases its sorption properties from metal ion uptake. Incorporate of phosphate group into lignin increase the metal ions sorption of lignin more than the other functional groups. The bleached pulp has higher sorption metal ions than lignin. The sorption of metal ions depends on the structure of ions exchanger electro negativity, steric and radius of metal ions.

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