CHARACTERIZATION AND PROPERTIES OF ION EXCHANGERS PRODUCED FROM LIGNIN PRECIPITATED AFTER PEROXYACID PULPING

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Pulping of bagasse by one-stage and three-stage peroxyacetic acid was carried out. Characterization of the precipitated lignin from the waste liquor of the pulping process was studied using infrared spectroscopy. Comparison between the molecular structure of peroxyacid lignin and kraft lignin was investigated. Different lignins were applied to phosphorylation reaction. The sodium binding capacity and metal ions absorption by these lignins were taken into consideration. Infrared spectroscopy of the produced phosphorylated lignin was investigated. The peroxyacid lignin was found to have lower OH, higher COOH, a higher level of phosphate groups, and a higher binding capacity for sodium compared to kraft lignin.

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INTRODUCTION

Chemical constituents of lignocellulosic materials can be separated by conventional and non-conventional pulping processes. The structure of the lignin produced non-conventional pulping processes, e.g. peroxyacetic acid pulping, is different than that produced from conventional pulping e.g. kraft pulping.

Lignin is considered as a natural polymer made up of phenyl propane units attached with each other with β-O-4 linkages. One of the most promising types of organosolv pulping is the peroxyacid pulping process. This pulping process produces high yield pulp nearly similar to kraft pulp. Peroxyacid reacts with lignin during pulping process; the reaction involves: (1) ring hydroxylation, (2) oxidative demethylation, (3) oxidative ring opening, (4) displacement of side chains, (5) cleavage of ether bonds, and (6) epoxidation (Gierer 1982).

Most lignin products are based on technical lignin separated from black liquor, which is a by-product from pulping processes. It is observed that the separated lignin from waste liquor of peroxyacid is more reactive than that separated from kraft waste liquor. Also, peroxyacid increases the carbonyl and the carboxyl group content, thus rendering the lignin more soluble in water and alkaline media (Poppius et al. 1993).

Lignin can be used in many applications, e.g. resin synthesis as Novolak and resol phenol lignin formaldehyde resins (Nada et al. 1994, 1999; Nada and Hassan 2003). Glasser et al. have synthesized polymers from lignin and isocyanate combination (Glasser

et al. 1984). Some lignin derivatives can be used as dispersants, emulsifiers, adhesives and ion exchangers (Nada et al. 2003; Nada and Hassan 2006; Lehrfeld 1996).

In this study, precipitation of lignin from one-stage and three-stage peroxyacetic acid pulping of bagasse waste black liquors was carried out. On the other hand, kraft lignin was precipitated from waste black liquor resulting from kraft pulping of bagasse. The molecular structure of these precipitated lignins was followed using infrared spectroscopy. Phosphorylation of the lignins to form cation exchange resins was carried out. The sodium binding capacity as well as the metal ions uptake of the produced phosphorylated lignin were determined.

EXPERIMENTAL

Materials:

The raw material used in this work was bagasse raw material delivered from Edfo Mill for Pulp and Paper Industry, Edfo, Egypt.

Peroxyacid pulping of bagasse was carried out in one stage for two hours using 16% peroxyacetic acid, and three stages using 8% peroxyacetic acid (Nada et al. 2004). Precipitation of lignin from waste black liquor produced from peroxyacetic acid pulping of bagasse was carried out using distilled water. Lignin was precipitated from kraft black liquor delivered from Edfo Mill, Edfo, Egypt, by using 10% sulfuric acid. After precipitation, lignin was filtered, washed with distilled water until neutrality and then air dried.

Infrared spectroscopy of precipitated lignin was carried out by "Bruker Vector 22 FTIR Spectrometer" using KBr disc technique. The reproducibility of these results was not quantified, and it is recognized that it would be valuable to carry out a future study showing replication and statistical analysis of peak absorbances in IR spectra.

Phosphorylation:

Lignin has been reacted with phosphorous oxychloride (POCl$_3$) in the presence of pyridine under reflux at 115°C for two hours according to (Lehrfeld, J. 1996; Nada et al. 2004, 2005).

Sodium Ion-Exchange Capacity:

The same technique used in previous work was used to show the ability of phosphorylated lignin to absorb metals (Nada et al 2006). For 0.2g of the phosphorylated material, 10 ml of 0.01 N NaOH was added and the mixture was stirred for 2 hours and left overnight. The material was filtered and washed with distilled water until neutrality. 20ml of 0.01 N HCl was added, and the mixture was left overnight, then the excess HCl was determined using 0.01 N NaOH. The sodium load was calculated as follows:

Sodium ion-exchange capacity = [(B – V) N x 1000] / W   where:
B = volume of 0.01 N NaOH consumed in titration of phosphorylated sample.
V = volume of 0.01 N NaOH consumed in titration of blank sample
N = normality of NaOH
W = weight of oven dry sample.

Determination of Incorporated Phosphate Groups onto Lignin:

0.1g of phosphorylated lignin was boiled in conc. HNO_3 (10 ml) until dissolution, cooled, and diluted to 100 ml in measuring flask. Phosphorous was determined using inductively coupled atomic emission spectroscopy (ICP-AES).

Ion Exchanger

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

The absorption binding capacity for the different ion exchangers was estimated using solutions of different concentrations from these metals.

RESULTS AND DISCUSSION

Infrared spectroscopy of lignin and phosphorylated lignin from one- and three-stage peroxyacid (PA) pulping and lignin from kraft pulping was studied and the results are discussed below.

Infrared Spectroscopy of Different Precipitated Lignins:

The relative absorbance of different groups in peroxyacid and kraft lignins was calculated by the ratio of intensity of different bands to the intensity of C-H vibration: stretching of aromatic ring at 1505 cm^{-1} (13), and the results are presented in Table 1.

Table1. Relative Absorbance of Different Groups in Peroxyacid and Kraft Lignins

Bands	Relative absorbance of lignin		
	Kraft lignin	1-stage PA lignin	3-stage PA lignin
3420 (OH)	1.201	0.932	1.06
2930 (CH of CH_2)	1.255	1.068	1.167
2850 (CH of CH_3)	1.391	1.191	1.253
1718 (C=O of COOH)	-	0.881	0.896
1650 (aldehyde C=O)	1.377	1.035	1.29
1375 (phenolic OH)	1.304	1.12	1.29
1122 (-O- linkage)	0.984	0.891	0.849

From Table 1, it is clear that lignin produced from peroxyacetic acid pulping of bagasse was more highly degraded and oxidized than the kraft lignin (the relative absorbance of OH at 3420 cm^{-1} of kraft lignin was more than that in case of peroxyacetic acid pulping lignin). This is due to the oxidation of the OH group in peroxyacid lignin to carboxylic group. On the other hand, the relative absorbance of OH band at 3420 cm^{-1} was higher in case of three-stage peroxyacid lignin than one-stage peroxyacid lignin. This can be explained by the use of high dose of peroxyacid in one-stage, while the same dose was taken in two steps in case of the three-stage peroxyacetic acid lignin.
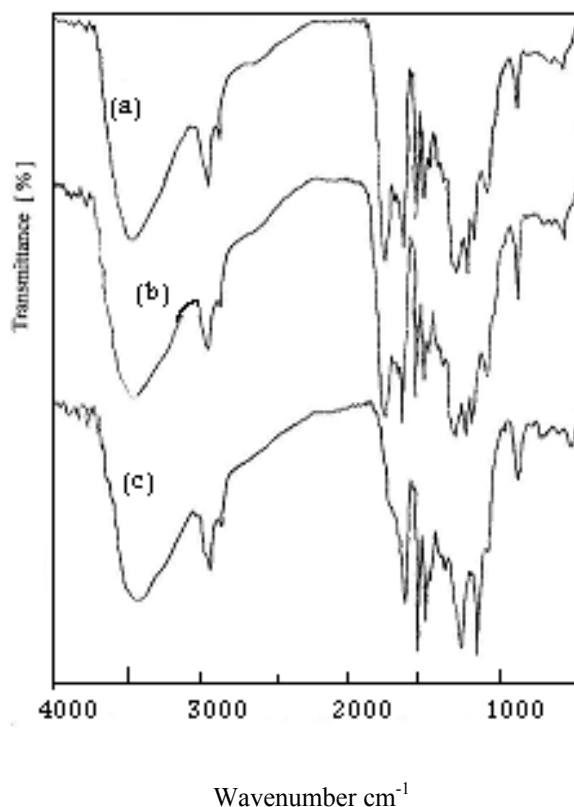
Wavenumber cm⁻¹

Fig. 1. IR spectra of precipitated lignin from different waste black liquors produced from: (a) one-stage peroxyacid pulping, (b) three-stage peroxyacid pulping, and (c) kraft pulping

From the same table, it is also clear that there was a formation of a new band at 1720 cm⁻¹, which characterizes the C=O of carbonyl groups, due to the oxidation that occurs in peroxyacid lignin. This band had higher relative absorbance in three-stage peroxyacid lignin than one-stage peroxyacid lignin. This band was formed due to the high oxidation effect of peroxyacetic acid on raw material, especially on lignin in a pulping process. This explains why the relative absorbance of OH group at 3420 cm⁻¹ is higher in kraft lignin than that in the case of peroxyacetic acid lignin.

The relative absorbance of lignin at 1650-1670 cm⁻¹ - which is characteristic of aldehyde or ketone groups – had a higher value in the case of kraft lignin than peroxyacid lignin due to the oxidation of peroxyacid and changing OH to COOH. This can be confirmed by the lower relative absorbance of the band at 1650-1660 cm⁻¹ in case of one-stage peroxyacid lignin than the three-stage process due to the higher oxidation effect of peroxyacid pulping in one-stage.

The relative absorbance of the CH band characteristic of CH_2 at 2930 cm⁻¹ and CH_3 at 2850 cm⁻¹ had lower value in peroxyacid lignin than kraft lignin. Finally, the relative absorbance of β-O-4 linkage was lower in the case of peroxyacid lignin than kraft lignin due to the higher oxidation effect of peroxyacid causing degradation between phenyl propane units of lignin molecules. The intensity of the CO band of phenolic groups at 1375 cm⁻¹ increased in the case of peroxyacid lignin due to the degradation which occurs at β-O-4 linkage during pulping process. The value of relative absorbance of this band was higher in case of one-stage lignin than three-stage lignin.

Cation Exchanger Preparation

Three-stage peroxyacid lignin and kraft lignin were modified by incorporation of phosphate groups onto them for use as cation exchanger. Reaction of phosphorous oxychloride with lignin can form a monomer anion in addition to a dimer anion, as indicated in the following equation (Scheme 1):

and
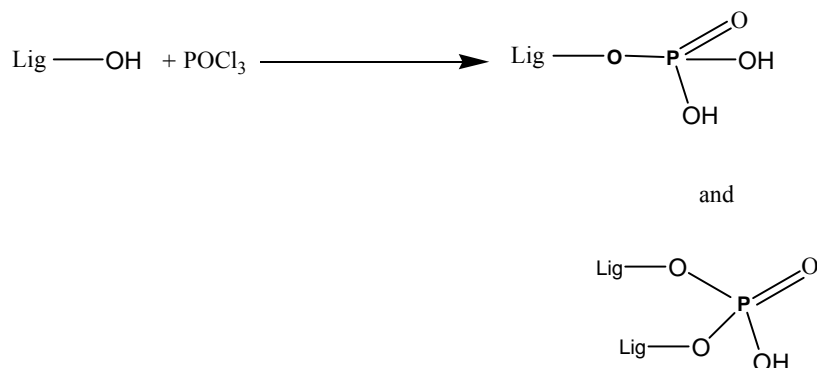
Scheme 1. Reaction of phosphorous oxychloride with lignin

It was found that the incorporated phosphate groups in peroxyacetic acid lignin were slightly higher than those in kraft lignin. This can be attributed to the high degradation in peroxyacid lignin, which increases the end groups in degraded lignin; so the reaction with phosphorous oxychloride increases, causing higher incorporated phosphate groups in peroxyacetic acid lignin. This means that kraft lignin contains fewer COOH and phosphate groups than peroxyacetic acid lignin and the groups have tendency for metal ions absorption.

It was found that the peroxyacetic acid lignin had a slightly higher incorporated phosphate groups (96 mg/g) than kraft lignin (90 mg/g). This can be attributed to the increase of the end groups formed in peroxyacetic acid lignin than in case of kraft lignin.

From infrared spectra (Table 2), it is clear that the incorporation of phosphate group onto lignin decreased the relative absorbance of C-OH group band due to the increase of the formation of C-O-P. This can be confirmed by the formation of new bands in the infrared spectra at 1200 cm^{-1} and 960 cm^{-1} characteristic to C-O-P groups.

Table 2. Relative Absorbance of Different Groups in Peroxyacid and Kraft Lignins

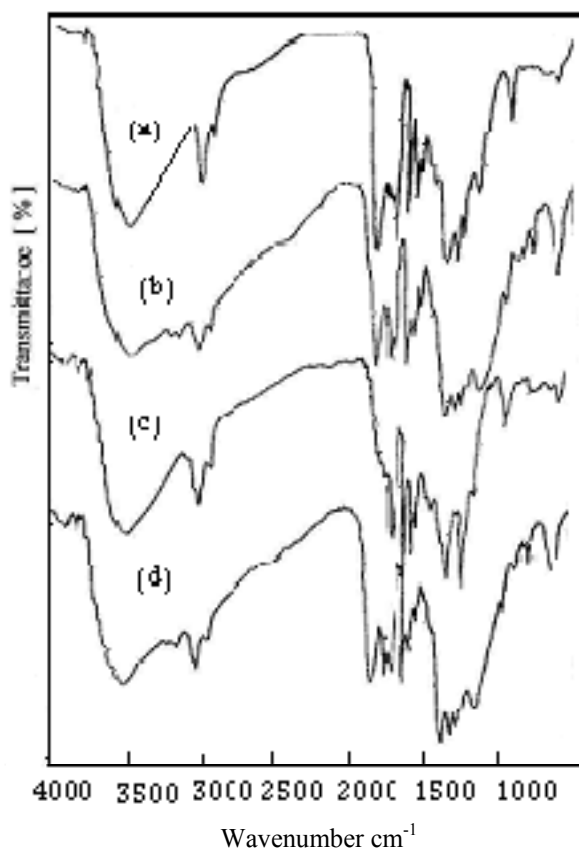| Bands	Unphosphor-ylated peroxyacid lignin	Phosphorylated peroxyacid lignin	Unphosphor-ylated kraft lignin	Phosphorylated kraft lignin
3424 (OH)	0.967	0.1	1.156	0.98
1200 (C-O-P)	-	1.25	-	1.04
960 (C-O-P)	-	0.84	-	0.795
2930 (CH$_2$)	1.18	1.02	1.25	1.04
2830 (CH$_2$&CH$_3$)	1.37	1.16	1.39	1.1

Fig. 2. IR spectra of (a) one-stage peroxyacid lignin, (b) phosphorylated peroxyacid lignin, (c) kraft lignin, and (d) phosphorylated kraft lignin

Also, from Table 2 it can be seen that the relative absorbance of bands at 2930 and 2830 cm^{-1}, which is characteristic of the CH vibration in CH_2 and CH_3, decreased by phosphorylation due to the degradation and oxidation, which may have occurred during phosphorylation process.

Sodium Binding Capacity

Sodium binding capacity gives an indication of the efficiency of the produced cation exchanger toward metal ions absorption. Figure 3 shows the sodium binding capacity of unphosphorylated and phosphorylated lignin.

In general, phosphorylated lignin had higher sodium binding capacity value than unphosphorylated lignin due to the incorporated phosphate groups. On the other hand, the phosphorylated peroxyacetic acid lignin had a higher sodium binding capacity than the phosphorylated kraft lignin. This can be attributed to the higher incorporated phosphate groups, in addition to the presence of COOH groups due to the oxidation of OH, which occurred during peroxyacid pulping of bagasse. Moreover, the unphosphorylated peroxyacetic acid lignin had a higher sodium binding capacity than the unphosphorylated kraft lignin due to the COOH content in peroxyacetic acid lignin resulting from oxidation of OH during pulping process as shown in Scheme 2.
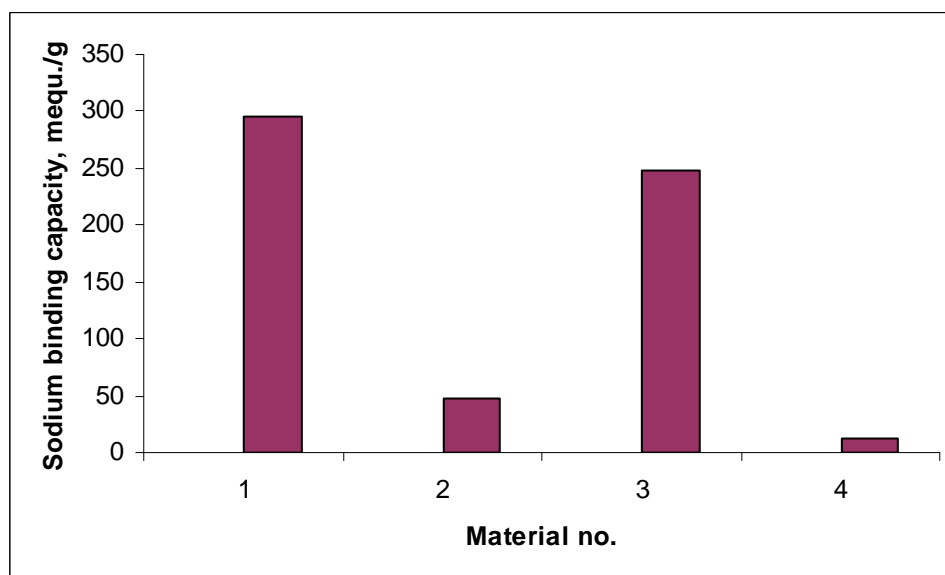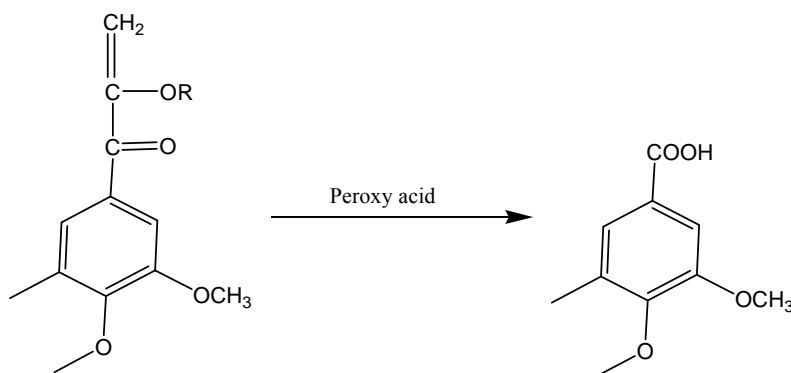
Fig. 3. Sodium binding capacity of (1) phosphorylated peroxyacetic acid lignin, (2) unphosphorylated peroxyacetic acid lignin, (3) phosphorylated kraft lignin, and (4) unphosphorylated kraft lignin.

Scheme 2. Oxidation of a lignin moiety by peroxyacid during kraft pulping

Metal Ion Absorption

The adsorption ability of unphosphorylated and phosphorylated lignins for metal ions was investigated. Figure 4 shows the metal ions uptake (Cr, Cu, Fe, Pb) from their mixture in solution containing 20 ppm of metal.

From this figure, it is seen that the phosphorylated lignin had a higher absorbance for metal ions than unphosphosphorylated lignin. On the other hand, the phosphorylated peroxyacetic acid lignin had a higher affinity toward metal ions uptake than the phosphorylated kraft lignin. This can be attributed to the higher content of phosphate groups, in addition to carboxyl groups that are incorporated in peroxyacetic acid lignin. The presence of two functional groups in phosphorylated peroxyacetic acid lignin

increases its affinity and selectivity toward different metal ions uptake. Also from the figure it is clear that the unphosphorylated peroxyacetic acid lignin had a higher affinity toward metal ions than the kraft lignin due to the presence of incorporated carboxyl groups in peroxyacetic acid lignin.

It is also clear that the metal ions uptake from their solutions by the phosphorylated lignin was not similar. Cr(III) and Fe(III) ions were more absorbed by the ion exchanger than other metals. This can be attributed to the charge and hydrated radius ion in the solution. Also, the difference of absorption affinity of metal ions by ion exchanger depends on the ionic radius and steric hindrance as well as the electronegativity of the metal ion (Lehrfeld, J. 1996).
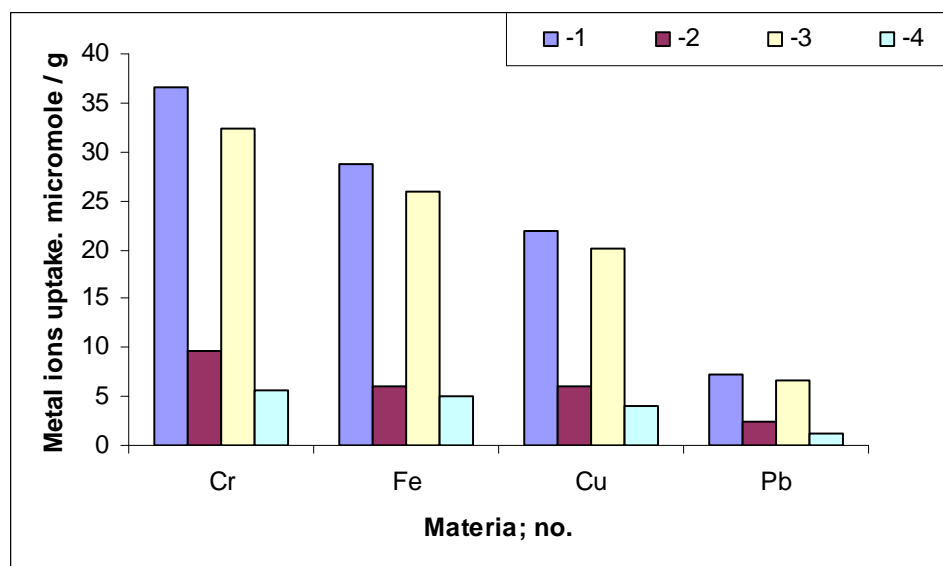

Fig. 4. Metal ion uptake (micromole/g) by (1) phosphorylated peroxyacetic acid lignin, (2) unphosphorylated peroxyacetic acid lignin, (3) phosphorylated kraft lignin, and (4) unphosphorylated kraft lignin

The binding capacity of an ion exchanger prepared from phosphorylated peroxyacetic acid lignin for different metal ions in solution (20 ppm conc. in every metal ion, which is equivalent to 0.02 mg of each metal ion in solution) was investigated and is presented in Fig. 5. The concentration of metal ions solution in their mixture was 50-500 ppm in 25ml.

It is clear that the binding capacity of phosphorylated peroxyacetic acid lignin was increased by increasing the metal ions concentrations. This can be attributed to the increase of contact between metal ions and ion exchanger. The increase reached its maximum at a metal ion concentration of 1000 ppm. Also, from the figure it is evident that the absorption of Cr was higher than other metal ions and had the following sequence:

Cr > Fe > Cu > Pb

The absorption of Pb was the lowest, due to its higher ionic radius than other metal ions.
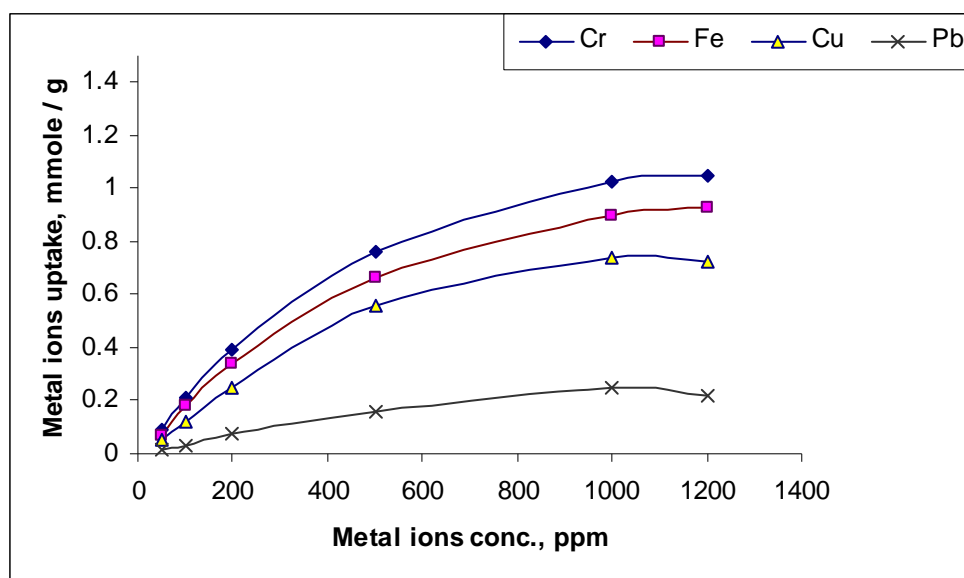
Fig. 5. Effect of metal ions concentration (ppm) on the binding capacity of these metals (mmole/g)

Effect of Ion Exchanger Concentration

In other trials, different weights of phosphorylated peroxyacid lignin were stirred in 25 ml of mixture of the previously mentioned metal ions and each was 100 ppm concentration.

It is clear that the metal ion absorption increased by increasing weight of ion exchanger up to 0.4g. This can be attributed to the increase of surface area of ion exchanger that is in contact with the metal ions. Further increase in the ion exchanger concentration caused a decrease in the metal ion absorption due to the coagulation of ion exchanger particles, which consequently decreased the surface area of the resin in contact with the metal ions in solution.
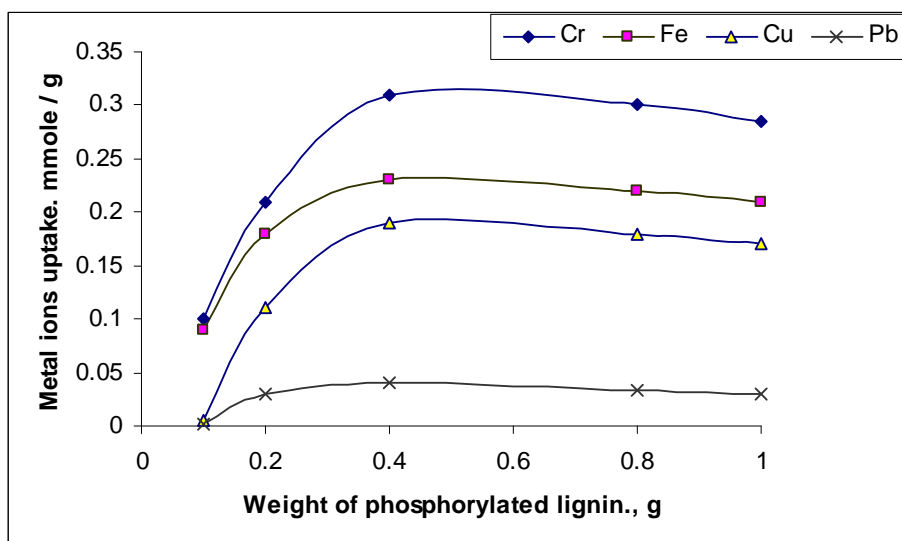

Fig. 6. Effect of weight of phosphorylated peroxyacid lignin resin on metal ions uptake (mmole/g)

CONCLUSIONS

1- Peroxyacetic acid lignin was found to have lower OH and higher COOH groups than kraft lignin.
2- Phosphorylated peroxyacid lignin had a higher level of incorporated phosphate groups than kraft lignin.
3- The sodium binding capacity and metal binding capacity of phosphorylated peroxy-acid lignin had higher values than phosphorylated kraft lignin.
4- The absorption of metal ions is affected by their concentrations in the mixture and by the weight of ion exchanger used. So, the increase in metal ion concentration increases the absorption capacity of ion exchanger, also it increases with increasing weight of resin up to a certain weight and then decreases or becomes constant.

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