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# Properties of ion exchangers produced from different pulps

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## ABSTRACT

Soda and peroxyacid pulp were prepared from different cotton baggies and characterized by FT-IR, X-ray diffraction, TGA, and DT**A** thermal analysis. The crystallinity, thermal stability, and efficiency of peroxide pulp are higher than that of soda pulp. Incorporation of functional groups e.g., -COOH and -$H_2PO_3$ into pulp increases its efficiency toward metal ions uptake, The absorption of metal ions depend on the incorporated functional groups and metal ion radii as well as electronegativity of metal ions.


## KEYWORDS

Pulp;
Ion exchangers;
FT-IR;
TGA;
DTA;
Metal ion uptake.

## INTRODUCTION

Cellulose is a high molecular weight linear polysaccharide. Its properties depend on the pulping process and its sources. It is hydrolyzed and treated chemically to prepare low molecular weight beside cellulose esters and ethers. The mainly degraded and hydrolyzed part in cellulose chains is amorphous regions[1]. Agricultural residues are a mixture of complex polysaccharides and lignin. Some of the isolated components of these mixtures (i.e., cellulose and starch) have increased value when new functionality is added. For examples, cationic and carboxymethyl cellulose have many industrial and commercial uses. By applying some of methodologies to un-proceeded residues, useful products could be obtained. A potential waste disposal problem would be minimized because these residues would now have some commercial utility as paper industry, artificial wood and cellulose derivatives. Some of these derivatives are carboxymethyl cellulose, nitrocellulose, cellulose phosphate and grafted cellulose which can be used as hydrogel and ion exchangers. Cellulose affords material of cost effective technologies of ion exchange[2-4]. Cellulose grafting with certain monomers is a simple technique to incorporate desired active functional groups on the backbone of polymer for absorption metal ions, water[5] and enzyme immobilization[6]. Moreover grafting or chemical reaction of cellulose gives it new properties, such as, hydrophobic or hydrophilic character and resistance to chemical and biological agents[7].

The aim of the present work is to investigate the effect of pulping process on the ion exchange properties of the produced metal. The effect of pulp hydrolysis on its properties is also carried out. The effect of incorporating different functional groups e.g., carboxylic and phosphate groups in cellulose were investigated. The prepared pulps were characterized and evaluated by Infra red spectroscopy, X-ray diffraction, and thermal analysis, (TGA and

DTA). The efficiency of the modified cellulose toward metal ion absorption were estimated.

## EXPERIMENTAL

### Materials

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); 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

Prehydrolysis of raw material was carried out before soda pulping process using 1.5% $H_2SO_4$ 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, $H_2O_2$ and $ClO_2$.

### Chemical analysis

Lignin, α-cellulose, hemicelluloses, and ash content was estimated by Tappi standard method (T13 wd-74), (T203 OS-61), (T19 wd-71) as mentioned elsewhere[8].

### 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[9].

### Lignin precipitation

Soda lignin was precipitated from the produced waste black liquor of soda pulping using 10% $H_2SO_4$. 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 and pulp

Lignin and pulp was hydrolysed with 5-15% $H_2SO_4$ acid under reflux for different times.

### Cellulose derivative

(a) Carboxylated lignin and pulp: It was prepared by oxidation of lignin or pulp with sodium chlorite at 70°C for 2hr. (b) Phosphorylated lignin or pulp: It was prepared according to the method of Lehrfeld[10]. (c) Crosslinking: Lignin or pulp was cross linked by epichlorohydren[11].

### Phosphorous determination

It was determined by dissolving 0.2g of lignin or pulp in conc. $HNO_3$ (10ml). After complete dissolution the volume was adjusted to 25ml in measuring flask using deionized water. The phosphorus was determined using ICP – AES Jobin Yvon J4/85 spectrometer.

### Sorption of metal ions

0.2g of sample was stirred in 25ml solution containing different metal ions (20 ppm for every metal ion), for 30 min. filter, and the remaining metal ions in the filtrate was determined using ICP analyzer.

### Spectroscopic analysis

### 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 $cm^{-1}$.

### Thermal analysis

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

## RESULTS AND DISCUSSION

### Effect of the method of pulping process on the properties of the produced pulp

## Ion exchange properties

The method of pulping of raw materials and bleachability of the pulp has a high effect on the properties of produced pulp. So, the ion exchange affinity of the produced pulp from peroxyacid and soda pulping of bagasse was investigated (TABLE 1). It is clear that the metal ions uptake by peroxyacid bagasse pulp is higher than that in case of the soda pulp. This can be attributed to the formation of carboxylic group in the pulp due to the pulping with peroxyacetic acid which causes some oxidation of the pulp during pulping process[12]. The formation of carboxyl group in the peroxy acid pulp increases its efficiency toward metal ions uptake. The formation of -COOH groups onto cellulose increases its affinity for metal ions sorption more than the hydroxyl groups as shown in Figure 1[13].

From infrared spectra Figure 1, it is clear that the peroxyacid pulp has a higher relative absorbance (ratio of intensity of absorption of any band/ intensity of band absorption at 1325cm$^{-1}$)[14] of carboxylic group at 1715 cm$^{-1}$ (0.35) than that in case of soda pulp (0.062). On the other hand, the relative absorbance of -OH group at 3420cm$^{-1}$ in case of peroxyacid pulp is lower than that in case of soda pulp due to the oxidation of the cellulose which occur during the peroxyacetic acid pulping.

From previous results, cellulose, have appreciable ion binding capacity which is due the manner by which cellulose is prepared.

## Hydrolysis of pulp

Hydrolysis of cellulose is heterogeneous reaction.

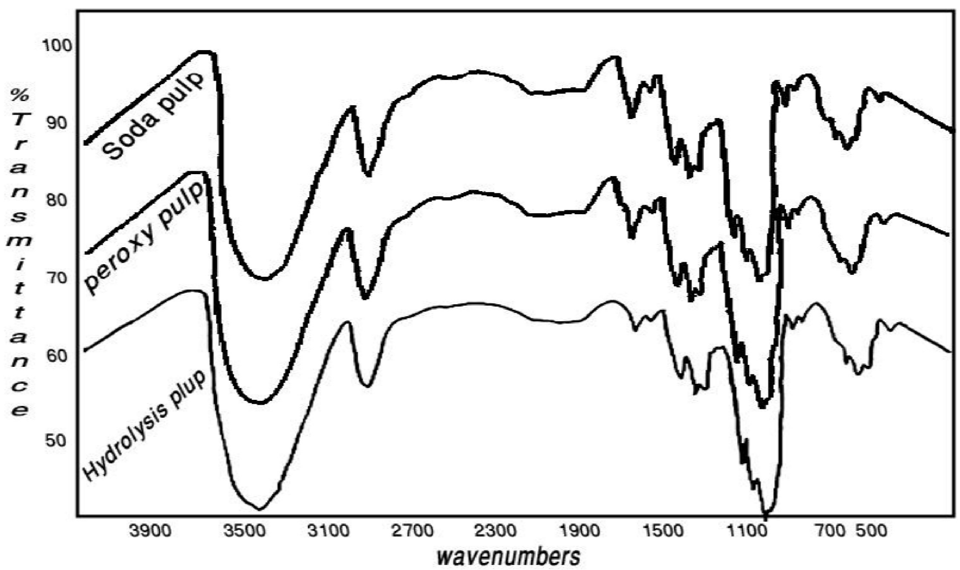



**Figure 1 : Infrared spectroscopy of soda, peroxyacid and hydrolyzed bagasse pulp**

Reaction influences by physical factor conditions (acid concentration and temperature), as well as physical state of cellulose. The sudden shift of physical structure and reaction pattern in response to acid concentration and temperature indicates that the main factor causing the change in cellulose structure is disruption of hydrogen bonding. The acid hydrolysis has a high effect on the cleavage of β-1-4 glucosidic bond in cellulose. The ion exchange affinity of hydrolyzed soda bagasse pulp toward metal ions uptake was studied (TABLE 1).

From TABLE 1 it is clear that the hydrolyzed pulp has slightly lower affinity toward metal ions uptake than the unhydrolyzed pulp. This is due to the increase in crystalline regions and lower of the amorphous region which is more active than the crystalline region. This can be confirmed by the infrared spectroscopy from which it is seen that crystallinity index (ratio absorbance

**TABLE 1 : Metal ion uptake by different functional groups in bagasse pulp**

| Material | Absorbed metal ions µmol/g | | | |
|---|---|---|---|---|
| | Cd | Mg | Zn | Hg |
| Soda pulp | 2.64 | 73.9 | 16.2 | 4.8 |
| Peroxyacid pulp | 2.9 | 78.4 | 18.9 | 5 |
| Hydrolyzed pulp*(100$^{O}$C,3h,10%HCl) | 2.48 | 71.4 | 16 | 4.61 |

***using 10% HCl at 100 $^{O}$C for 3 hours**

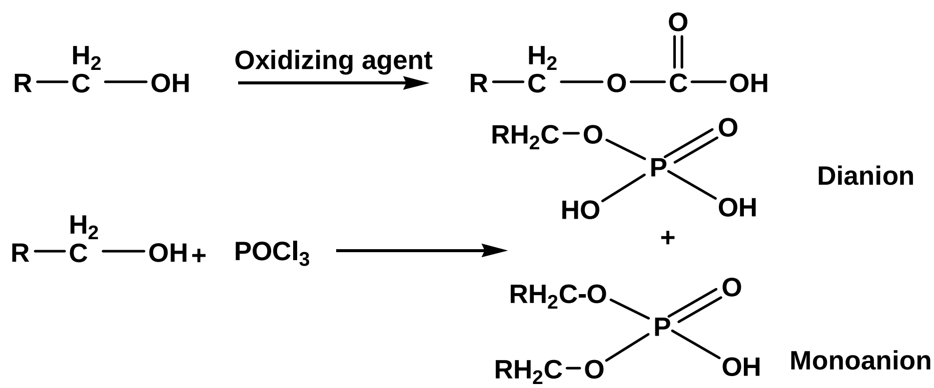
of band of $CH_2$ vibration at 1425/absorbance of band CH vibrate at 900 $cm^{-1}$)[15]. It is found in case of hydrolyzed pulp (2.25) while in untreated pulp (2.03). On the other hand, the mercerization depth (ratio of band absorption at 1375/band absorption at 1325 $cm^{-1}$) of the hydrolyzed pulp is lower than the unhydrolyzed pulp[16] due to the decrease of amorphous part by hydrolysis.

## Function groups

TABLE 2 shows the metal ions uptake by phosphorylated and carboxylated bagasse pulp. It is seen that the phosphorylated and carboxylated bagasse pulp has a higher affinity toward metal ions uptake than the untreated pulp. On the other hand, the phosphorylated bagasse pulp has a higher affinity for metal ions sorption than the carboxylated bagasse pulp. This can be due to the higher power of phosphate groups to absorb metal ions from their solutions. Multiple functional groups may be placed on the same repeating unit on one in close proximity. These reactive sites may lead to some degree of selectivity rejection of cations having large ionic radii due to the steric hinderance factors or selective adsorption due to the polydentate bonding. The organic derivative prepared from the bagasse pulp and oxidizing agent to form carboxylate cellulose half ester. Phosphorus oxychloride can react with bagasse pulp at a single site and the produced phosphate can remain as a dianion, or it react with two sites on the (OH) bagasse pulp backbone, forming monoanion to react with a cation (Scheme 1)[17].

**TABLE 2 : Effect of different function groups incorporated onto pulp**

| Material | Absorbed metal ions µmol/g | | | |
|---|---|---|---|---|
| | Cd | Mg | Zn | Hg |
| Soda pulp | 2.64 | 73.9 | 16.2 | 4.8 |
| Carboxylated pulp | 4.32 | 91.8 | 20.1 | 5.9 |
| Phosphorylated pulp | 17.7 | 95.7 | 27.4 | 7.5 |
| Cross linked Phosphorylated pulp | 21.1 | 100.3 | 29.1 | 8.6 |




Scheme 1

From TABLE 2, it is clear that, the cross linked phosphorylated pulp has a higher affinity toward metal ions uptake than the not cross linked phosphorylated pulp. This is because the cross linking of the pulp with epichlorohydrin before phosphorylation decreases dissolution of the pulp during phosphorylation process. Also, the cross linker of pulp increases the chains which attached with cellulose and increases the -OH group and consequently increases the incorporated phosphate group, which it is found in the phosphorylated pulp 85 ppm/g while it is in the cross linked 96.4 ppm/g.

The produced ion exchanger absorbed the metal with different ranges. This is due both steric and electronic effects. Also the efficiency of the produced ion exchangers toward metal ions uptake can be affected by the radius of metal ions. Boyd[19] concluded that ion exchange absorption affinities are determined chiefly by the magnitude of the charge and the hydrated radius of the ion in the solution.

## Soda pulp and soda lignin

TABLE 3 shows the metal ions uptake by pulp prepared by soda pulping and the precipitated lignin from

**TABLE 3 : Sorption of metal ions by soda pulp and soda lignin**

| Material | Absorbed metal ions µmol/g | | | |
|---|---|---|---|---|
| | Cd | Mg | Zn | Hg |
| Soda pulp | 2.64 | 73.9 | 16.2 | 4.8 |
| Soda lignin | 0.77 | 70.6 | 6.2 | 3.9 |

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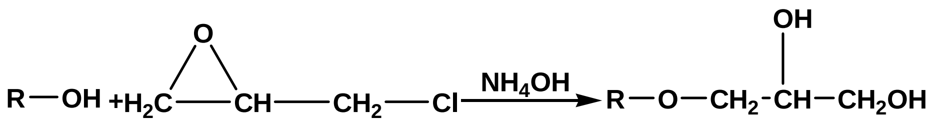
the produced waste black liquor from the pulping process.

From the table it is clear that the bagasse pulp absorb metal ions more than the lignin. This is due to the difference in physical structure of lignin and pulp in which the cellulose in pulp is arranged as chains above each other. This chains has crystalline part and amorphous part that was active for penetration of metal ions solution which increase the contact between metal ions and pulp, and consequently increases the sorption of metal ions. But in case of lignin it is found as polymer not as chain which crosslinkes molecules of phenyl propane unit which decreases the affinity of lignin to sorb metal ions. Also, the cellulose has more hydroxyl groups which link more metal ions than lignin.

In general, the hydroxyl functionality on all of produced pulp is enabling to substitution with a wide variety of electrophilic reagents. Multiple functional groups as -OH, -COOH, - $H_2PO_3$ may be placed on the same repeating units or on one in close proximity. These reactive sites of different functional groups may have to some degree of the selective reaction of cations, a large ionic radii due to steric hindrance factors or selective absorption.



## X-ray diffraction

To give more information about the effect of hydrolysis for bagasse pulp with HCl, beside the infrared spectroscopy, X-ray diffraction for unhydrolyzed and hydrolyzed bagasse pulp were applied. The X-ray diffraction patterns were recorded on X-ray diffractometer by reflection method.

The difractogram of cellulose Figure 2 Shows two peaks with θ-range 21-23 corresponding to crystal graphic from of cellulose and broaded peaks with 2 θ range 15-19°. The value of 2 θ angle at which the given peaks are observed and are changed during cellulose hydrolysis. The crystallinity of cellulose was estimated by segal, et al[18] using the following equation.

**Crystallinity index = $I_{00}$ ($I_{002}$ - $I_{am}$)/ $I_{00}$x100**

Where 002 to the peak intensity corresponding to 002 plane at 2 θ = 27.8 for cellulose. $I_{am}$ is the peak intensity of the amorphous fraction at 2 θ =16. In our experiments the hydrolyze cellulose has much higher crystallinty than unhydrolyzed cellulose (TABLE 4).

From TABLE 4, it is clear that the crystallinity index of hydrolyzed bagasse is higher than unhydrolyzed one. This is due to the degradation of amorphous part during hydrolysis process.

## Thermal analysis of different pulps

Thermal analysis of the soda and peroxyacid bagasse pulps was determined to show the effect of pulping method on the thermal properties of the produced pulps. The thermal degradation of soda and peroxy pulp in nitrogen atmosphere has been extensively studied. The

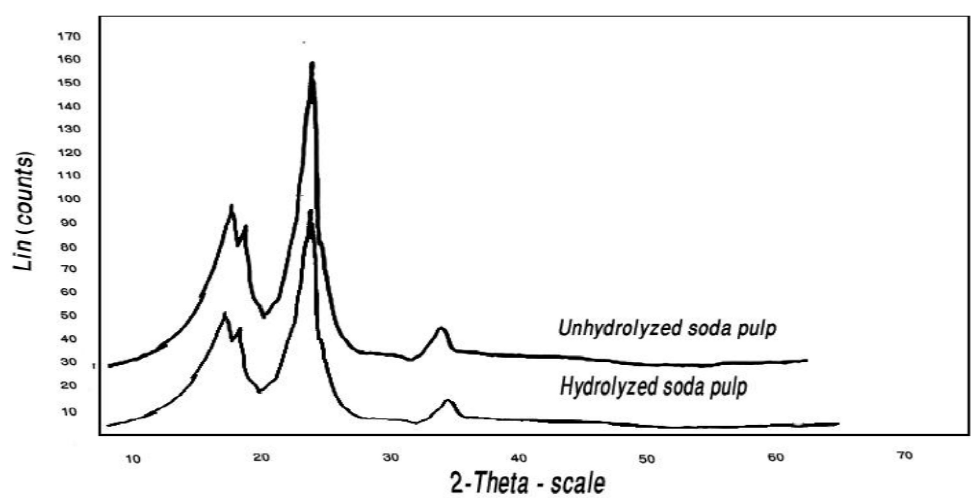



**Figure 2 : The x-ray diffraction of unhydrolyzed and hydrolyzed pulp**

**TABLE 4 : X-ray diffraction of unhydrolyzed and hydrolyzed bagasse pulps**

| Material | Position of 2 θ | | Crystallinity |
|---|---|---|---|
| | 001 | 002 | |
| Bleached bagasse pulp (unhydrolyzed) | 15.465 | 22.692 | 46 |
| Hydrolyzed bagasse pulp | 14.999 | 22.770 | 52 |

degradation of the pulp is composed of set of concurrent and consecutive reaction. The rate of thermal decomposition of the peroxy pulp is lower than soda pulp. This can be attributed to its higher crystallinity and incorporated –COOH which produced in cellulose during peroxyacetic acid pulping process.

The experimental results show two decomposition temperatures one is minor decomposition temperature at which the pulp began to degrade and combustion. From table it is clear that the minor decomposition temperature of peroxyacid pulp is 300 $^{0}$C is higher than in case of soda pulp (280 $^{o}$C) and the loss of weight at these two temperatures was 6 and 10% for peroxy acid pulp and soda pulp respectively. On other hand, it is found another decomposition temperature (major decomposition temperature) at which the pyrolysis of pulp and formation of gas is found. The major decomposition temperature of the peroxyacid pulp is higher than the soda pulp. This means that the peroxy acid pulp is more stable than the soda pulp. The differential thermal analysis curves of the peroxy acids and soda pulp was

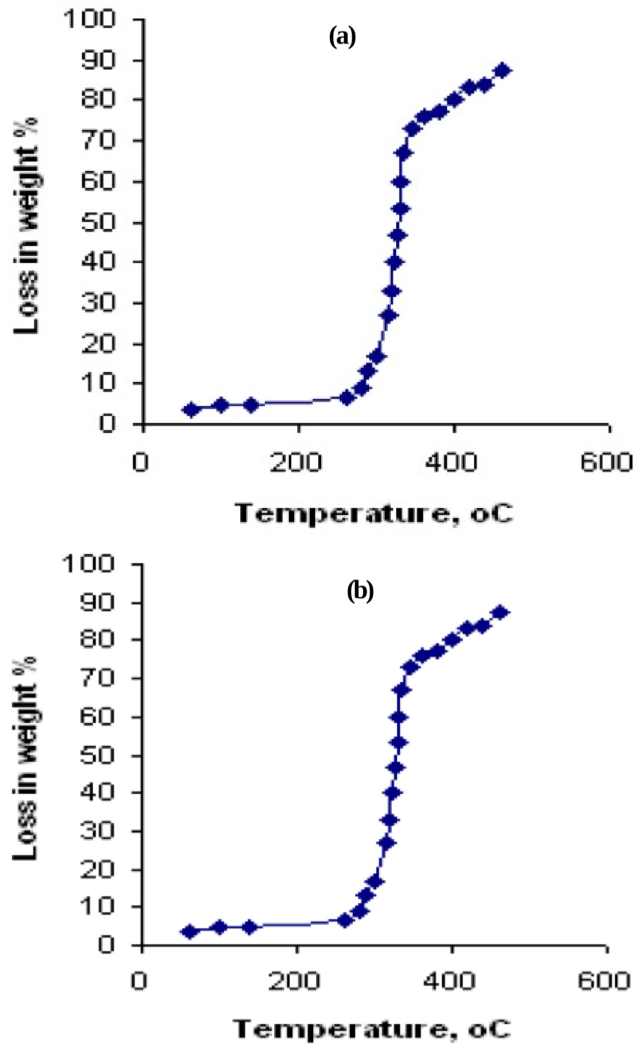



Figure 3 : TGA of (a) soda and (b) peroxyacid pulps

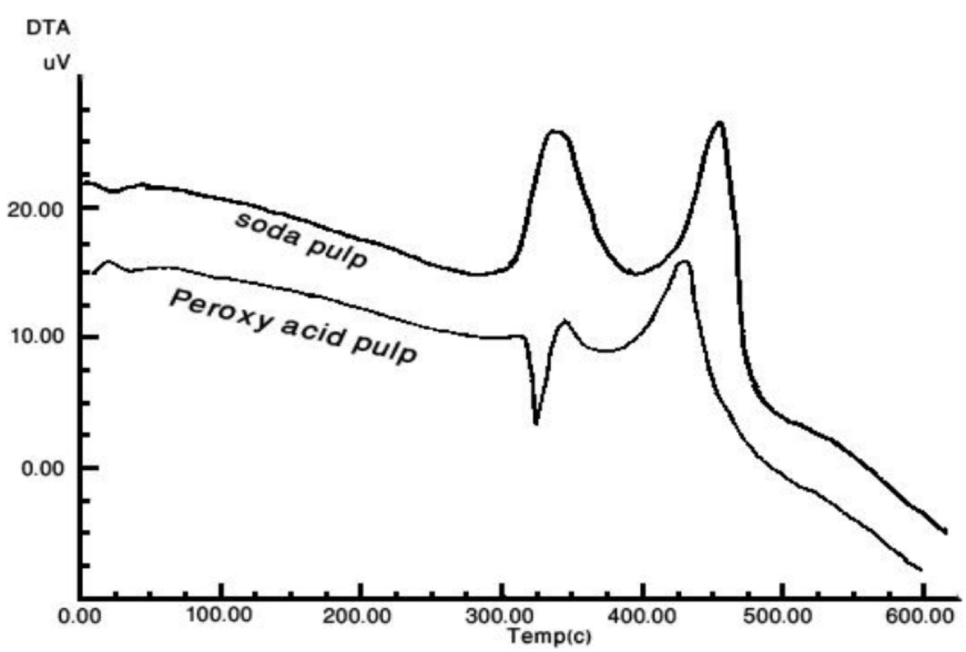



Figure 4 : DTA curves of soda and peroxyacid pulps

seen in Figure 4

### The differential thermal analysis (DTA) curves of the peroxyacid and soda pulps

From the figure, it is clear that DTA in case of soda pulp have three peaks, one endothermic a 50-60°C which is due to the evaporation of the humidity and the other two exothermic at 333°C and 461°C. In case of peroxyacid three peaks were found, two endothermic and one exothermic, one at 60-65°C which is related to the water evaporation and the second endothermic peak at 340°C. The third one is exothermic peak at 471°C. It is clear from DTA curves that the temperature of peaks in case of peroxyacid pulp is higher than that of soda pulp.

## CONCLUSION

Efficiency of bleached pulp toward metal ions uptake is higher than lignin, i.e. the metal ions uptake by pulp was higher than that of lignin. The hydrolyzed pulp has lower efficiency toward metal ions uptake than the untreated pulp. Peroxyacid bleached pulp has a higher affinity toward metal ions uptake than soda bleached pulp (The kind of raw materials (agricultural wastes) and the pulping process have a highly effect on the affinity of lignocellulosic material toward metal ions uptake). Metal ions uptake is highly affected by the kind of functional groups incorporated onto the cellulosic material (Incorporation of different functional groups e.g. carboxyl and phosphate into pulp increase its affinity toward metal ions uptake). Cross-linking of cellulose with epichlorohydrin increases its efficiency toward metal ions sorption**.** Crystalinity index of hydrolyzed cellulose is higher than un-hydrolyzed cellulose **(**Peroxyacid and hydrolyzed pulps have higher crystallinity than soda pulp). Incorporation of phosphate groups onto cellulose increase its efficiency toward metal ions uptake more than carboxylated groups. Thermal stability of cellulose derivatives has the following sequence: cellulose phosphate >carboxylated cellulose > untreated cellulose. Also, peroxyacid pulp has higher stability toward thermal treatment than soda pulp.

The absorption of metal ions by ion exchanger was depending on the incorporated functional groups and metal ion radii as electronegativity of metal ions.

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