

Physicochemical Studies of Cation Ion Exchange Wood Pulp

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Abstract: Wood pulp with different functional groups (phosphorylated, sulphonated and phosphorylated carboxylated) with or without crosslinking is preparation. Molecular structure of the prepared cation exchanger is analyzed by infrared. A new band was seen at 1200, 1400 and 1713 cm^{-1} for phosphorylated, sulfonated and carboxylated wood pulp respectively. Cross linked of prepared cation exchangers increases its efficiency toward metal ions uptake. The efficiency of the produced ion exchangers depends on the incorporated functional groups. Crosslinked ion exchanger has higher efficiency toward metal ion uptake than the uncrosslinked ion exchangers. Also, the quantity of absorbed metal ion by ion exchanger depends on the properties of metal ion. Such, the radius, electronegativity as well as the stearic phenomina. The dielectric constant (ϵ) and AC electrical conductivity were studied with frequencies over the rang (200 KHz to 5 MHz) for different incorporated functional groups wood pulp at different temperature. Generally, the dielectric constant decreased and the conductivity increased with increasing frequencies.

Key word: Wood pulp materials, Infrared, Atomic absorption, Dielectric constant, AC conductivity.

INTRODUCTION

Synthesis of ion exchangers from agricultural wastes can be prepared by chemical modification copolymerization crosslinking and incorporation of functional groups (Nada, 1986; Laskiewicz and Weisb, 1999. Nada *et al.*, 1990; Nada and Hassan, 2006; and Laszlo, 1996). Ion exchangers are broadly employed for the treatment of process water and wastewater. Agricultural residues represent a cheap and environmentally safe source of material for preparation of ion exchangers (Hehifield, 1996 and Nada and Adel, 2006). The incorporation of certain groups to lignocellulose material is used to increase their efficiency toward cation exchange ability (Lin *et al.*, 2005; Nada and El-Wakeel, 2006 and Vashmgrou, 1995). The major fields of application of these polysaccharides ion exchangers are protein isolation, chromatography waste water treatment capturing of mercury, and removal of ammonia from air. Derivalization of the agricultural residues can aim to produce chelating anion or cation exchangers. Epichlorolydren is a commercially used as cross linking agent for preparation of acid cation exchangers (Laszkiewicz, and Domsik, 1989 and Nada, *et al.*, 2007). Infrared spectroscopy is used to follow the molecular structure of cellulose and its derivatives particularly in studying the fine structure (Antal., *et al.*, 1985. Nada, *et al.*, 2000). intermolecular and intra- molecular force structure (Nada., *et al.*, 2002) as well as interaction of function groups of molecular with other molecules. Chemical modification have a highly effect on the thermal stability of lignocellulose materials (Yu levdek., *et al.*, 1967).

In general, most of polymers are insulators because of their low conductivity. The conductivity depends on the thermally generated carriers and also on the addition of suitable dopants (Mehendru, *et al.*, 1997 and Shinka, *et al.*, 1989). Although charge transport in polymers was a problem with great technological implication, the current understanding of the elemental process involved is still unsatisfactory (Bassler, 1984). Polymers are amorphous or semi – crystalline substances. In amorphous substances there were many localized charge carrier levels called trapping sites and the carrier mobility was very low. The transport mechanism in amorphous materials was more complicated than in crystalline materials, where a long range order exists. Dielectric constant and AC conductivity studies are used to investigate the conduction mechanism of synthetic polymer materials. Many review articles (Havriliak, Havriliak, 1996; Lindsey Patterson, 1980; Roling, Non-Cryst, 1999; Sullivan, Deutsch, 1975; Burchard, 1983). deal with this subject, presenting theoretical and experimental aspects and summaries of many experimental data of this substance class.

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The aim of this work is to study the effect of incorporation of different functional groups, as phosphate, sulfate, carboxyl and crosslinking onto with wood pulp on metal ions absorption. On the other hand, the infrared spectroscopy was used to study the molecular structure of the prepared cation exchanger. Also, the effect of the incorporated functional group on dielectric properties and AC electrical conductivity wood pulp was studied.

MATERIALS AND METHODS

- 1- Raw material used in this study is paper grade pulp. The chemical constituent of this pulp is α - cellulose 85 %, hemicellulose 14% and Ash 0.05 %.
- 2- Preparation of Cation Exchanger:

The phosphoylation and sulfonation of wood pulp was carried out according to (Nada, *et al.*, 2002) 5 g of wood pulp steeped in cold pyridine for 10 minutes and then added 5ml of POCl₃ or chlorosulfuric acid added in 20ml methylene chloride drop by drop. Then this mixture was refluxed for 2 hour at 115 °C in oil bath. Then final product was poured into ice water and then filter washed the precipitated with water till neutrality and then with acid (1N HCl) and then with distilled water till neutrality. Then washed with methanol and finally dried in air. Carboxylated of phosphorylated wood pulp was carried out using sodium periodate (NaClO₂) technique (Mackawo and Koshijima, 1984).

3- Metal Ion Uptake:

0.2 g of prepared cation exchanger was studied with rotating in 25 ml of different metal ion (Cu, Co, Fe, Mg, Mn, Ni) and every metal ion was 20 ppm for 30 mins. After stirring, the content filtered, and the metal ions was determined in filter using Thermo-Elemental S4 fullautomatic atomic absorption spectrometer equipped with deuterium continuum background corrector. A burner-nebulizer (100 mm with single slot for an air acetylene C₂H₂) was utilized as an absorption cell. The light sources were Thermo- Elemental hollow cathode lamps.

Infrared:

A Jasco Model 300E Fourier transform infrared spectrometer was used to measure the vibrational spectra of the investigated samples. The samples were measured using the KBr disc technique.

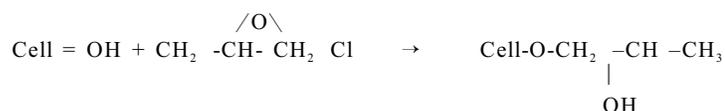
Electrical properties:

Measurements of the AC conductivity and dielectric constant were carried out on samples in the form of a disc of about 1 cm diameter and 0.16 cm thickness. The two surfaces of each sample were coated with silver paint (BDH). The dielectric constant and AC conductivity were measured using an RLC bridge (HIOKI Model 3530, Japan).

RESULTS AND DISCUSSION

Infrared Spectroscopy:

Table (1) shows the relative absorbance of different bands of different groups in wood pulp and derivatives. Comparing between wood pulp, sulfonated, phosphorylated and crosslinking phosphorylated wood pulp. From Table and Fig. (1,2), a new band is seen in the spectra of sulfonated and phosphorylated wood pulp at 1400 and 1200 cm⁻¹ respect. Also a new band is seen at 962 cm⁻¹ which characteristic also to phosphate groups. The relative absorbance of OH at 3400 cm⁻¹ of sulfonated wood pulp is lower than the wood pulp and phosphorylated wood pulp. The crosslinking phosphorylated wood pulp has a higher relative absorbance of OH than phosphorylated wood pulp. Thus can be due to that the crosslinked wood pulp has high braces which increase from contact between phosphorousoxychloride and wood pulp. On the other band, the phosphorylated wood pulp has a lower absorbance of bands at 1200 and 960 cm⁻¹ than crosslinked phosphorylated wood pulp. Moreover, the relative absorbance of CH₂ bands at 2930 & 1425 and 1325 cm⁻¹ of crosslinked phosphorylated wood pulp thus can be seen from the following equation



From table it is clear also that , the degradation of wood pulp due to phosphorylation is lower than sulfonation process .Thus can be confirmed of lower relative absorbance of -O- band at 1112 cm⁻¹ in case of phosphorylated wood pulp than sulfonated wood pulp . the crystallinity index of phosphorylated wood pulp is lower than the sulfonated wood pulp due to lower degradation of phosphorylated wood pulp than the sulfonated wood pulp. The Mercerization depth of wood pulp derivatives is higher than that in case of wood pulp. From table, it is seen also that, the relative absorbance of sulfonated group at 1400 cm⁻¹ is higher than that the phosphorylated group incorporation in wood pulp. This mean that the incorporation of sulfate group into wood pulp is higher than that incorporated phosphate groups.

Infrared of ion exchange of more than incorporated group. Table (1) shows that the relative absorbance of phosphorylated wood pulp and phosphorylated carboxylation wood pulp. From table, it is clear that the phosphorylated wood pulp has higher relative absorption of phosphate group at 1200 cm⁻¹ than the phosphorylatd carboxylated wood pulp. Also due to carboxylation a new band was seen at 1718 cm⁻¹ which characteristic to carboxylated group. Degradation of cellulose chain in case of carboxylated wood pulp is higher than the phosphorylated wood pulp.

Table 1: Infrared spectra of wood pulp and its derivatives.

Sample	OH 3379 cm ⁻¹	CH ₂ 2902 cm ⁻¹	CHO 1638 cm ⁻¹	CH ² 1428 cm ⁻¹	2 nd OH 1162 cm ⁻¹	1rdOH 1037 cm ⁻¹	-O- 1112 cm ⁻¹	COOH 1720 cm ⁻¹	C-O-P 870 cm ⁻¹	C-O-P 1200 cm ⁻¹	C-O-S 1400 cm ⁻¹	CrI	Mercerized depth
Untreated W.P	2.82	1.13	0.5	0.98	1.78	2.48	2.17	-	-	-	-	2.8	1.11
Sulfonated W.P	2.67	0.9	0.37	0.93	1.61	2.3	2	0.1	-	-	1.4	2.6	1.19
Phosphorylated W.P	2.9	0.92	0.39	0.9	1.73	2.5	1.95	-	0.32	1.1	-	2.5	1.25
Phosphorylated W.P+Crosslinked	3	1.17	0.57	1.93	1.9	2.61	2.31	0.2	0.25	1.2	-	3	0.99
Phosphorylated W.P+carboxylation	2.71	1	0.81	1.02	0.56	1.56	2.23	0.65	0.16	1.1	-	1.97	1.02
Phosphorylated W.P +Crosslinked + carboxylation	2.8	2.89	1.51	1.54	1.81	2.51	2.14	0.4	0.2	1.15	-	2.28	1.34

Table 1: shows that the relative ion exchange of more than incorporated group.

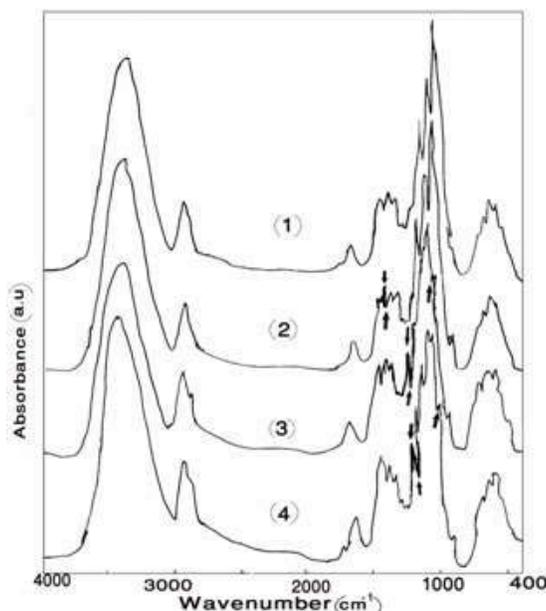


Fig. 1: Absorption spectra of wood pulp (1) wood pulp sulfonation (2) wood pulp phospholylation (3) wood pulp phospholylation crosslinking (4).

Metal ions uptake:

Table (2) show the metal ion uptake of wood pulp and its derivatives. It is clear that the phosphorylated wood pulp has the higher affinity toward metal ion uptake than sulfonated and untreated wood pulp, although the relative absorbance of C-O-S is higher than C-O-P. i.e. the incorporated sulfonated group onto wood pulp is higher than that incorporated of phosphorylated groups. This can be attributed to that, react with OH of cellulose to form half ester with one ionizable proton while phosphorous oxychlorid can react at a single site

form dianion and monoanion as shown in structure I. it can react with two sites on biopolymer backbone crosslink them and result to only monoanion to react with a cation. The difference of ability sorption of ion exchange to metal ions can be affected radius of ion, steric, electronic effect and hydrated radius of ion as well as hard acid. Multiple functional group incorporated in wood pulp lead to some degree of selectivity to rejection of cations having large ionic radii due to steric hindrance factor or selective absorption due to polydentate bonding. The sulfate monoester, a half ester, has a smallest size and better able to reside in the interspace of the biopolymer matrix. Phosphorus oxychloride can react at a single site and the product can remain as dianion or it react with two sites on biopolymer backbone crosslink them and result in monoanion to react with a cation (Lahmer, *et al.*, 1950).

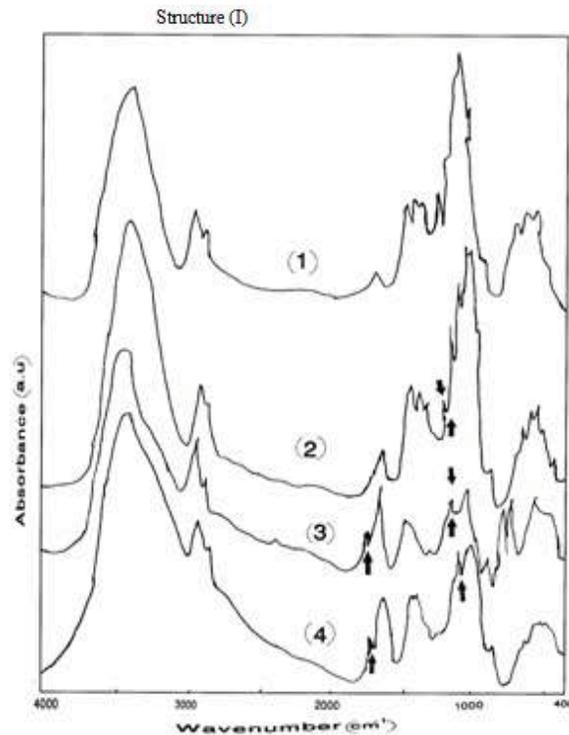
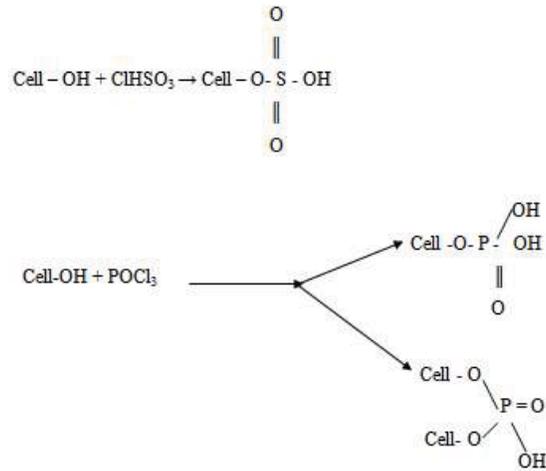


Fig. 2: Absorption spectra of wood pulp phosphorylation (1) wood pulp phosphorylation crosslinking (2) wood pulp phosphorylation carboxylation (3) wood pulp phosphorylation crosslinking carboxylation (4).

Table 2: Metal ion uptake from wood pulp and its derivatives

Samples	$\mu \text{ mol / g}$					
	Cu	Co	Fe	Mg	Mn	Ni
untreated W.P	3.9	5.5	5.6	13.4	9.1	4.4
Sulfonated W.P	9.9	10.8	15.4	41.1	18.1	10.6
Phosphorylated W.P	15.9	12.5	37.7	93.2	20.1	13.8
Phosphorylated W.P + crosslinking	17.8	14.8	38.2	98.4	28.4	17.8
Phosphorylated W.P + carboxylated	16.3	16.2	33.3	99	20.5	17.2
Phosphorylated W.P +crosslinking +carboxylated	19.8	17.4	354.7	99.8	21.2	21.0

Crosslinking of cellulose prior to or followed by chemical modification control the swelling of the produced cellulose derivatives and permit high degree of substitution. So from infrared spectra it is clear that the relative absorbance of C-O-P band at 1200 cm of crosslinked phosphorylated wood pulp is higher than uncrosslinked one. This mean that it has a high phosphate group (Simkovic, 1996). From Table (2) it is seen that the crosslinked phosphorylated wood pulp has higher affinity to metal ions uptake than uncrosslinked one. This is due to the increase of incorporated phosphate group in crosslinked phosphate wood pulp thus can be observed from the relative absorbance of C-O-P band at 1200 cm^{-1} which has a higher value than the relative absorbance of uncrosslinked phosphate. Also the crosslinked phosphate wood pulp is more branched than uncrosslinked one which increase from its efficiency toward metal ion uptake. Also, beside the effect of crosslinked material to increase the incorporated functional groups, it stabilize the cellulose for the preparation of weakly acidic cation exchanger (Simkovic, 1996). From Table (2), it is clear that the selectivity of absorbent metal ions by the ion exchangers is not the same. On the other hand, the affinity of metal ions by different derivatives of wood pulp is related to the charge and the hydrated radius of the metal ion. Also adsorption of the metal ions onto the ion exchangers can be attribute to terms columbic interaction and intrinsic absorption. Columbic interaction results from the electrostatic energy of interaction between absorbents and absorbates. The charge of substrates as well as softness and hardness of the charge on both sides are mostly responsible for the amount of absorption. On the other hand, the ion exchange of incorporated phosphate and carboxylate groups has a high tendency toward absorption of some metal ion than the ion exchange which incorporated phosphate group only.

In general, from table it is clear that the crosslinked phosphate and carboxylate group ion exchange has a higher affinity toward metal ion uptake than the other ion exchangers.

Electrical studies:

Dielectric constant (ϵ')

Dielectric constant measurements on wood pulp and its derivatives have been made over the frequency range of 200 Hz to 5 MHz in the temperature range of (303 – 433 K). The variation of dielectric constant wood pulp and its derivatives as a function of frequency at different temperatures are shown in Figs. 3 (a – f). From these figures, it is clear that the dielectric constant almost increases with increasing of temperature. This increase can be attributed to the orientation of the dipoles (which formed from the charge carriers) in the direction of the applied electric field.

In general, temperature has a complicated influence on the dielectric constant, which in turn depends on electronic and ionic polarization, dipole orientation polarization, space charge polarization, etc. The variation of the dielectric constant with frequency could be used to elucidate which type of contributions is present. The space charge polarization contribution is mainly noticeable in the low frequency region. In contrast, dipole orientation polarization can be exhibited by materials even up to 10^{10} Hz, while electronic and ionic polarization always exists below 10^{13} Hz.

Since higher values of the dielectric constant are observed in lower frequency regions at which the space charge polarization contribution is predominant (Elshafie, *et al.*, 1999). It can also be seen that, the dielectric constant almost decreases with increasing frequencies. This may be due to the fast variation of the field accompanied with the applied frequency and the electric dipoles are no longer able to rotate sufficiently fast to follow the field variation. This will lead to a decrease in the dielectric constant which increasing the frequency.

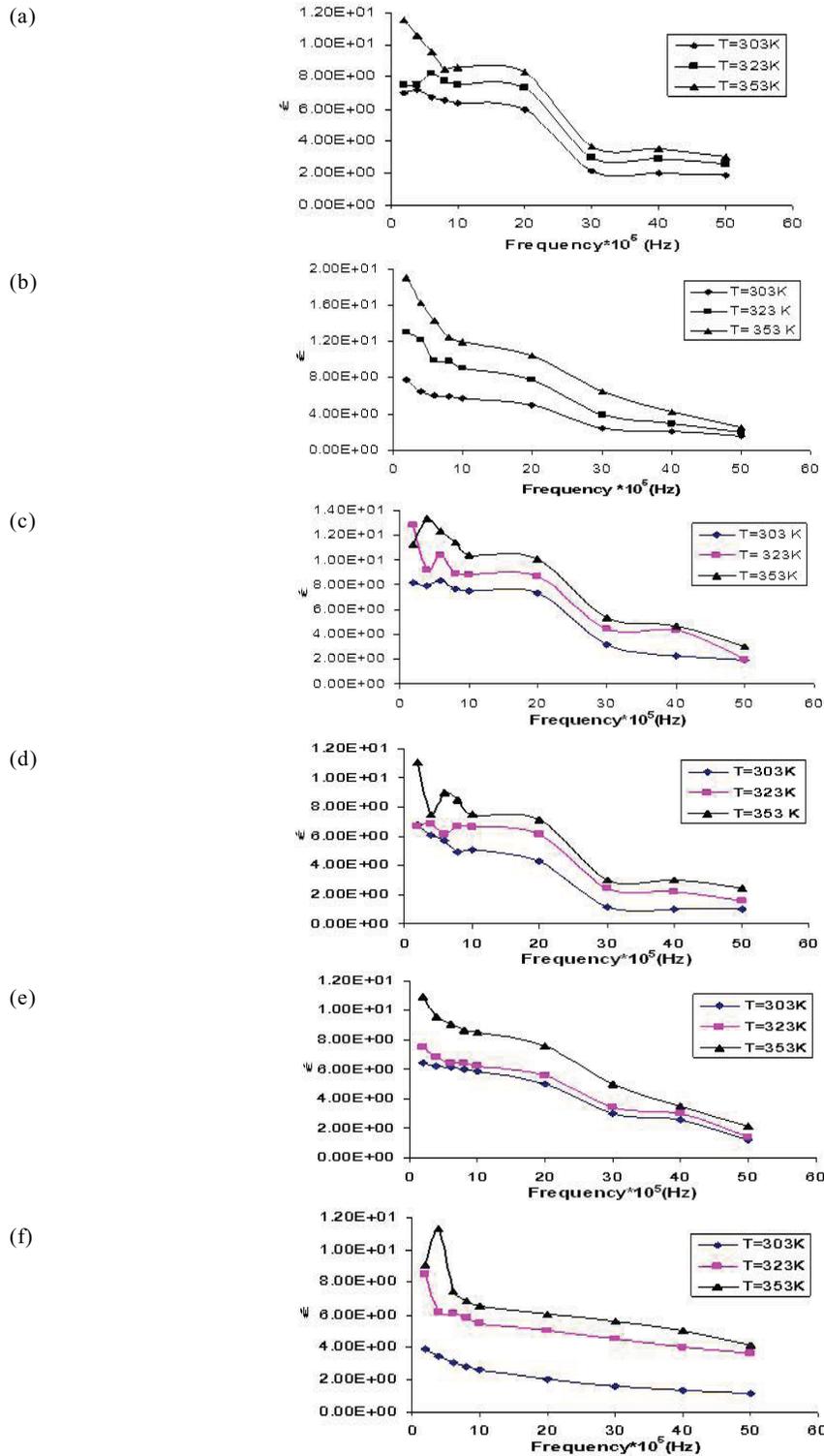


Fig. 3: (a-f): Dielectric constant(ϵ') as a function of frequencies at T = 303,323 and 353 K for wood pulp (a) wood pulp sulfonation (b) wood pulp phospholylation (c) wood pulp phospholylation crosslinking (d) wood pulp phospholylation carboxylation(e) wood pulp phospholylation crosslinking carboxylation (f).

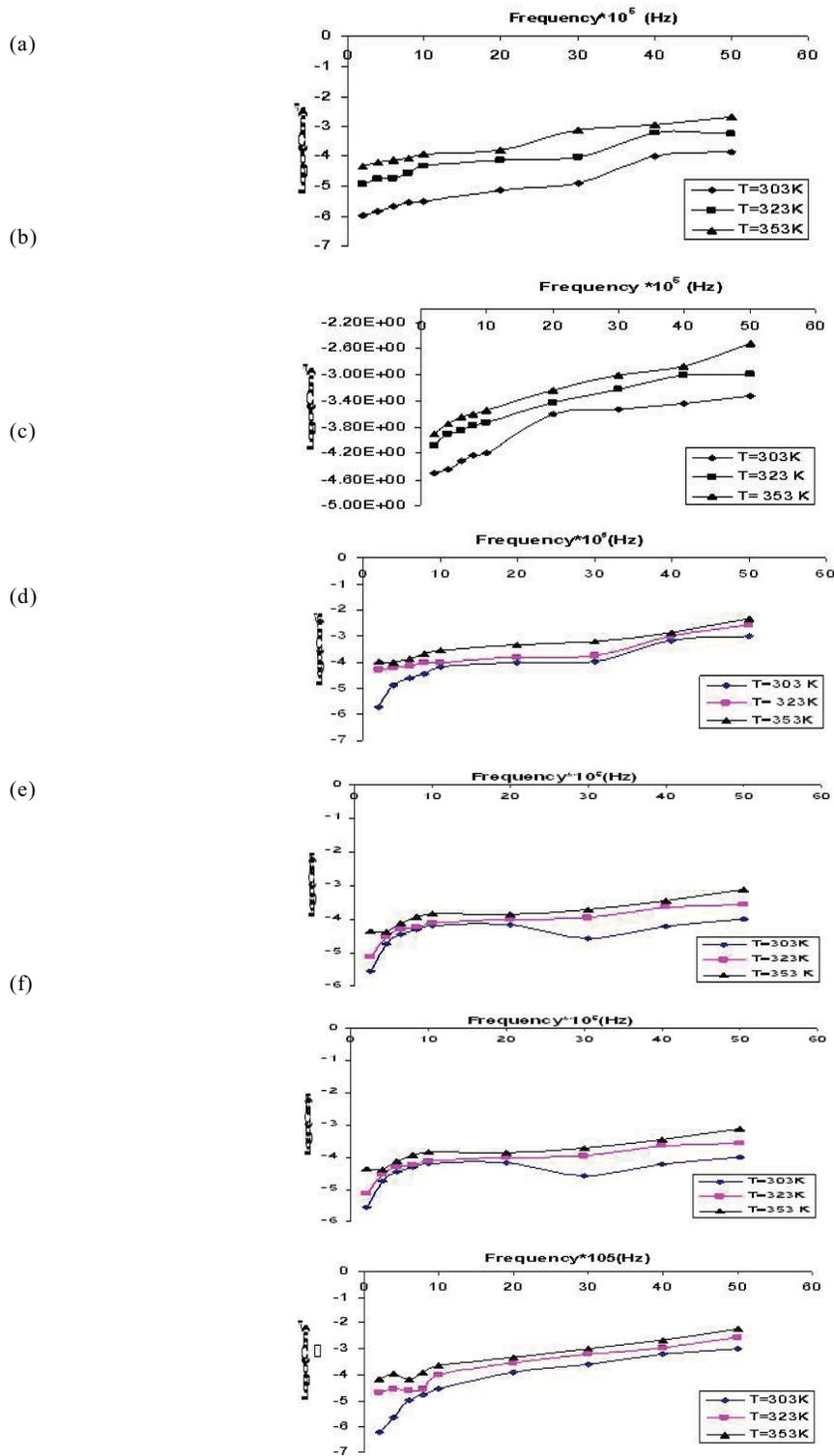


Fig. 4: (a-f): AC conductivity as a function of frequencies at T = 303,323 and 353 K for wood pulp (a) wood pulp sulfonation (b) wood pulp phospholylation (c) wood pulp phospholylation crosslinking (d) wood pulp phospholylation carboxylation(e) wood pulp phospholylation crosslinking carboxylation (f).

AC electrical conductivity:

The dependence of AC electrical conductivity on the frequencies at different temperatures (303 – 433 K) of wood pulp and its derivatives are shown in Figs. 4(a-f) the conductivity increases with increasing temperature and this behavior was acceptable because the thermal energy activates the charge carriers and increases their mobilities with the result of increasing conductivity. An empirical relation can express the frequency dependence of AC conductivity (Elliott, 1987 and Saleh, *et al.*, 1993) as follows: $\sigma_{AC} \propto (2\pi f)^n$

Where n is not a constant for all substances, but it is a function of temperature, approaching unity at low temperatures and 0.5 or less at high temperature. Also the conductivity increases with increasing frequencies, due to the electrons in a molecular orbital excited to a higher energy level and tunneling through a potential barrier to a non-occupied state of a neighboring molecule. The available experimental results on the frequency dependence of AC conductivity have revealed a considerable similarity of behavior for the samples under investigation.

Conclusion:

1. Crosslinking for wood pulp increase the incorporated functional group.
2. Phosphate group increase the resistance of the produced ion exchange
3. Crosslinking of ion exchange increases from the metal ion absorption.
4. Absorption of metal ions is highly affected by the incorporated functional groups.
5. Absorption of metal ion by ion exchanger is affected by the electronegativity and atomic radius of metal ions.
6. The dielectric constant and AC conductivity are depending on the dynamic of polysaccharides.

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