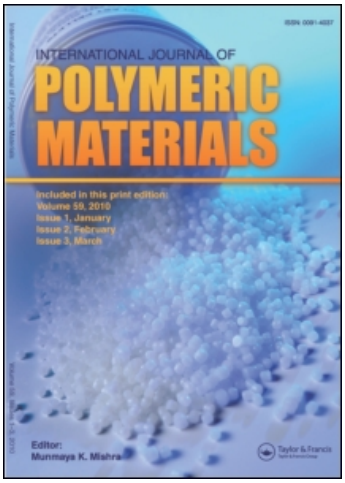

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Preparation, Characterization and Properties of Paper Sheets Made from Chemically Modified Wood Pulp Treated with Metal Salts

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Preparation, Characterization and Properties of Paper Sheets Made from Chemically Modified Wood Pulp Treated with Metal Salts

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Three chemically modified wood pulps (CEWP, AOWP and CmEWP) were prepared and used as a substrates for paper sheets. The effect of treating the chemically modified wood pulps with $CuCl_2$ and $FeCl_3$ salts on the mechanical and thermal properties of the formed paper sheets, in addition to their antimicrobial action on some microorganism were studied. The prepared sheets were characterised by IR-spectra, micro-analyses and magnetic succeptibility measurements. The thermal degradation of the prepared sheets has been investigated by means of non-isothermal TG measurements using Coats and Redfern model. The method of least squares was applied to estimate the appropriate order of degradation reaction (n), and consequently the activation parameters. The results obtained reveal that, paper sheets containing Cu(II) ions have a higher strength properties, thermal stabilities, antimicrobial action and magnetic property than paper sheets prepared from untreated and $FeCl_3$-treated modified pulps. Paper sheets prepared from treating the derivatives of partially cyanoethylated wood pulp (AOWP and CmEWP) have high magnetic succeptibility value compared with paper formed from adding Fe_2O_3, as conventional filler for magnetic paper manufacture. The regression equation which represents the relation between mechanical properties (Q_z), crystallinity index and activation energy was also proposed.

Keywords: Paper; wood pulp; metal salts; properties

INTRODUCTION

Applications of modified celluloses in inorganic analytical chemistry have been given a great deal of attention during many years. Modified

celluloses can be used for removal of heavy metal ions from waste or sea water, *i.e.*, as absorbants, much more effectively than natural cellulose. Therefore attempts to introduce chelating groups, carboxyl, nitrogen containing groups and phosphate, to the backbone of cellulose by chemical modification have been carried out by many authors [1 – 6].

Cyanoethylation of cellulose regards as a one of chemical modification tools for introducing nitrogen containing groups through cellulose backbone. Cyanoethylation of cellulose can be traced back to the pioneering work of MacGregor *et al.*, in the 1940s [7]. Since the partial cyanoethylated of cotton cellulose has been extensively studied to improve its durability, such as thermal, chemical and microbiological substance. Also, highly substituted product was used as an electric material because of its high dielectric constant [8]. The chemical modification by cyanoethylation to improve the mechanical properties of paper sheets has been reported [19, 10].

Persual of literature reports the binding of heavy metal ions by amidoximated wood, the tendency of recovery the metals from absorbents are not completely desorbed by acid solution, and the decrease of the durability of absorbents in repeated use [4, 11 and 12].

In this study, we report the properties (mechanical, thermal and biological action) of paper sheets prepared from partially cyanoethylated wood pulp (CEWP) and derivatization of amidoximated and carbomylethylated wood pulps (AOWP and CmEWP) from it, as adsorbents to Cu(II) and Fe(III) from their salt solutions. The prepared sheets were characterized by IR-spectra, micro-analytical analyses and magnetic succeptibility measurements. For comparison, the properties of paper sheets prepared from wood pulp and chemically modified wood pulps are also studied.

EXPERIMENTAL

Materials

a) Paper Substrates

– Paper grade kraft soft wood pulp, was delivered from Rakta Paper Mill, Alexandria, Egypt. The pulp was chemically analysed as α-cellulose [13], pentosans [14], lignin [15] and ash.

- Partially cyanoethylation of wood pulp and its derivatives (amidoximated and carbomylethylated wood pulps) were prepared according to the procedures described in references [16, 17]. Partially cyanoethylation was carried out on pre-beaten wood pulp (SR° 30).

b) Metal Salts

Analytical grade copper chloride dihydrate and ferric chloride hexathydrate were used for preparing a solutions of metal ions.

Handsheets Paper Making and Strength Properties Measurements

The prepared chemically modified wood pulps were continued to beating till SR° 40–45, followed by soaking in 10 m mole aqueous solutions of $CuCl_2$ and $FeCl_3$, in liquor ratio 100 : 1, and incubated at room temperature (~ 22°C) for 15 hrs., then subjected to handsheet formation, according to Swedish standard method (S.C.A.). The prepared sheets, from untreated and metal salts treated modified pulps, were conditioned at relative humidity 65% and temperature 20°C before testing the breaking length, tear factor and burst factor [18]. The ash content of the prepared sheets was also estimated, as an indication to the metal content in paper samples (as metal oxides).

For each test at least five measurements were carried out, and the arithmatic mean of the obtained results was calculated.

Other Measurements

Infra-red Absorption Spectra

IR-spectra of untreated and metal salts treated modified pulps were obtained in the region from 4000–200 cm^{-1}. The apparatus used was Insco FT/IR-300E, Fourier Transform Infrared Spectrometer, using the KBr technique.

Micro-analyses

Carbon, hydrogen and nitrogen contents of paper samples were determined by the Microanalytical Unit of Cairo University. The

metal percentage adsorbed by chemically modified pulp was determined by atomic absorption spectrometer to the remaining metal salt solutions.

Magnetic Measurements

Measurements of magnetic succeptibility (mass, c.g.s.) were carried out using Gouy balance and Hg $[Co(SCN)_4]$ as calibrant.

Thermal Analysis

The thermogravimetry analysis (TGA) of the paper samples was run on a Shimadzu-50 thermal analyzer under nitrogen atmosphere, at flow rate of 30 ml. $min.^{-1}$ and a rate of heating 10°C $min.^{-1}$ The measurements were made relative to calcined alumina.

Biological Evaluation

The antimicrobial actions of the paper samples on Bacillus stabtilis NRRL B-543, Escherichia coli NRRL B-210, Salmonella typhi, Pseudomonas aeruginosa, and Aspergillus niger were carried using the technique of a gar plate method [19]. The former four micro-organisms as example of bacteria and the latter one as example of fungus.

Scanning Electron Microscope (SEM)

A scanning electron microscope Nanolab 7 produced by SEMCO Instrument Co. Ottawa–Canada, was used. The photographig conditions were all kept constant all over the experiments. Acceleration voltage of electron beam 20 kV, the time taken for a photograph is 60 sec. Scanning electron microscopic structures were observed at magnification of X 500.

RESULTS AND DISCUSSION

Table I represents the chemical constituents of the paper grade kraft soft wood pulp which was used as a paper substrate.

TABLE I Chemical analysis of wood pulp

Chemical constituent	*value* *
α-Cellulose, %	86.55
Pentosans, %	7.00
Lignin, %	trace
Ash, %	0.187

* It is the mean values of the triplicate measurements.

Mechanical Properties

Table II shows the effect of treating the chemical modified wood pulps [partially cyanoethylated (CE), amidoximated (AO) and carbomylethylated (CmE) wood pulps (W.P.)] with copper chloride and ferric chloride solutions on the mechanical properties of the formed handsheets. The mechanical properties of paper sheets prepared from wood pulp and chemically modified wood pulps were taken for comparison. It is seen that the mechanical properties of paper sheets made from wood pulp were promoted either by chemical modification or metal salts treated modified pulps. The treatment by copper chloride exerts a considerable increase in the mechanical properties of modified pulps than the treatment by ferric chloride.

TABLE II Mechanical properties and permeability of paper sheets prepared from untreated and treated chemically modified wood pulps with metal salts

Paper Sample	*Breaking length, m*	*Tear factor*	*Burst factor*	Q_z	*Permeability ml./min.*	*Ash, %*
Wood pulp (W. P.)	4281.50	108.07	33.07	1132.68	180	0.19
Cyanoethylated wood pulp (CEWP)	4413.49	109.63	45.93	1169.67	205	0.18
CEWP-$CuCl_2$	5358.13	116.21	34.05	1403.65	420	3.87
CEWP-$FeCl_3$	4458.87	105.63	36.43	1176.64	233	7.69
Amidoximated wood pulp (AOWP)	5535.16	117.74	39.03	1452.42	303	0.21
AOWP-$CuCl_2$	5670.08	125.03	20.19	1485.08	875	4.14
AOWP-$FeCl_3$	5136.70	103.77	38.21	1345.61	555	6.24
Carbomylethylated wood pulp (CmEWP)	4652.13	122.70	25.30	1230.71	> 1000	0.20
CmEWP-$CuCl_2$	6009.70	127.46	34.25	1574.72	1000	4.83
CmEWP-$FeCl_3$	5789.28	127.74	28.33	1518.27	> 1000	5.36

For the purpose of comparison, the mechanical properties (breaking length, m, burst factor and teafactor) are together in the modified formula which has suggested by Jayme [20] and known as the quality number, Q_z. The data of the quality number (Tab. II) show that, derivatization of CmEWP pulp from partially CEWP exerts a higher influence (improvement) on the paper properties of wood pulp than other modifications (partially cyanoethylation and amidoximation of W.P.). This is related to in addition to the remaining CN groups present in the vicinity of the hydroxyl groups can participate in hydrogen bonding formation, the treatment of partially CEWP by H_2O_2 facilitate the formation of *N*-methylene amide cross links between amide groups or amide and the remaining free hydroxyl groups [16], this may interupt the formation of gap between adjacent chains and increasing the permeability value (Tab. II), as mainifasted from SEM-graphs (Figs. 1 – 3).

The data of Q_z also show that, the highest value is that of paper formed from $CuCl_2$-treated CmEWP. The paper sheets of $CuCl_2$-

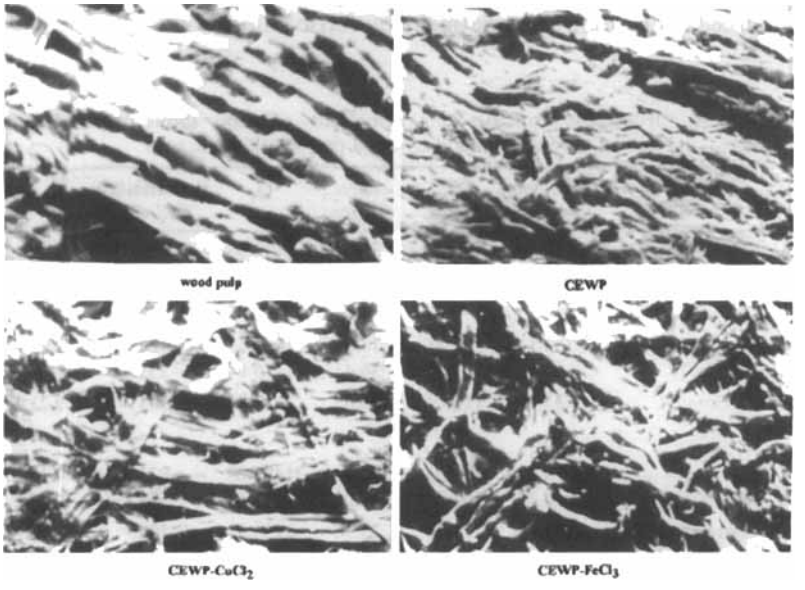

FIGURE 1 SEM photographs of paper sheets prepared from untreated and metal salts treated partially cyanoethylated wood pulps (CEWP).

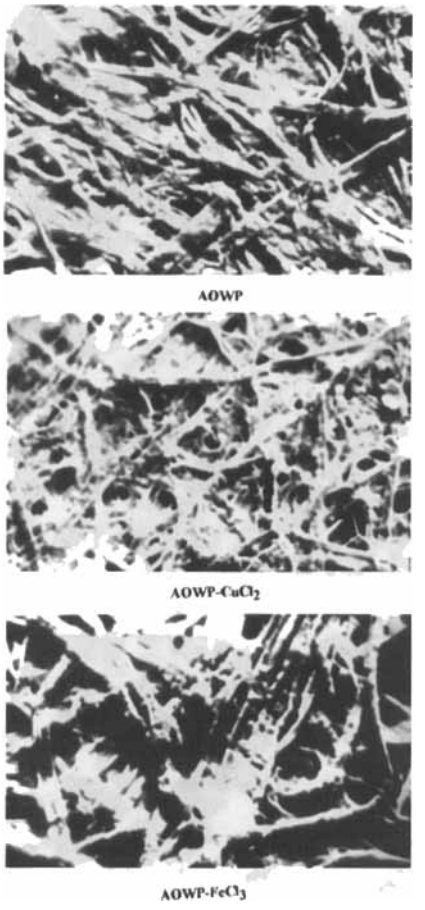

FIGURE 2 SEM photographs of paper sheets prepared from untreated and metal salts treated amidoximated wood pulps (AOWP).

treated the derivatives of CEWP (AOWP and CmEWP) have superior Q_z value than $CuCl_2$-treated CEWP, this is attributed to increase the number of lone pair electrons on oxygen and nitrogen atoms, which coordinate with metal ions. However, due to the oxidation effect of $FeCl_3$ to some hydroxyl groups, destruction of weak hydrogen bonds and subsequent reordering of the chains with the formation of new and relatively stronger hydrogen bonds [21], the Q_z values of the

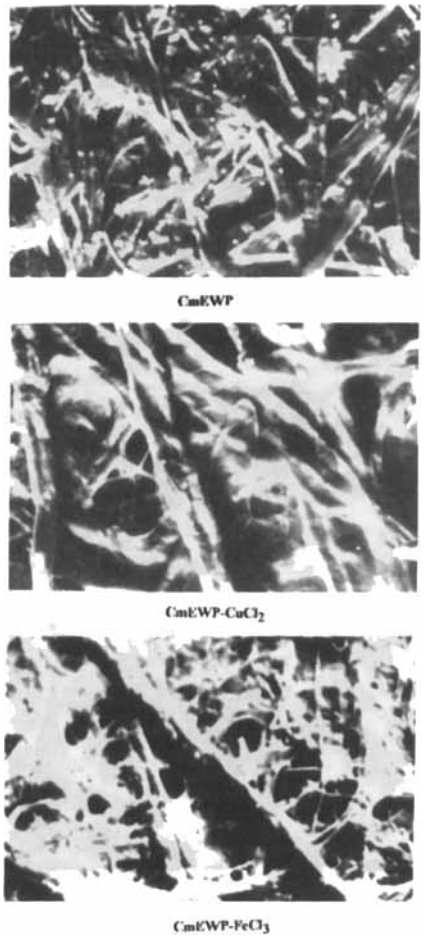

FIGURE 3 SEM photographs of paper sheets prepared from untreated and metal salts treated carbomylethylated wood pulps (CmEWP).

formed paper sheets from $FeCl_3$-treated modified pulps are lower than $CuCl_2$-treated pulps, and these values are relatively higher than paper sheets made from untreated modified pulps.

The values of permeability and ash content (Tab. II) of the formed paper sheets in addition to SEM-graphs also confirmed the inclusion of metal ions through cellulose chains.

IR-spectra

Tables III and IV show the main infra-red absorption bands and IR-measurements [asymmetry index, mean hydrogen bond strength (MHBS) and crystallinity index [22,23] of paper sheets under investigation. The relative absorbance of band was calculated as the ratio of the absorbance at the subscript wave-number to the absorbance of the wave-number at $\sim 1328\,cm^{-1}$, which corresponds of CH rocking of ring.

From Table III it is clear that, the IR-spectrum of paper sheet made from untreated wood pulp shows characteristics broad bands at $3421\,cm^{-1}$ and $2916\,cm^{-1}$ due to OH and hydrogen bonds (intra and inter molecular hydrogen bonds). The bands at wave-number $1637\,cm^{-1}$, $1428\ cm^{-1}$, $1369\ cm^{-1}$ and $894\ cm^{-1}$ corresponding to C = O (stretching vib.), OH (bending vib.), CH (bending vib.) and CH (rocking vib.), respectively.

In the IR-spectrum of paper sheet made from partially CEWP, the band maximum corresponding to stretching vibration of OH was shifted to lower wave number (from $3421-3400\ cm^{-1}$) with the appearance of a new bands at 2260 and $2140\ cm^{-1}$ arising from $C \equiv N$ group. This is attributed to substituting the 1^{ry} hydroxyl groups of glucopyranose units by polar cyanoethyl groups, which leads to increase the bonding strength between fiber chains and the degree of order (as a result of treatment with alkali during its preparation), as manifested from increasing the values of MHBS, asymmetry index and crystallinity index, compared with those values of sheet formed from unmodified wood pulp (Tab. IV).

The spectra of paper sheets formed from treating the partially CEWP by hydroxyl amine hydrochloride and hydrogen peroxide confirm the formation of hydroxamic acid and amide groups, respectively. Whereas, the relative absorbance of band corresponds to C = O at $\sim 1664\,cm^{-1}$ increased, in addition to the blue shift of the band maxima correspond to OH (str.) from $3400\ cm^{-1}$ to $3430\,cm^{-1}$ and increased its relative absorbance in the case of spectrum of AOWP paper sheets. It can be also seen that, complete amidoximation and carbomylethylation of partially cyanoethylated wood pulp has not been reached due to the remaining of $C \equiv N$ band.

TABLE III Main IR-absorption bands of paper sheets prepared from untreated and treated chemically modified wood pulps with metal salts

Paper Sample	ν_{OH} (*stretching*)		ν_{CH} (*stretching*)		$\nu_{C\equiv N}$ (*stretching*)		$\nu_{C=O}$ (*stretching*)		ν_{OH}(*bending*)		ν_{CH} *or* ν_{NH} (*bending*)		ν_{CH} *or* ν_{NH} (*rocking*)		$\nu_{700-200\,cm^{-1}}$	
	cm^{-1}	*E*	cm^{-1}	*E*	cm^{-1}	*E*	cm^{-1}	*E*	cm^{-1}	*E*	cm^{-1}	*E*	cm^{-1}	*E*	cm^{-1}	*E*
Wood pulp (W.P.)	3421	1.66	2916	1.06	–	–	1637	0.74	1428	0.98	1369	1.02	894	1.03	231	0.93
CEWP	3400	1.49	2902	1.01	2260	0.52	1670	0.99	1430	0.99	1373	1.03	900	0.78	559	1.09
					2140	0.50									237	1.8
CEWP-$CuCl_2$	3384	1.54	2902	1.02	2260	0.51	1670	0.99	1430	1.00	1373	1.05	900	0.79	617	1.09
					2150	0.48									237	1.85
															217	1.48
CEWP-$FeCl_3$	3421	1.82	2902	1.25	2260	0.47	1664	1.05	1429	1.01	1373	1.05	900	0.84	559	1.23
					2150	0.45									239	1.84
															220	1.31
AOWP	3446	2.10	2902	1.41	2260	0.41	1664	1.05	1430	0.99	1373	1.04	900	0.77	561	1.00
					2140	0.41									237	1.60
AOWP-$CuCl_2$	3430	1.53	2902	0.95	–	–	1655	1.20	1430	1.03	1375	1.03	900	0.78	559	1.15
					–	–									237	1.92
															559	1.13
AOWP-$FeCl_3$	3430	1.48	2902	1.04	2260	0.49	1664	1.05	1430	1.00	1373	1.03	895	0.83	285	1.06
					2140	0.49									237	0.96
CmEWP	3440	1.38	2902	0.91	2260	0.41	1670	1.04	1430	0.99	1373	1.03	900	0.77	559	0.77
					2140	0.43									239	1.89
CmEWP-$CuCl_2$	3400	1.55	2902	0.89	2260	0.50	1670	1.1	1430	1.01	1373	1.03	900	0.77	559	1.12
					2140	0.51									237	1.77
CmEWP-$FeCl_3$	3400	1.37	2902	0.89	2260	0.49	1670	1.07	1430	1.00	1375	1.03	900	0.78	559	1.13
					2140	0.49									343	1.01
															237	1.95

For the IR-measurements Table IV shows that the MHBS, asymmetry index and crystallinity index of AOWP and CmEWP paper sheets are higher than those values of CEWP paper sheets. This is attributed for the case of AOWP sheets to the ability of forming inter and intra molecular hydrogen bonding between OH and NH of hydroxamic acid groups with unsubstituting OH groups of glucopyranose units; while for the case of CmEWP sheets, in addition to the formation of hydrogen bonds between polar C $\equiv$ N groups, and OH groups, the formation of *N*-methylene amide cross link between cellulose chains is possible [16]. This view was emphasized from increasing the permeability of formed sheet, and consequently the relatively high porous surface structure of paper was noticed than other sheets (Figs. 1–3).

The results in Table IV show that, the IR-measurement of paper sheets made from treating the chemically modified wood pulps with $CuCl_2$ solution, especially asymmetry index and crystallinity index, increased compared with paper sheets of untreated modified pulps. This is attributed to the formation of chelated bonds between the introduced chelating groups (nitril, hydroxamic and amide) with Cu(II) ions. The red shift of the band corresponds to OH group (str.) for $CuCl_2$-treated CEWP sheet from 3400 to 3385 cm^{-1}, with decreasing the relative absorbance of the bands at 2260 and 2150 cm^{-1}

TABLE IV IR-measurements of paper sheets prepared from modified pulps and metals treated chemically modified wood pulps with metal salts

Paper Sample	$A_{max}\,cm^{-1}$	*Asymm. Index*	*M.H.B* A_{OH}/A_{CH}	*Cr. I* $A_{1430\,cm^{-1}}/A_{900\,cm^{-1}}$
Wood pulp (W. P.)	3421	1.391	1.227	0.944
Cyanoethylated wood pulp (CEWP)	3400	1.643	1.465	1.270
CEWP-$CuCl_2$	3385	1.786	1.505	1.271
CEWP-$FeCl_3$	3421	1.580	1.457	1.198
Amidoximated wood pulp (AOWP)	3446	2.000	1.494	1.293
AOWP-$CuCl_2$	3430	2.650	1.607	1.319
AOWP-$FeCl_3$	3430	2.140	1.421	1.206
Carbomylethylated wood pulp (CmEWP)	3440	1.720	1.520	1.281
CmEWP-$CuCl_2$	3400	2.190	1.734	1.311
CmEWP-$FeCl_3$	3400	2.000	1.538	1.284

indicating that the unsubstituting hydroxyl group of glucopyranose units and C ≡ N groups act as a coordination sites. While, the nitril and/or hydroxamic acid and amide groups are a major coordinating sites for the case of $FeCl_3$-treated modified pulps, as clear from the unchanged the band maxima of OH (str.). The decrease in the relative absorbance (E) corresponds to C ≡ N group for metal treated modified pulps is related to the delocalization of lone pair electrons of N after coordination with metal ions.

Table IV also shows that, the crystallinity index and asymmetry index of sheets formed from AOWP and CmEWP are higher than those values of sheets from CEWP. This is related to the presence of more lone pair electrons on N and O which coordinated with metal ions.

For the cases of $FeCl_3$-treated modified pulps, the values of crystallinty index is lower than $CuCl_2$-treated modified pulps. This is attributed to the oxidation effect of iron [21], as manifested from increasing the value of $E_{C=O}$ group at 1670 cm^{-1}. Since the MHBS refers to the number of hydroxyl groups of cellulose pulp entering the hydrogen bonds, therefore its value also decreased for $FeCl_3$-treated modified pulps than $CuCl_2$-treated one.

The observed unchanged in the position of the band maxima correspond to OH (str.) of metal treated modified samples with increasing the MHBS and the (E) of this band, may be attributed to the presence of coordinated water (as the case of metals treated CEWP and $CuCl_2$-treated CmEWP), in addition to themselves liberation of primary hydroxyl groups in C_6 from hydrogen bonds associated with other groups after the metal ions introduced into cellulose chains [24]. The liberation is relatively higher than coordination.

The unchanged in the position of the bands correspond to CH (str.) at 2902 cm^{-1} of metal salt treated pulp may be related to the effect of interaction between the nitrill, hydrogen, hydroxamic acid, or carbomylethylated groups and the metal ions on the environment of $-CH_2$ is not evident, due to the porous structure of produced paper sheets, as clear from increasing the permeability value (Tab. II) and SEM-graphs (Figs. 1 – 3).

The IR-spectra of metal salts- treated modified pulps (Tab. III) show an increase in the relative absorbance of the bands in the region from 700 – 200 cm^{-1} with the appearance of a new bands, compared

with paper samples prepared from chemically modified pulps, this observation confirm the formation of M —O and/or M —N bonds [25, 26].

From the IR-spectra (Tabs. III and IV) and elemental analyses data listed in Table V it is clear that, the unsubstituting hydroxyl groups of glucopyranose units and cyanoethyl groups and/or hydroxamic acid or carbomylethylated group are the sites of polychelation with Cu(II) ions; while for $FeCl_3$-treated modified pulps the substituted chelating groups are more possible sites than free hydroxyl groups. The $CuCl_2$ reacts with glucopyranose unit of CEWP, AOWP and CmEWP in a 1:3, 1:4, and 1:2 molar ratio, respectively, and in a molar ratio 2:1, 2:1 and 3:1, for the case of $FeCl_3$ with the prementioned adsorbents.

Also, from the difference in the found percentage of metal ion (Tab. V) compared with its theoretical calculation, it is predicted that the number of glucopyranose units including one Cu(II) ion are 14, 22, and 10 for the case of CEWP, AOWP and CmEWP, respectively; while these values become 6, 15 and 9, respectively for the number of glucopyranose units including one Fe(III) ion.

Magnetic Property

Table V shows the values of mass susceptibility (X_g c.g.s.) of the paper sample under investigation. It is clear that the derivatization of amidoximated and carbomylethylated wood pulp from partially cyanoethylated wood pulp improves the magnetic property. The paper sheet prepared from AOWP has superior mass susceptibility than other modified pulps (CEWP and CmEWP). For metals (Cu(II) and Fe(III) salts)-treated CEWP, the X_g of the prepared sheets is lower than that prepared from CEWP. However, treating the AOWP and CmEWP with $CuCl_2$ promote their magnetic properties. For all chemically modified pulps, the paper sheets prepared from $CuCl_2$-treated pulps have a higher magnetic properties than those made from $FeCl_3$-treated pulps.

The decrease in X_g values of sheets prepared from metals-treated CEWP, compared with untreated one confirm that the lone pair of electrons on nitrogen atoms are coordinated with metal ions. While, the increase of its value for the case of $CuCl_2$-treated AOWP and CmEWP than CEWP paper sheets indicate that the chelation of Cu(II)

TABLE V Micro-analysis of paper sheets preapred from untreated and treated chemicall modified wood pulps with metal salts

Paper Sample	*C*, %	*H*, %	*N*, %	*M*, %*	H_2O, %**	$X_g(10^{-9})$ *c.g.s.*
Wood pulp (W. P.)	48.2	4.8	–	–	–	–
Cyanoethylated wood pulp (CEWP)	47.0	5.7	2.90	–	–	5999.6
CEWP-$CuCl_2$	42.1	5.7	2.70	2.5	2.0	2338.1
CEWP-$FeCl_3$	40.8	5.9	2.65	4.8	4.9	3526.7
Amidoximated wood pulp (AOWP)	47.2	6.1	3.10	–	–	6759.7
AOWP-$CuCl_2$	43.1	5.4	2.94	2.8	–	18775.9
AOWP-$FeCl_3$	40.9	5.2	2.85	3.9	–	5579.0
Carbomylethylated wood pulp (CmEWP)	46.2	6.2	2.50	–	–	13332.9
CmEWP-$CuCl_2$	39.9	5.7	2.44	3.1	3.7	48147.9
CmEWP-$FeCl_3$	41.3	5.6	2.42	3.1	–	6507.1

* Mean values of the percent of metal adsorbed by modified pulp, which estimated by atomic absorption of the remaining solution, and the metal content in the ash residue.
** The percent of coordinated water was calculated from the difference between H,% calculated and found, taken into account the moisture content in paper sample.

ions through the liberation of hydrogen atoms from hydroxyl of hydroxamic acid or amide groups (ionic bond) is more possible than the coordination of lone pair electrons on nitrogen and oxygen atoms (covalent coordinated bond).

On the basis of the value of mass susceptibility of paper sheets prepared from adding Fe_2O_3, as a conventional additive used for preparation of magnetic paper ($X_g = 5.59 \times 10^{-6}$ c.g.s.), we expect that all prepared paper sheets either from three chemically modified pulps or metals treated AOWP and CmEWP are used as magnetic paper.

Thermal Analysis

TG curves for paper sheets prepared from wood pulp, the three chemically modified pulps and metal salts treated modified pulps are shown in Figures 4–6. There are three degradation stages in all paper

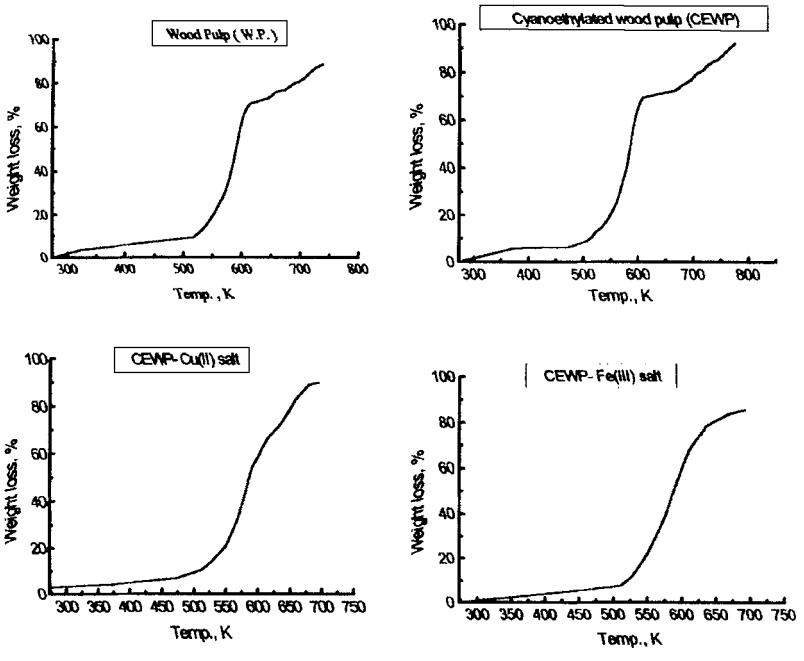

FIGURE 4 Weight loss *vs.* temperature for thermogravimetric analysis of paper sheets prepared from untreated and treated cyanoethylated wood pulp with metal salts.

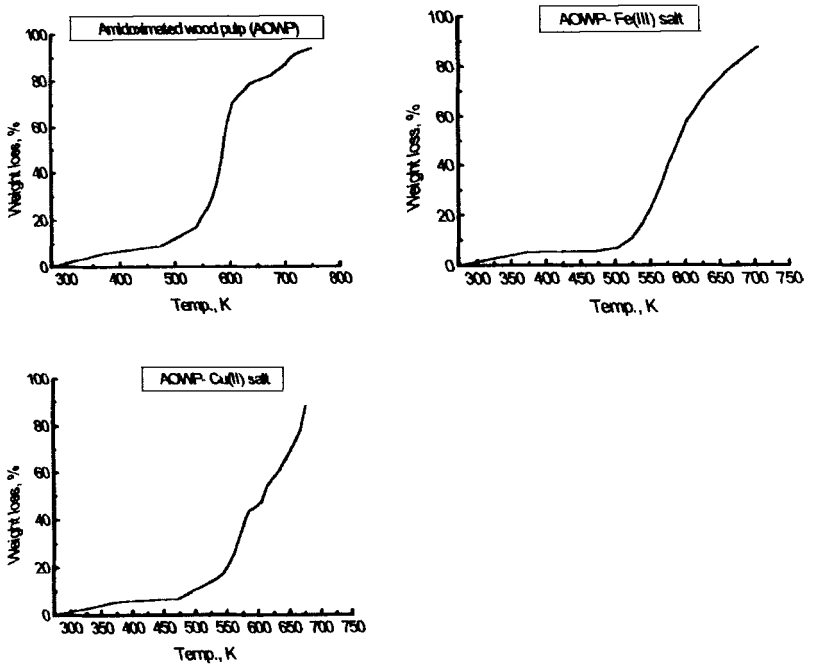

FIGURE 5 Weight loss, % *vs.* temperature for thermogravimetric analysis of paper sheets prepared from untreated and treated amidoximated wood pulp with metal salts.

samples studied. At lower temperature, *i.e.*, below 244°C (1st degradation process), the weight loss is due to the evolution of sorbed moisture in addition to the coordinated water molecules in the case of metal salts treated pulps. The second process in the range from 244–397°C due to the decomposition of cellulose, leading to the formation of carboxyl and carbonyl groups, evolution of carbon dioxide and carbon monoxide, and formation of carbonaceous char. The third process in the range from 241–500°C due to the oxidation of charred product [27].

The starting temperatures and weight loss percentages for the second and third degradation processes (two main degradation processes, and regard as 1st and 2nd-stages) are tabulated in Tables VI–VIII. It is clear that the start temperatures of the two degradation processes of sheets made from chemically modified pulps

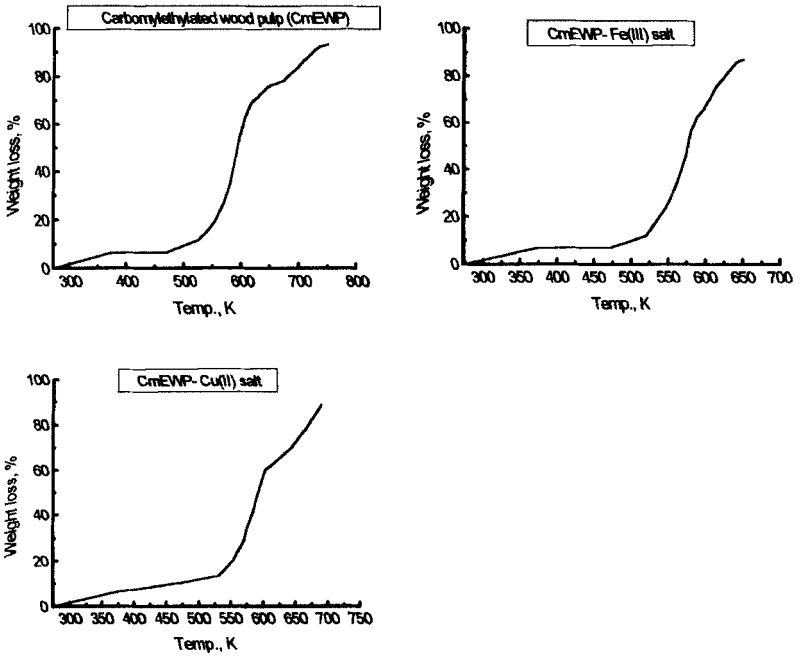

FIGURE 6 Weight loss, % *vs.* temperature for thermogravimetric analysis of paper sheets prepared from untreated and treated carbomylethylated wood pulp with metal salts.

are higher than that made from unmodified pulp. Maximum raise in the start temperatures were noticed for sheets made from AOWP. This is attributed to, in addition to the formation of hydrogen bond between nitrogen atoms of remaining cyanoethylated groups with neighboring hydrogen, the hydroxyl groups of hydroxamic acid groups enhanced the formation of intramolecular hydrogen bonding with hydroxyl groups in other glycopyranose units. Therefore, more energy is needed for decomposition. This view was emphasized from increasing the values of MHBS and asymmetry index of AOWP paper sheets than sheets made from other modified pulps (Tab. IV). For the case of paper sheets prepared from metal salts treated modified pulps, the raise of starting temperature, compared with untreated modifed pulps, is only observed for first main degradation stage (second

TABLE VI Activation energies (E_a), frequency factor (A), order of degradation (n) and weight loss percent for the thermal degradation of paper sheets prepared from partially cyanoethylated and metal salts treated cyanoethylated wood pulps (CEWP)

Paper Sample	*Stage*	*Temp. range, °C*	*−r*	*Se*	$E_a(kJ\,mol^{-1})$	$A(s^{-1})$	*n*	*weight loss, %*
Wood pulp (W. P.)	first	244–341	0.997	0.105	106.8	1.04×10^{6}	0.5	70.83
	second	382–500	0.996	0.153	213.4	3.43×10^{11}	1.5	93.33
CEWP	first	259–334	0.997	0.110	164.6	8.19×10^{10}	1.0	69.60
	second	392–468	0.990	0.249	263.9	9.11×10^{14}	1.5	92.49
DEWP-$CuCl_2$	first	268–324	0.994	0.168	206.8	5.91×10^{14}	1.0	59.09
	second	356–421	0.983	0.396	312.8	6.97×10^{20}	2.0	89.78
CEWP-$FeCl_3$	first	238–362	0.996	0.138	113.3	4.40×10^{6}	1.5	78.46
	second	394–429	0.983	0.397	295.6	9.22×10^{17}	2.0	85.71

TABLE VII Activation energies (E_a), frequency factor (A), order of degradation (n) and weight loss percent for the thermal degradation of paper sheets prepared from amidoximated and metal salts treated Amidoximated wood pulps (AOWP)

Paper Sample	*Stage*	*Temp. range, °C*	$-r$	*Se*	$E_a(kJ\,mol^{-1})$	$A(s^{-1})$	*n*	*weight loss, %*
Wood pulp (W. P.)	first	244–341	0.997	0.106	106.8	1.04×10^{6}	0.5	70.83
	second	382–500	0.996	0.153	213.4	3.43×10^{11}	1.5	93.33
AOWP	first	274–332	0.998	0.098	223.7	8.97×10^{15}	1.0	70.80
	second	406–476	0.993	0.263	350.3	3.42×10^{21}	2.0	93.81
AOWP-$CuCl_2$	first	271–312	0.986	0.179	275.9	2.36×10^{21}	1.0	43.33
	second	332–397	0.971	0.440	327.0	1.41×10^{23}	2.5	88.79
AOWP-$FeCl_3$	first	250–335	0.993	0.217	155.8	2.8×10^{10}	1.5	60.83
	second	350–432	0.989	0.389	310.0	8.0×10^{20}	2.5	87.89

TABLE VIII Activation energies (E_a), frequency factor (A), order of degradation (n) and weight loss percent for the thermal degradation of paper sheets prepared from carbomylethylated and metal salts treated carbomylethylated wood pulps (CmEWP)

Paper Sample	*Stage*	*Temp. range, °C*	$-r$	*Se*	$E_a(kJ\,mol^{-1})$	$A(s^{-1})$	*n*	*weight loss, %*
Wood pulp (W. P.)	first	244 – 341	0.997	0.106	106.8	1.04×10^{6}	0.5	70.83
	second	382 – 500	0.996	0.153	213.4	3.43×10^{11}	1.5	93.33
CmEWP	first	253 – 344	0.998	0.364	136.5	2.27×10^{8}	1.0	69.17
	second	400 – 476	0.986	0.090	313.9	1.47×10^{19}	2.0	93.34
CmEWP-$CuCl_2$	first	265 – 329	0.996	0.141	185.7	5.60×10^{12}	1.0	60.00
	second	368 – 415	0.988	0.337	468.0	9.36×10^{32}	2.0	88.83
CmEWP-$FeCl_3$	first	247 – 329	0.992	0.192	124.0	1.73×10^{7}	1.0	65.91
	second	341 – 376	0.995	0.233	408.1	2.94×10^{29}	2.5	86.94

process) of paper sample from $CuCl_2$-treated CEWP and $CuCl_2$-CmEWP. The starting temperature of $CuCl_2$-AOWP is higher than paper sheets of unmodified wood pulp.

It is also clear that, the treatment of modified wood pulps with metal salts leads to a reduction of weight loss of the first main degradation stages. The reduction in the case of $CuCl_2$-AOWP is higher than other modified pulps treated with $CuCl_2$, and $CuCl_2$-treated modified pulps is higher than $FeCl_3$-treated pulps. The latter case is attributed to the oxidation nature of $FeCl_3$ on unsubstituting OH groups of glugopuranose units and OH gps. of hydroxamic acid groups in the case of AOWP paper sheets [11, 21].

Calculation of the Activation Energies (E_a)

TG data can be analyzed in order to estimate the activation energy of the thermal degradation process. In this work, the analysis was conducted using the method adopted by Coats and Redfern [28]. The general correlation equation used in the Coasts and Redfern method is

$$\log_{10}\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = \log_{10}\left[\frac{AR}{aE_a}\left(1-\frac{2RT}{E_a}\right)\right] - E_a/2.3\,RT$$

where α is fractional conversion, n is the order of degradation reaction, a is the heating rate (in $k\,min^{-1}$), R is the gas constant (in $kJ\,mol^{-1}\,K^{-1}$), T is the temperature (in K), A is the frequency factors (s^{-1}), and E_a activation energy.

Plotting the left-hand-side values of the equation, *i.e.*, $\log_{10}[(1-(1-\alpha)^{1-n})/(T^2(1-n))]$ against $1/T$ using various values of n, should give a straight line with the most appropriate value of "n" [29]. Thus, the method of least square is applied for the equation, taking values of "n" ranging from zero to 3.0 with increment of 0.5, and calculating for each value of "n", the correlation coefficient, $-r$, standard error estimation, SE. The "n" values which corresponds to the maximum $-r$, and minimum Se is the order of degradation process. The activation energies and frequency factor were calculated from the slope and intercept, respectively, of the Coats and Redfern equation with the most appropriate value of "n".

Figures 7–9 show the plots of $-r$, Se and E_a as a function of n, for the first main degradation stages of all paper samples studied. The kinetic parameters (E_a, A) and appropriate order of degradation for each process are given in Tables VI–VII. It is clear that, the appropriate order of degradation for the first main degradation stage of paper made from modified and $CuCl_2$-treated modified pulps follow the first order, this indicate that the order of reaction does not depend on the type of modification, or treating the modified pulps by $CuCl_2$. While for the second main degradation stages, the corresponding, n, values are from 1.5–2.5.

Tables VI–VIII also show that, the chemically modification of wood pulp by partially cyanoethylation, amidoximation, carbomyl-

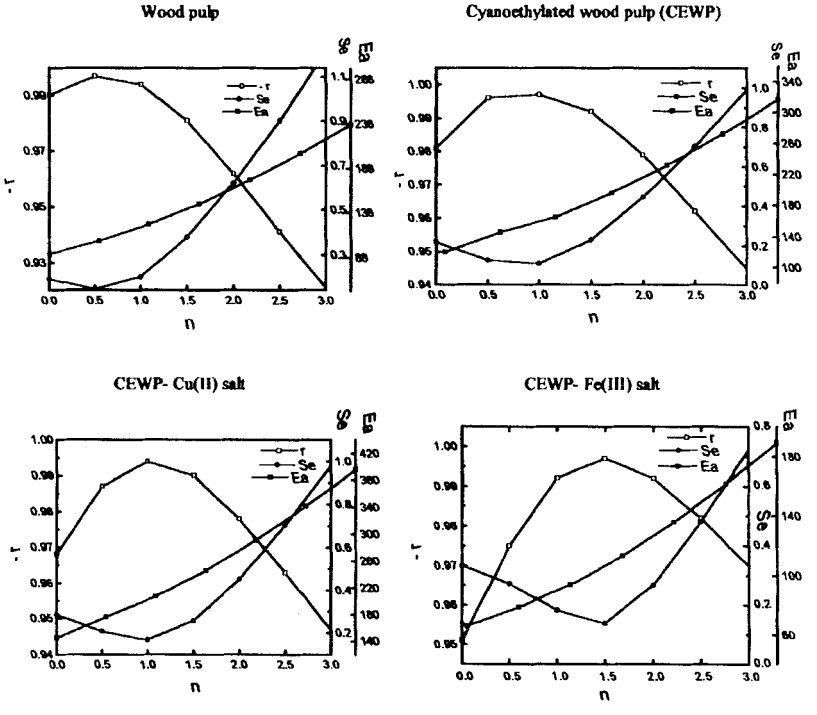

FIGURE 7 Statistical determination of "n" and "E_a" of the main (2^{nd}) thermal degradation stages of paper sheets prepared from untreated and treated CEWP with metal salts.

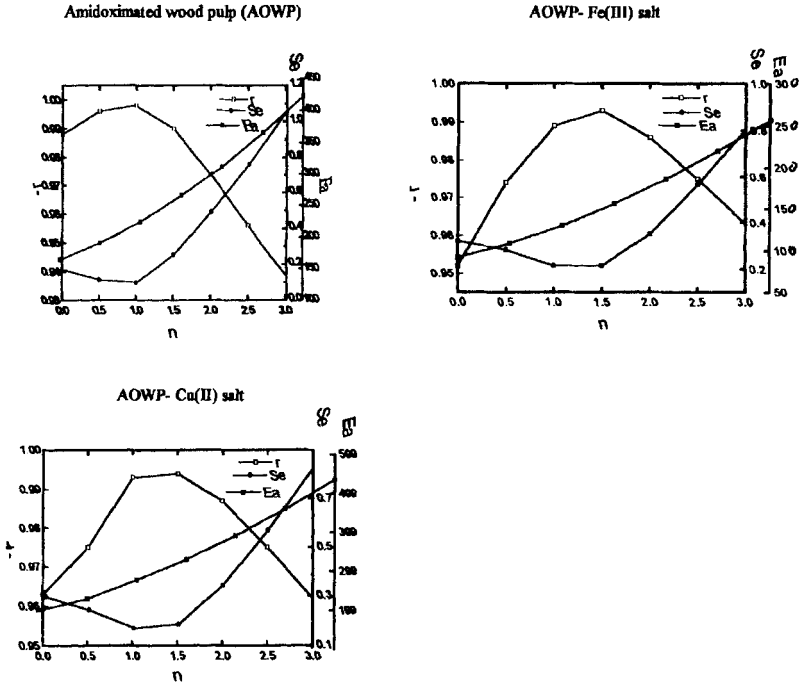

FIGURE 8 Statistical determination of "n" and "E_a" of the main degradation stages of paper sheets made from untreated and treated amidoximated wood pulp with metal salts.

ethylation, and metal salts treated the modified pulps improve the thermal stabilities of the prepared paper sheets. From the values of ΣE_a of the two main process it can be seen that, the stabilities of the paper sheets decrease in the order $CuCl_2$-CmEWP > $CuCl_2$-AOWP > AOWP > $FeCl_3$-CmEWP > $CuCl_2$-CEWP > $FeCl_3$-AOWP > CmEWP > CEWP > $FeCl_3$-CEWP > W.P.

The improvement in thermal stabilities of paper sheets made from treated AOWP and CmEWP with $CuCl_2$ than the case of treating the CEWP, this is related to the presence of many lone pair electrons on N and O atoms which capable to form coordinate bond with metal ions. However, due to the oxidation nature of $FeCl_3$ to free OH groups, the thermal stability (ΣE_a) of $FeCl_3$-AOWP paper sheet is lower than that paper of $FeCl_3$-CmEWP. The measurements of crystallinity index

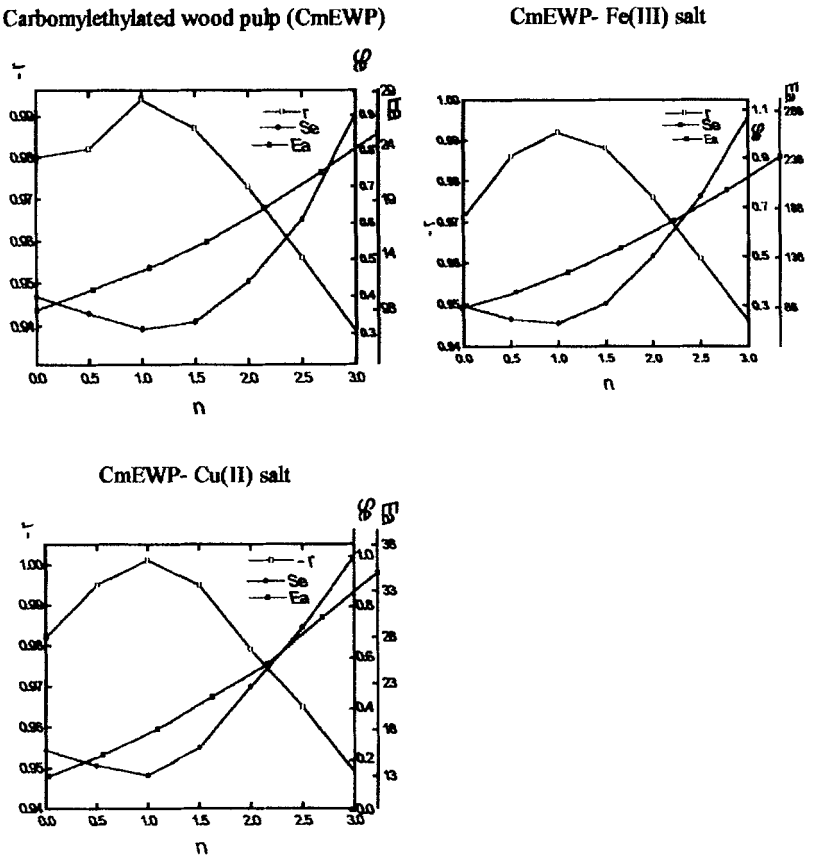

FIGURE 9 Statistical determination of "n" and "E_a" of the main degradation stages of paper sheets made from untreated and treated carbomylethylated wood pulp with metal salts.

(X_1), mechanical properties, which represents by quality number (Q_z; X_2) and activation energy (Y) are correlated by the following regression equations [30]:

– For metal salts treated CEWP:

$$Y = -372.1 + 283.3X_1 + 0.0991X_2 \quad (R^2 = 0.99996)$$

– For metal salts treated AOWP:

$$Y = -26616.7 - 12425.4X_1 + 41.7X_2 - 9555.2X_1^2 - 7.73X_2^2 \quad (R^2 = 1.000)$$

– For metal salts treated CmEWP:

$$Y = 181835 - 238579X_1 - 33.5X_2 + 89963X_1^2 + 0.0012X_2^2 \quad (R^2 = 1.000001)$$

The values of the determination coefficients, R^2, confirm the accuracy of the equations is very high.

Biological Evaluation

The data obtained in Table IX showed that, introducing the Cu(II) ions into chemically modified pulps during its treatment with $CuCl_2$ solution improve the antimicrobial action of the prepared paper sheets, compared with paper formed from chemically modified and $FeCl_3$-treated modified pulps. The most active paper was paper sample from $CuCl_2$-treated CmEWP, whereas this paper has relatively high inhibitory effect to all the tested microorganisms except pseudomonas aerugenosa. This highly inhibitory effect may be related to relatively increase the percent of Cu(II) ions adsorbed by CmEWP.

TABLE IX Antimicrobial action of paper samples on some microorganisms

Paper sheet tested	*B. subtilis*	*E. coli*	*S. typhi*	*P. aerugenosa*	*A. niger*
Wood pulp (W.P.)	–	–	–		–
Cyanoethylated wood pulp (CEWP)	–	–	–	–	–
CEWP-$CuCl_2$	+ +	+	+	–	+ +
CEWP-$FeCl_3$	–	–	–	–	–
Amidoximated wood pulp (AOWP)	–	–	–	–	–
AOWP-$CuCl_2$	+	+	+	–	+
AOWP-$FeCl_3$	–	–	–	–	–
Carbomylethylated wood pulp (CmEWP)	–	–	–	–	–
CmEWP-$CuCl_2$	+ + +	+ +	+ +	–	+ + +
CmEWP-$FeCl_3$	–	–	–	–	–

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