J. Mater. Environ. Sci. 2 (3) (2011) 259-270
ISSN : 2028-2508

The role of extracted alkali lignin as corrosion inhibitor

Abdel mnim Altwaiq [a], Sa'ib J. Khouri [a], Salah Al-luaibi [b*], Robert Lehmann [c], Heiko Drücker [c], Carla Vogt [c]

[a]*Chemistry Department, Petra University, Amman 11196, Jordan*
[b]*Chemistry Department, Basra University, Basra, Iraq*
[c]*Institute of Inorganic Chemistry, Leibniz University, Hanover, Germany*

Received in 06 May 2011, Revised 20 May 2011, Accepted 20 May 2011.

*Corresponding authors. Tel : +9647801000106, E-mail: salah_al_labeia@yahoo.com

Abstract

Various experiments were carried out on three alloys immersed in HCl solutions to determine quantitatively the role of extracted alkali lignin in inhibiting the corrosion. The corrosion monitoring techniques include weight loss method, quantification of metal ion contents in the corrosive solutions and surface analysis methods using scanning electron microscope and micro beam x-ray fluorescence. The results obtained from the three independent methods present a clear evidence of inhibition behavior of extracted alkali lignin in the corrosion of different alloys immersed in HCl solutions. The inhibition efficiency of alkali lignin increased with increasing its concentration.

Keywords: alkali lignin, inhibitor, immersion test, weight loss.

1. Introduction

Many investigations were conducted to examine extracts from natural substances to slow or inhibit the corrosion process. The extracts contained mixtures of compounds having oxygen, sulfur and nitrogen elements, which help in the corrosion inhibition process. Natural compounds used as inhibitors to develop new cleaning chemicals for green environments have been selected because they are environmentally friendly, readily available, and renewable sources for a wide range of needed inhibitors [1-7].

Lignin forms the woody cell walls of plants and the cement material between the plant walls, and classified as the second most abundant biopolymer in the world after cellulose[8]. Alkali lignin is lignin isolated with alkali and precipitated by means of mineral acids [9-12]. Several recent publications [13-14] have reported that 70% of the lignin taken from different lignocelluloses materials is extracted with diluted alkali at temperature below 100 °C.

Lignin is a highly-branched, three dimensional biopolymer with a variety of functional groups providing active centers for chemical and physical interactions. The chemical functional groups in lignin are phenolic, hydroxyl, carboxyl, benzyl alcohols, methoxyl and aldehyde that make lignin useful as a corrosion inhibitor. Lignin also has a high surface area (180 m^2 g^{-1}) that exhibits surface activity [11, 12]. Due to its content of oxygen atoms and multiple bonds, akali lignin adsorbs on the metal surface forming a barrier between the metal and the corrosive environment [12, 16, 17]

The aim of the present study is to examine the inhibition behavior of extracted alkali lignin in the corrosion of different metals and alloys. The current study attempts also to extract pure alkali lignin from wood by using a simple extraction method suggested before [13, 14]. The corrosion and corrosion inhibition processes were studied by different techniques, which include weight loss analysis, surface analysis on the corroded metals by scanning electron microscope (SEM), and micro-beam x-ray fluorescence (µ-XRF), in addition to quantification of metal contents in the corrosive solutions by inductively coupled plasma–optical emission spectroscope (ICP-OES). The effects of many laboratory conditions such as concentration of the suggested inhibitor, acidity of the corrosive media and time of immersion were studied in order to comprehend the corrosion and corrosion inhibition processes.

2. Experimental

2.1. Alkali lignin extraction

Hard wood samples from a 25 years old maple tree were provided from a private garden in Hanover in Germany. After the outer barks were peeled off, the log was chipped and dried. The chips were ground to size between 70–120 mesh. After drying at 50 °C for 24 hours, the grinded wood chips were subjected to an alkaline extraction by 7.5 % (w/v) NaOH at 90–100 °C for 6 hours under continuous agitation conditions. The ratio (m/M) of wood to liquid in the extraction was 1:10. After gravity filtration, the filtrate was acidified by drop-wise addition of 5.0 M sulfuric acid to a pH around 5.50. The hemicelluloses were isolated from the hydrolysates by precipitation of the neutralized hydrolyze in the three volumes of ethanol. After filtration, the pellets of the hemicelluloses were washed with 70% ethanol and air-dried. After evaporation of ethanol, the alkali-soluble was obtained by precipitation at pH 1.50 from the corresponding supernatants acidified by drop-wise addition of 5.0 M sulfuric acid under continuous agitation. The precipitates were isolated by filtration with glass filter and washed with warm diluted solution of sulfuric acid 1% (v/v) to remove the dissolved polysaccharides. The precipitate was then dried in the oven at 125 °C to obtain pure alkali lignin [14]. Fig. 1 shows the extraction procedure of pure alkali lignin from maple wood tree.

2.2. Solutions preparation

Solutions of different concentrations of HCl were prepared by dilution of concentrated HCl 37% (w/v) (From Merck) using deionized water. All of chemicals and solvents used are of analytical reagent (AR) grade. All solutions were prepared by using deionized water.

2.3. Coupons preparation

The selected Alloys in this study have different oxidation potentials. The alloys include mild steel alloy with European number S235JR, stainless steel alloy with European norm 1.4301, X5CrNi18-10 and aluminum zinc alloy with German material number 3.4365 and European number 7075.

The percent (%) chemical compositions of the mild steel coupons are 0.17 C, 1.40 Mn, 0.55 Cu, 0.035 P, 0.035 S, 0.012 N, and balanced Fe. Coupons of stainless steel alloy have chemical compositions of 68.88% Fe, 0.05% C, 18.0% Cr, 10.0% Ni 1.0% Si, 2.0% Mn, 0.05% P, 0.01% S, and 0.01% N. The percent chemical compositions of the aluminum zinc alloy are 5.1–6.1 % Zn, 1.2–2 % Cu, 2.1–2.9 % Mg, 0.40% Si, 0.50% Fe, 0.30% Mn, 0.18–0.28% Cr, 0.20% Ti, and balanced Al.

Rectangular coupons of the selected materials were cut into 6.0 cm × 2.0 cm × 0.2 cm dimensions. Pre-treatment of the surface of coupons was carried out by grinding with emery paper of 100–800 grit, rinsing with deionized water, degreased with acetone, dried, then rinsed with deionized water and dried in the oven at 125 °C before used.

2.4. Weight loss measurements

Each experiment in weight loss measurement was carried out in a flat glass bowl containing 450 mL of the corrosive solution (HCl). Three clean weighed coupons were hanged and immersed vertically in the vessel. The bowl was covered by parafilm to prevent any evaporation and contamination. After the time elapsed, the cleaning procedure consisted of wiping the coupons with a paper tissue and washing with acetone, then rinsing by deionized water and drying in the oven at 125 °C. Weight loss was determined by weighing the cleaned samples before and after hanging the coupon into corrosive solutions in the absence and presence of various concentrations of alkali lignin under different conditions (listed in section 2.5). The average weight loss of the three coupons was taken to calculate the corrosion rate. Because alkali lignin doesn't dissolve in acidic solution, it was added to the corrosive solution dissolving in a 10 mL of ethylene glycol. A 10 mL of ethylene glycol was also added to the corrosive solutions without alkali lignin.

2.5. The laboratory conditions of coupons immersion tests:

I. Three different alloys; mild steel, stainless steel and alloy of aluminum and zinc.

II. Five concentrations of extracted alkali lignin; 100, 300, 700, 1000 and 1500 mg/kg

III. Different concentrations of the corrosive solution; 0.10 – 1.0 M of HCl.

IV. Immersion times between 3 hours and 1 day in the most cases

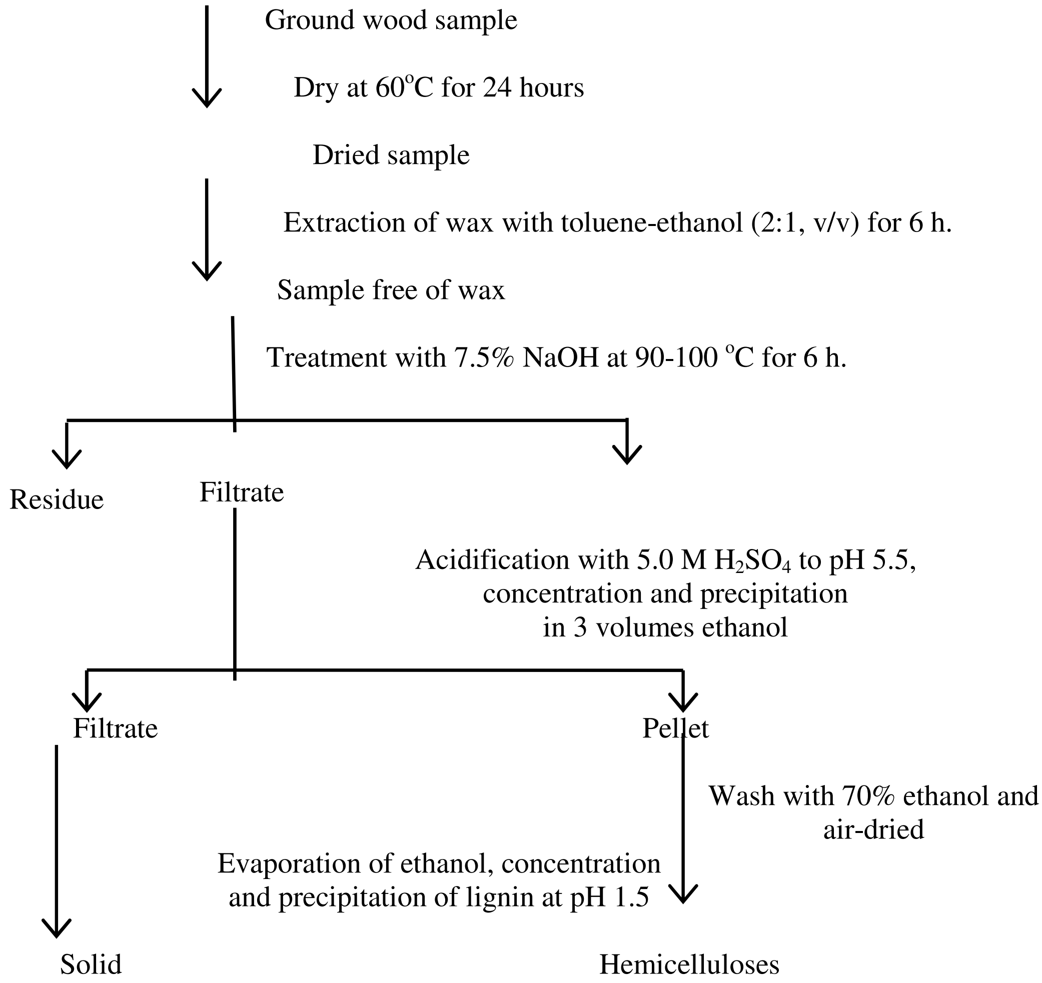

Figure 1 The scheme for extraction of pure alkali lignin from maple wood tree.

2.6. Identification of metal contents of corrosive solutions

Quantitative analysis of the major metals (Fe, and Al) contents present in the corrosive solutions has been performed by using SPECTRO ARCOS inductively coupled plasma–optical emission spectrometer (ICP-OES) (Spectro analytical instruments GmbH, Kleve, Germany) with axial plasma observation. The instrument features a Paschen-Runge spectrometer amount, employing the proprietary Optimized Rowland Circle Alignment (ORCA), consisting of two hollow section cast shells, optimized small volume and 32 linear CCD detectors, the wavelength range 130 and 770 nm can be simultaneously analyzed. Peristaltic pump was used to feed the nebulization system with sample solution. The measured elemental intensities were evaluated by Smart analyzer software. The chosen analytical emission lines (nm) were as follows: Fe (238.204, 259.941) and Al (267.078). The operating conditions for ICP-OES measurements are listed in Table.1.

Table 1 The operating parameters for ICP-OES measurements.

Parameters	**Setting**
Power (W)	1450
Plasma Torch	quartz, fixed, 3.0 mm injection tube
Nebulizer	cross flow
Spray chamber	axial
Coolant flow rate (L min $^{-1}$)	13
Nebulizer gas flow rate (L min^{-1})	0.8
Auxiliary gas flow rate (L min^{-1})	0.8
Sample aspiration rate (mL min^{-1})	2.0

2.7. Surface analysis on the corroded metals

Scanning electron microscope (SEM) was used to study corrosion and corrosion inhibition processes by taking images with different magnifications on the surfaces of the corroded coupons in absence and presence of alkali lignin. The model of the SEM is XL 30 (Phillips Electronics N.V., Eindhoven, Netherlands,) equipped with an Oxford energy dispersive spectrometer system model EDAX ZAF quantification (standardless), version 2.50, with 20 kV acceleration voltage of the electrons. The instrument was equipped with a very thin detector window so that light elements with Z = 5 (boron) can be measured. Images were taken by using two different detectors; secondary electron (SE) detector for topographical contrast and backscattered electron (BSE) detector for material contrast. Each sample was analyzed at three different locations to ensure reproducibility.

An Eagle µProbe II (Roentgenanalytik Messtechnik GmbH, Taunusstein, Germany) with Si(Li) detector and EDAX Vision 32 software (EDAX Business Unit, AMETEK GmbH, Taunusstein, Germany) was used to map the surfaces of the corroded metals in order to identify the elements present in the corrosion products, their distribution pattern, and their relative concentrations. This instrument contains a rhodium anode in the X-ray tube and a poly capillary lens with a spot size of around 50 µm. The working conditions on the mapping were 40 kV acceleration voltage, 220 mA and a live time measuring period of 2 seconds for each point. The distance of measured points on the samples was approximately 50 µm.

3. Results and discussion

3.1. Weight loss method

The simplest and longest-established method of estimating corrosion process is weight loss analysis. The basic measurement which is determined from corrosion coupons is the weight loss taking place over the period of exposure being expressed as corrosion rate [18, 19]. The corrosion rate (CR) and the percentage inhibition efficiency (IE %) were calculated using the following two equations [20] :

$$\text{Corrosion rate (CR)} = \frac{\text{weight loss (g)} \times \text{K}}{\text{alloy density (g cm}^{-3}) \times \text{exposed area (cm}^{2}) \times \text{exposure time (hr)}} \quad \text{.....(1)}$$

$$\text{Inhibition efficiency (IE \%)} = \left(\frac{\text{CR}_1 - \text{CR}_2}{\text{CR}_1}\right) \times 100 \quad \text{..(2)}$$

where K is a constant, CR_1 and CR_2 are the corrosion rates in the absence and presence of inhibitor, respectively. The corrosion rate can be calculated in a variety of units with an appropriate value of K as indicated in Table. 2.

The corrosion rates of mild steel alloy immersed in 1.0 M HCl were calculated by weight loss method under different immersion times (3, 6, 12, 18 and 24 hours). The K value that used in the calculation is 8.75×10^4. Fig. 2 indicates that the presence of alkali lignin does not stop the corrosion completely, but rather inhibits the corrosion process by reducing the corrosion rate. It is noticed that the inhibition strength depends directly on the concentration of alkali lignin.

As shown in Fig. 3, the corrosion current of the aluminum zinc alloy has relatively high value in 1.0 M HCl solution, meaning higher corrosion rates, and then corrosion rates of the alloy significantly decreased with alkali lignin present in the corrosive medium. In contrast, due to the aggressive medium (1.0 M HCl) and the moderate corrosion resistance of the investigated alloy, the corrosion inhibiting effect of alkali lignin became weaker by increasing the immersion time. Figs. 4 and 5 show the inhibiting effect of alkali lignin in the corrosion of aluminum zinc alloy coupons immersed in solutions of 0.10 and 0.40 M HCl, respectively. Tables 3–5 show the inhibition efficiencies of different concentrations of alkali lignin in the corrosion of the mild steel and the aluminum zinc alloy with HCl solutions at different immersion times. In most cases the inhibition efficiencies of alkali lignin decrease with the increase of the immersion time.

The corrosion rates of stainless steel coupons were very low (2 mm y^{-1}) and show a small difference in the presence and absence_of alkali lignin. This small difference may be not taken as an eventual result due to the primitive method that was used.

Table 2 The different corrosion rate units with the appropriate value of the constant K.

desired corrosion rate unit	**area unit**	**K-factor**
mils/year (mpy)	in^2	5.34×10^5
mils/year (mpy)	cm^2	3.45×10^6
millimeters/year (mmy)	cm^2	8.75×10^4

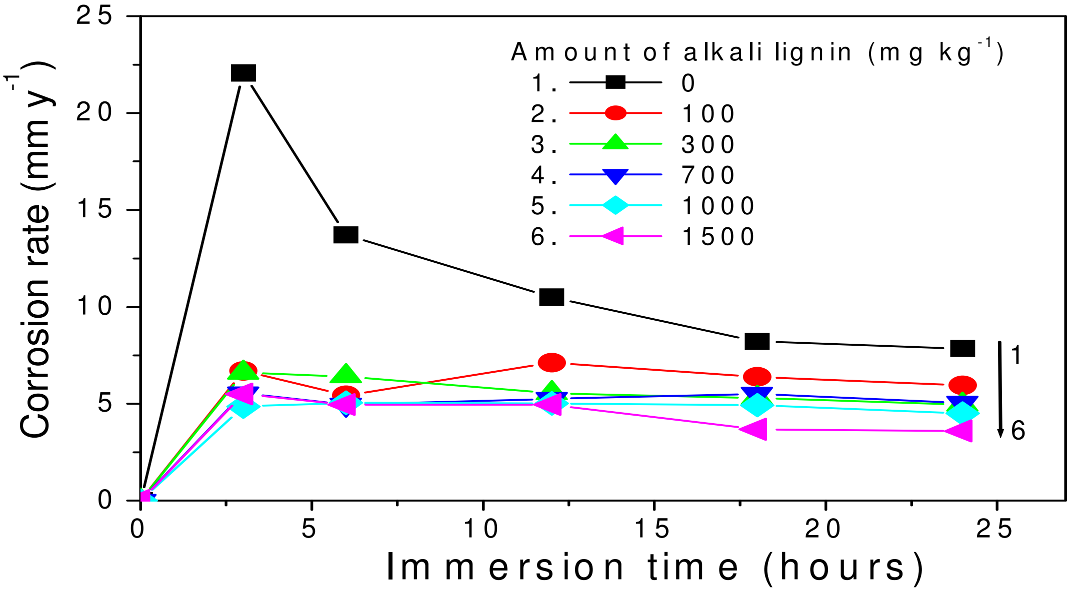

Figure 2 The corrosion rates of mild steel alloy in 1.0 M HCl in absence and presence of different concentrations of alkali lignin.

Table 3 The Inhibition efficiencies of different concentrations of alkali lignin in corrosion of mild steel alloy in 1.0 M HCl under different immersion times.

Alkali lignin concentration (mg kg^{-1})	**Inhibition efficiency (IE %)**				
	3 hours	6 hours	12 hours	18 hours	24 hours
100	70.5	60.4	32.3	22.5	36.9
300	70.0	60.3	47.1	35.6	37.2
700	74.8	63.9	50.7	45.5	44.3
1000	78.1	63.1	52.2	51.4	51.2
1500	75.1	63.9	64.9	54.6	54.1

Table 4 The Inhibition efficiencies of different concentrations of alkali lignin in corrosion of aluminum alloy in 1.0 M HCl under different immersion times.

Alkali lignin concentration	**Inhibition efficiency (IE %)**				
(mg kg^{-1})	3 hours	6 hours	12 hours	18 hours	24 hours
100	59.1	61.5	11.9	10.3	7.9
300	68.3	70.87	14.1	11.7	5.9
700	82.5	81.7	19.3	15.9	14.1
1000	86.7	85.5	47.0	34.4	29.2
1500	86.7	85.4	31.5	34.4	21.2

Table 5 The Inhibition efficiencies of different concentrations of alkali lignin in corrosion of aluminum alloy in 0.40 M HCl under different immersion times.

Alkali lignin concentration	**Inhibition efficiency (IE %)**				
(mg kg^{-1})	3 hours	6 hours	12 hours	18 hours	24 hours
100	46.0	49.8	62.7	62.9	56.8
500	61.8	73.0	70.1	63.1	61.2
1000	70.0	76.8	70.1	63.1	47.1

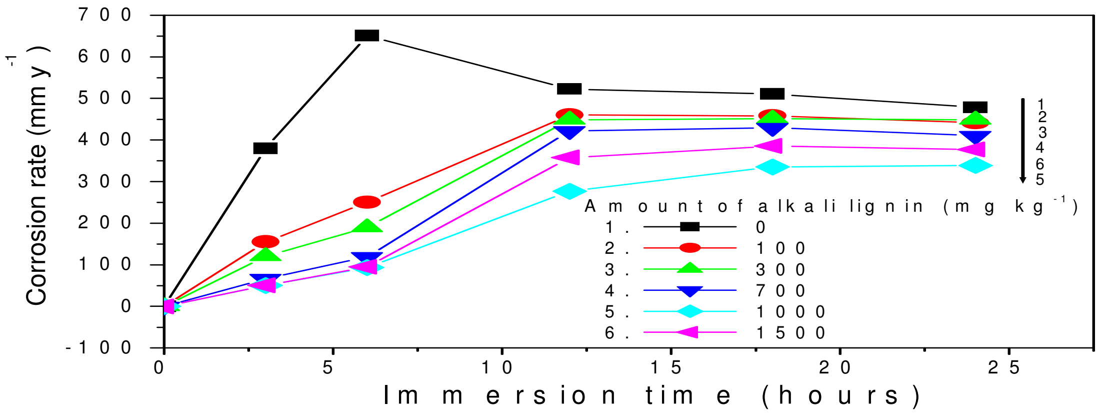

Figure 3 The corrosion rates of aluminum zinc alloy in 1.0 M HCl in absence and presence of different concentrations of alkali lignin.

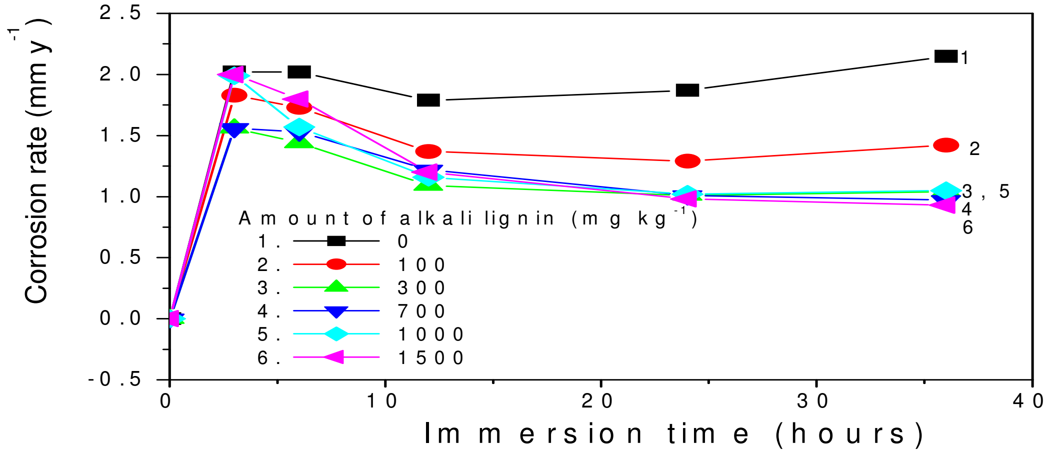

Figure 4 The corrosion rates of aluminum zinc alloy in 0.10 M HCl in absence and presence of different concentrations of alkali lignin.

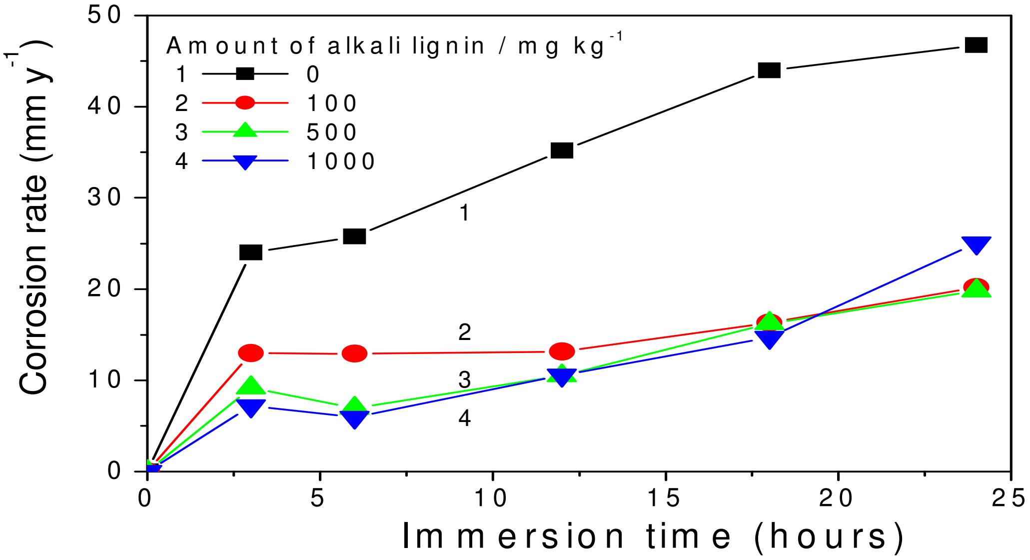

Figure 5 The corrosion rates of aluminum zinc alloy in 0.40 M HCl in absence and presence of different concentrations of alkali lignin.

3.2. Quantification of metal ions contents in the corrosive solutions

The Fe and Al ions contents in the corrosive solutions in the presence and absence of alkali lignin were identified to test the effect of alkali lignin on the corrosion process. Fig. 6 shows reduction of Fe ions concentrations when alkali lignin was presented in the corrosive solution. These results are a further evidence of the inhibiting effect of alkali lignin against corrosion of the mild steel alloy.

The results obtained from quantification of Al ions contents in the corrosive solutions under different immersion times are in good agreement with weight loss measurements. Fig. 7 demonstrates the decrease in aluminum ions contents in the presence of alkali lignin in the corrosive solution (0.40 M HCl).

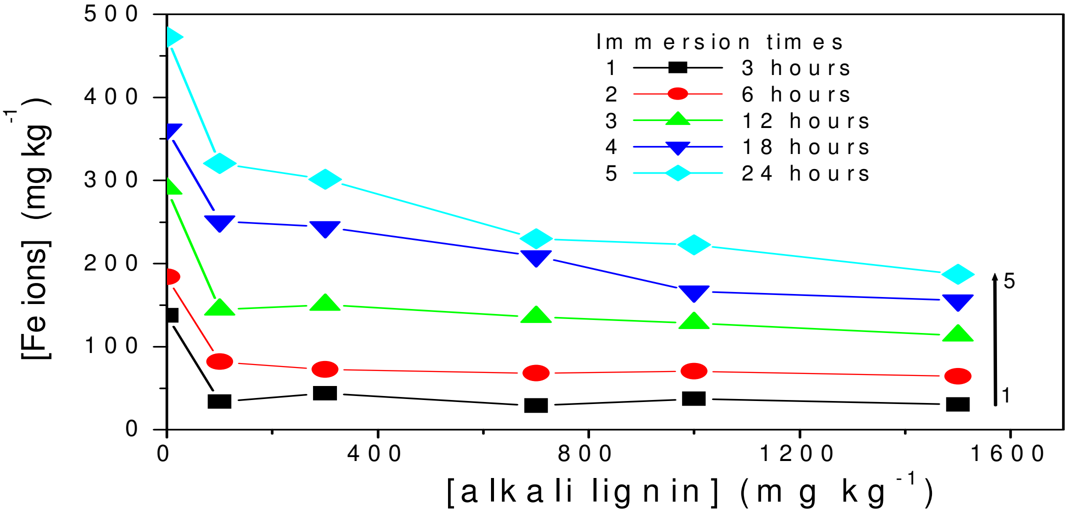

Figure 6 The variation of Fe ions concentrations in the corrosive solution (1.0 M HCl) resulted from mild steel corrosion in absence and presence of different concentrations of alkali lignin under different immersion times.

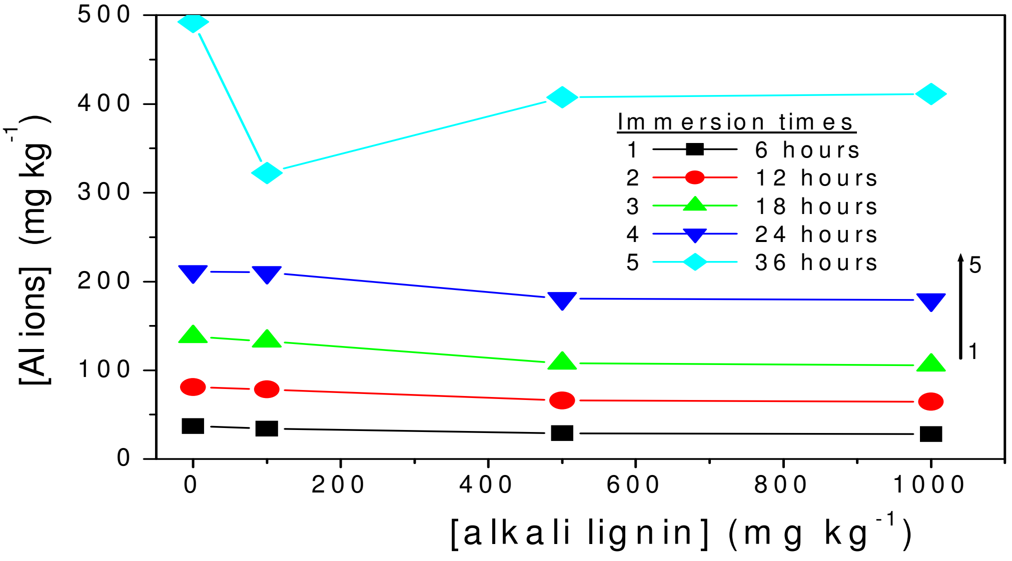

Figure 7 The variation of Al ions concentrations in the corrosive solution (0.40 M HCl) resulted from Al alloy corrosion in absence and presence of different concentrations of alkali lignin under different immersion times.

The quantification of Fe ions contents in the solutions obtained from corrosion of stainless steel coupons are shown in Fig. 8. As indicated in Fig.8, there is inhibiting effect of alkali lignin against corrosion of stainless steel alloy, but this effect was not strong enough. As the corrosion rate without inhibitor is slow, the effect of alkali lignin in this case appears weak.

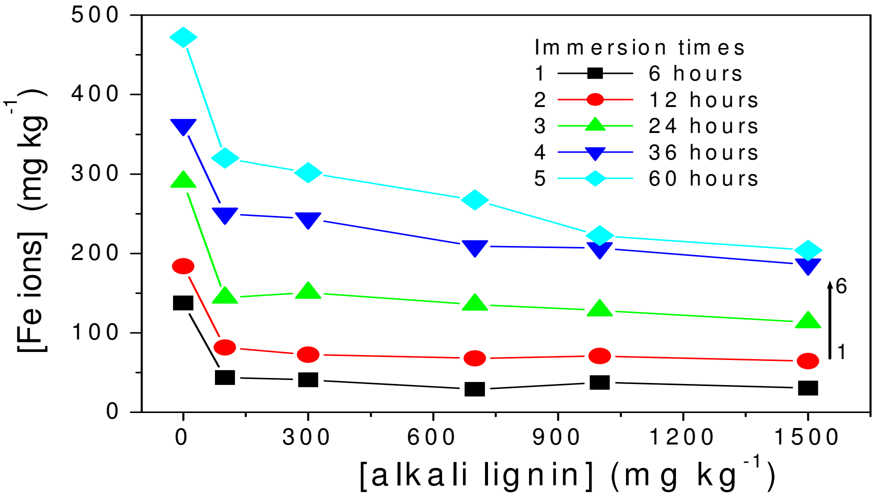

Figure 8 The variation of Fe ions concentrations in the corrosive solution resulted from stainless steel corrosion in the absence and presence of different concentrations of alkali lignin under different immersion times.

3.3. Surface analysis on the corroded coupons

Because corrosion is fundamentally a surface phenomenon, it is useful to apply surface analysis like SEM and μ-XRF on the corroded metals. SEM micrographs of the corroded surface of mild steal coupons immersed in 0.10 M HCl solutions in the absence and presence of alkali lignin with 120 and 2000 magnifications are shown in Fig. 9. By the comparison of SEM images at the same magnifications, it is indicated that the corrosion of mild-steel coupons in the presence of alkali lignin is weaker than in the case of absence of alkali lignin that proves again the inhibiting effect of alkali lignin against corrosion of mild steel alloy in 0.10 M HCl solution.

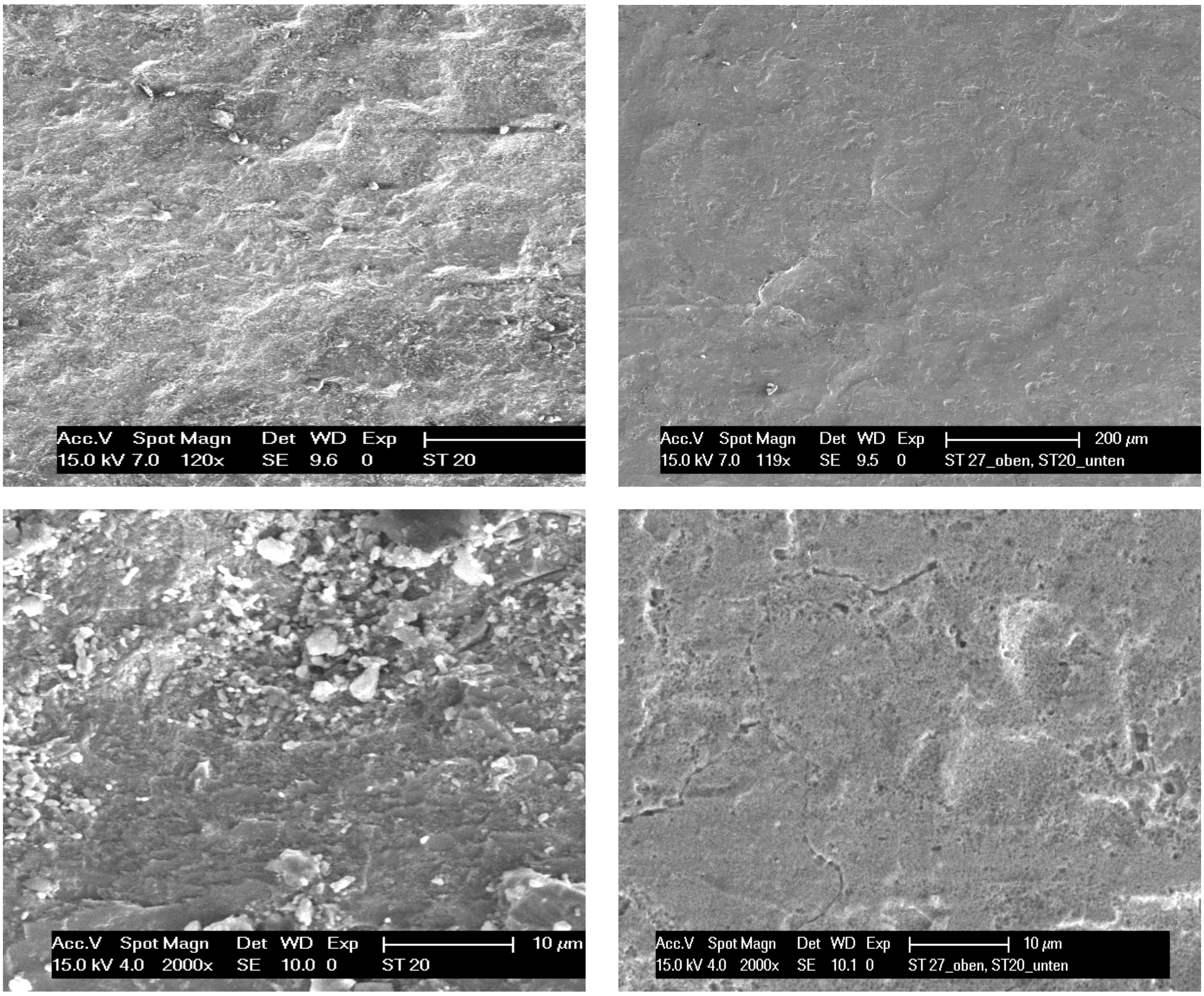

Figure 9 The SEM images of the corroded surface of mild steel coupons in 0.10 M HCl solution in the absence (left side) and presence of alkali lignin (right side).

Another evidence of inhibiting effect of alkali lignin against corrosion of the aluminum zinc alloy is the images obtained from SEM measurements. Fig. 10 shows these images using SE and BSE detectors with 100 and 500 magnifications. These images indicate that the corrosion of aluminum zinc alloy coupons in the presence of alkali lignin is weaker than in the case of absence of alkali lignin.

Micro beam x-ray fluorescence (µ-XRF) is a modification of the traditional XRF where x-rays are focused into a much smaller spot size with diameters in the micrometer scale. Mapping on the surfaces of the corroded coupons by µ-XRF represents a powerful tool in the localization of the corrosion products. Images produced from mapping as that demonstrated in Fig. 11 represent a further evidence of the inhibiting effect of alkali lignin in the corrosion of steel coupons immersed in 1.0 M HCl. Fig. 11 shows clearly that there is more Cl concentration, which related to the corrosion product, on the corroded coupons in the absence of alkali lignin than in the case of the presence of alkali lignin.

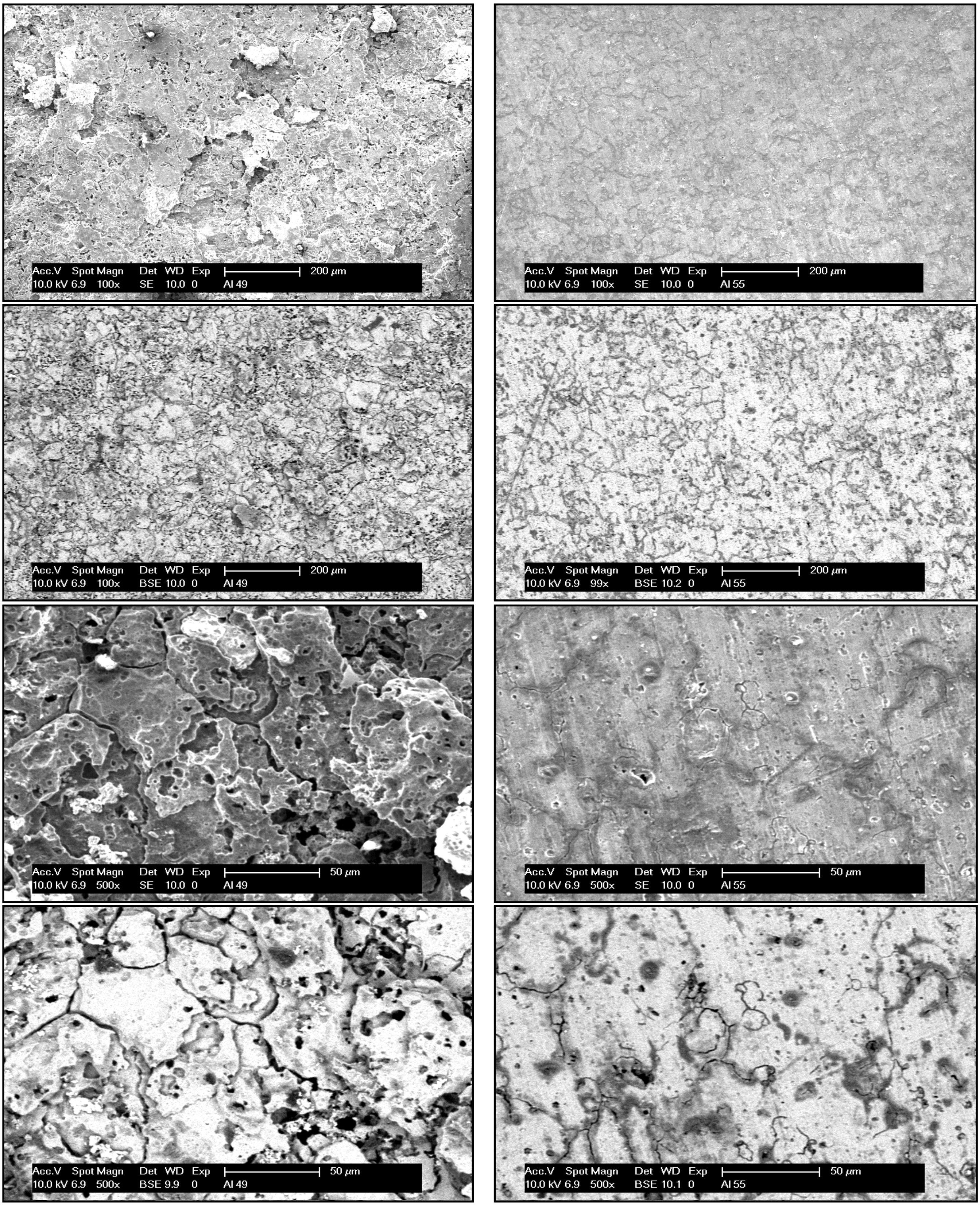

Figure 10 The SEM images of the corroded surface of aluminum zinc alloy coupons in 0.10 M HCl solutions in the absence (left side) and presence of alkali lignin (right side).

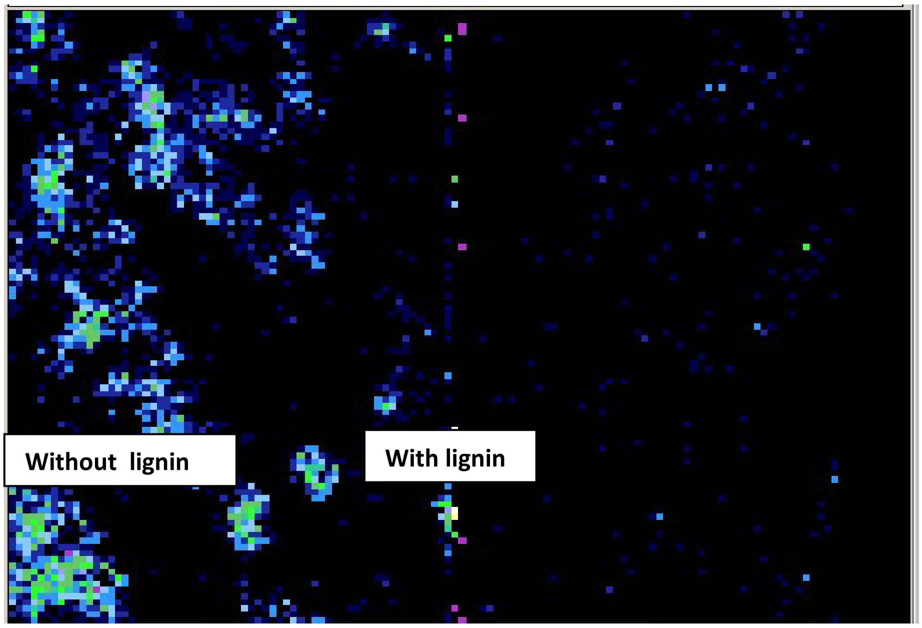

Figure 11 The mapping images of two different corroded areas on the mild steel coupons immersed in a solution of 1.0 M HCl in the absence and presence of alkali lignin and the distribution images of Cl atoms in the two areas, the hell regions indicate more concentrations of Cl atoms.

Conclusion

Three independent monitoring methods indicate the inhibition behavior of alkali lignin against corrosion of the investigated alloys in HCl solutions. Alkali lignin imparts various degrees of corrosion inhibition depending upon the metallurgical make up of the substrate and the composition of the corrosive medium. It is noticed that the inhibition strength depends directly on the concentration of alkali lignin. Alkali lignin was extracted successfully from sawdust of a maple wood tree.

Acknowledgment

I wish to express my deep gratitude and appreciation to the German Research Foundation (DFG) for financial support. I would like to thank also Mrs. Stella Kittel, Mr. Tobias Klande and all members in the working group of Prof. Carla Vogt for their cooperation and kind hosting.

References

1. Raja, P.B. Sethuraman, M.G., *Mat. Lett.* 62 (2008) 113.
2. Benkaddour, M., Hammouti, B. Bendahhou, M. Aouniti, A. , *Appl. Surf. Sci.* 25 (2006) 6212.
3. Amin, M.A. Abd El-Rehim S.S., El-Sherbini, E.E. Bayoumi, R.S. *Electrochem. Acta* ,52 (2007) 3588.
4. Jai, J. W.S. Wan A., *International conference on environmental research and technology* (2008) 865
5. Okafor, P.C. Ikpi, M.E. Uwah I.E., Ebenso, E.E. Ekpe, U.J. . Umoren,S.A. *Corros. Sci*. 50 (2008) 2310,
6. Abdel-Gaber, A.M. Abd-El-Nabey, B.A. Sidahmed, I.M. El-Zayady, A.M. Saadawy, M. , *Corros. Sci*. 48 (2006) 2765
7. El-Naggar, M.M., *Corros. Sci*. 49 (2007) 2226.
8. Houtman,C.J., *Holzforschung*,53,6(1999)585.
9. Sarakanan, K.V. Ludwig, C.H.,' *Lignins: Occurrence, Formation, Structure and Reactions'*, Wiley-Interscience, New York,(1971).175
10. . Argyopoulos, D.SS. Manachem,B. in: D.L. Kaplan (Ed.), *Biopolymers from Renewable Resources*, Springer, Berlin, (1998) 292.
11. Alder,E., *Wood Sci. Technol*. 11(1977) 169.
12. Dence, C.W. Lin, S. Y. *General structural features of lignin,*Springer, Berlin, (1992) 31.
13. Al-luaibi, S. . Awad N and Mohamed, I,. *Iraqi J. Polymer* 11 (2007) 59.

14. Sun, R Fang,. J. Rowlands, P., *Polym. J.* 30 (1998) 289.
15. Li, J. Gellerstedt, G. Toven, K., *Bioresource Technol.* 100(2009) 2556
16. National Association of Corrosion Engineers (NACE), Standard Test Method- Laboratory Corrosion
17. Sastri, V.S. Corrosion inhibitors. *Principles and applications*, John Wiley and sons Ltd, (1998) 253
18. Baboian R. (ed.), ASTM, (2005) 295
19. Freeman, R.A. Silverman, D.C*, Corrosion*, 48 (1992) 463.
20. Boeriu, C.G. Bravo, D. Gosselink, R.J.A. van Dam, J.E.G., Ind. *Crop. Prod.* 20 (2004) 205.

(2011) http://www.jmaterenvironsci.com