

Inhibition of C-steel corrosion in alkaline solution using some reducing sugars

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Abstract

Three reducing sugars, namely glucose, fructose and maltose were tested as inhibitors of C-steel corrosion in alkaline solution. Their inhibition efficiencies were measured using weight loss and potentiostatic polarization techniques. It was found that the addition of any of the three sugars reduce the corrosion rate of C-steel. The inhibition efficiency decreases according to the order; glucose > fructose > maltose. The adsorption of glucose molecules on the C-steel surface follows Langmuir adsorption isotherm, whereas the adsorption of fructose or maltose do not obey it. It was found also that the three sugars act as anodic inhibitors where their oxidation reactions interfere with the anodic corrosion reaction of C-steel. The inhibitive effects of the tested sugars were discussed in view of their relative reducing power. Furthermore, uv-visible spectra were recorded for the test solutions after the completion of weight loss experiments. The recorded spectra suggested a formation of metal-sugar complexes.

Keywords: C-steel; Corrosion inhibition; Reducing sugars; UV-visible spectra.

1. Introduction

C-steel is one of the most important alloys which frequently used in wide industrial applications. In particularly, it used in manufacture of petroleum pipe lines, pumping stations for agricultural water irrigation. Corrosion problems arise as a result of interaction of the aqueous solutions with C-steel leading to high economic loss. Therefore, the decreasing of C-steel corrosion rate is very important process. One of the important methods used to decrease the corrosion rate is addition of corrosion inhibitors. Much works were devoted to find out suitable inhibitors for C-steel corrosion in different aggressive solutions [1-6]. The used compounds may be inorganic oxidants or organic compounds containing nitrogen, sulfur or oxygen. Although many of the inhibitors used have high inhibition efficiencies, the usage of them still undesired due to their dangerous effects on human and environment.

It should be mentioned here that the first used corrosion inhibitors were naturally occurring substances extracted from various parts of different plants. The synthetic chemicals are, then used for several decades. Recently, many works were conducted to use of the environment friendly substances instead of the harmful synthetic chemicals [7-11]. Some saccharides were reported to be possible inhibitors for corrosion of aluminum and zinc pigments in aqueous alkaline solutions [12, 13]. The present work is devoted to test some of reducing saccharides (sugars), namely glucose, fructose and maltose as corrosion inhibitors for C-steel in alkaline solution. Weight loss measurements and polarization technique were used for evaluation of the inhibition efficiencies of the used saccharides. The uv-visible spectra of the aggressive alkaline solutions resulted from weight loss measurements, were also recorded.

2. Experimental

C-steel of type L-52 is used in preparing the electrode for the present study. For potentiostatic studies, a cylindrical rod of it is embedded in araldite with exposed surface area of 1.0 cm², and used as working electrode. The electrode was polished with different grades of emery papers, degreased with acetone and rinsed by running distilled water.

Potentiostatic polarization studies were carried out using Meinsberger Potentiostat / Galvanostat, with software zum ps6 remote for the calculation of corrosion parameters. Three-compartment cell with a saturated calomel reference electrode (SCE) and a platinum foil auxiliary electrode was used. The potentiostatic curves were obtained by application of potential with the scanning rate of 5 mV/sec. The corrosion current and potential were obtained from the point of intercept of anodic and cathodic Tafel lines. The inhibition efficiency IE was calculated using the following equation:

$$IE = [(I - I_i)/I] \times 100$$

Where I and I_i are the corrosion rates in free and inhibited solutions, respectively.

Coupons of C-steel with dimensions of (1 x 2 x 0.2 cm) were used for weight loss measurements. IE was calculated from the weight loss measurements using the equation:

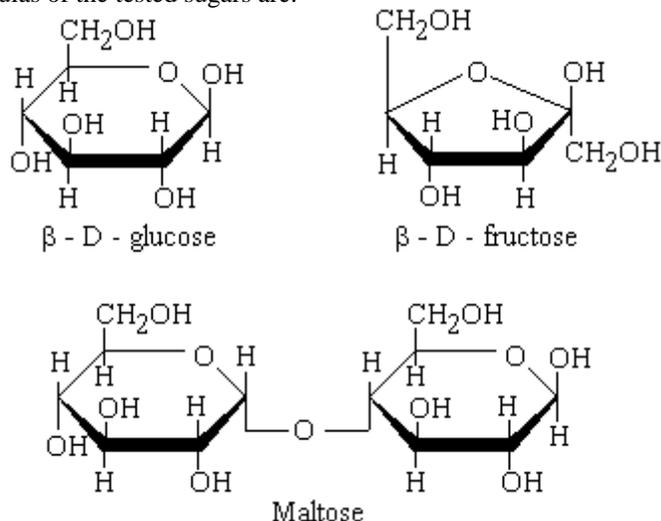
$$IE = [(W - W_i) / W] \times 100$$

Where W and W_i are the weight loss of the coupon in free and inhibited solutions, respectively.

The uv-visible absorption spectra of the tested solutions were recorded using Jasco, V 530 UV/VIS spectrophotometer.

All the chemicals used for preparation of the test solutions were of analytical grade and the experiments were carried out at room temperature, $25 \pm 1^\circ\text{C}$.

The structure formulas of the tested sugars are:



3. Results and discussion

3.1. Weight loss measurements

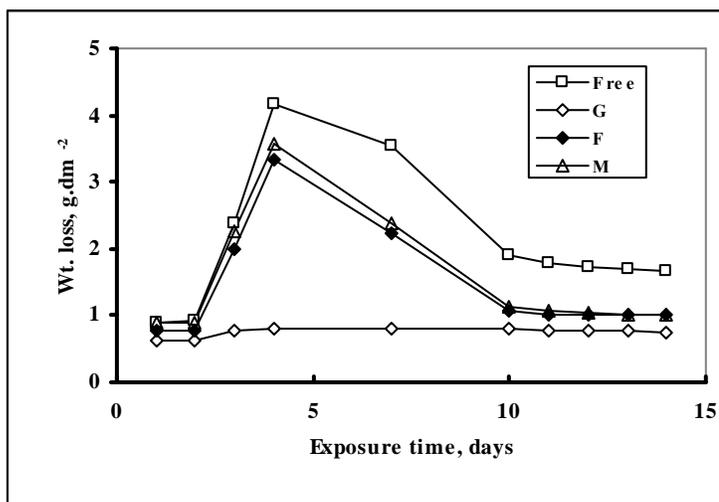


Fig (1): The loss of C-steel weight as a function of exposure time.

Fig (1) represents the weight loss of C-steel, in 1.0 M NaOH solutions devoid of and containing 0.05 M of glucose, fructose or maltose, as a function of exposure time. Among the whole exposure period, the loss of C-steel weight due to its exposure to the free alkaline solution is always higher than those resulted due to the solutions containing any of the three additives. This result indicates the inhibitive effect of the added sugars, on C-steel corrosion in alkaline solution. The figure reveals also that the loss of weight, in all solutions, is very small during the first two days of exposure. For all solutions, except that contains glucose, the weight loss increases markedly and reaches its maximum at the fourth day. After this, the weight loss decreases again and finally reaches steady values depending on the solution composition. On the other hand, the loss of weight in glucose containing solution is almost constant during the whole period of exposure.

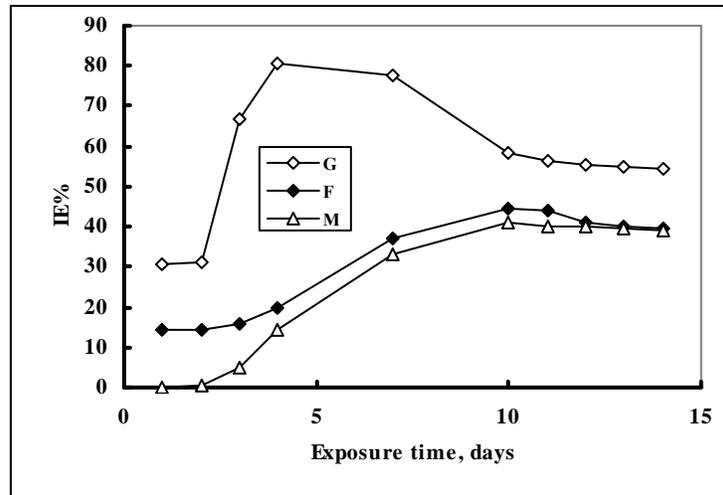


Fig (2): Variation of IE with exposure time.

The variation of inhibition efficiencies of the three sugars with the period of exposure is represented in Fig (2). Several remarks could be recognized in this relationship. As general, the relative inhibition efficiencies of the three sugars have the same order during the whole exposure period i.e. glucose has the highest and maltose has the lowest values. Moreover, the apparent decrease in inhibition efficiency of glucose at the long periods is due to the decrease of C-steel dissolution in the free alkaline solution. However, the inhibition efficiencies of fructose and maltose increase because the same reason. The decrease of C-steel corrosion rate could be attributed to the formation of a passive film on its surface.

Table (1): Effect of sugars concentration on dissolution rate of C-steel in 1.0 M NaOH solution.

Additives	W. loss (g/dm ²)	IE%	
0.0 M glucose	4.167	----	----
0.0005	3.958	5.00	0.05
0.001	3.791	9.00	0.09
0.005	2.730	34.48	0.3448
0.01	2.083	50.00	0.5
0.05	0.804	80.70	0.8155
0.0 M fructose	4.167	----	----
0.0005	4.00	4.00	0.04
0.001	3.875	7.00	0.07
0.005	3.595	13.72	0.1372
0.01	3.514	15.66	0.1566
0.05	3.338	19.89	0.1989
0.0 M maltose	4.167	----	----
0.0005	4.013	3.69	0.0369
0.001	3.925	5.79	0.0579
0.005	3.776	9.38	0.0938
0.01	3.708	11.00	0.11
0.05	3.564	14.47	0.1447

Table (1) contains the values of weight loss of C-steel coupons resulted due to their exposure, for four days, to solutions of 1.0 M NaOH, devoid of and containing different concentrations of glucose, fructose or maltose. The period of the four days was chosen because it corresponds to the maximum dissolution rate of C-steel in the free alkaline solution. The inhibition efficiencies of different concentrations of the added sugars are given in the table. It is common practice to assume that the inhibitive

effect of the added compound is a result of adsorption of its molecules on the metal surface. Therefore, there is a direct relationship between the inhibition efficiency and the fraction of surface covered by the adsorbed molecules (θ). Thus, the values of (θ) were calculated using the equation; $\theta = IE / 100$, for different concentration of glucose and given in Table (1). Inspection of Table (1) reveals that the inhibition efficiency increases as the sugar concentration is increased. Moreover, the inhibition efficiency increases, for the all studied concentrations, in the order: maltose < fructose < glucose.

The observed inhibition action of the used reducing sugars is attributed to the adsorption of their molecules on C-steel surface. The adsorbed layer of sugar molecules isolates the metal surface from the aggressive medium leading to decreasing the corrosion rate. To find out the mode of adsorption of sugar molecules on C-steel surface, the relationship between sugar concentration (C) and the surface coverage (θ)

should be obtained. Therefore, graphic representations of the relationships between $\log C$ and $(\log \frac{\theta}{1-\theta})$, for the three sugars, are given in Fig (3).

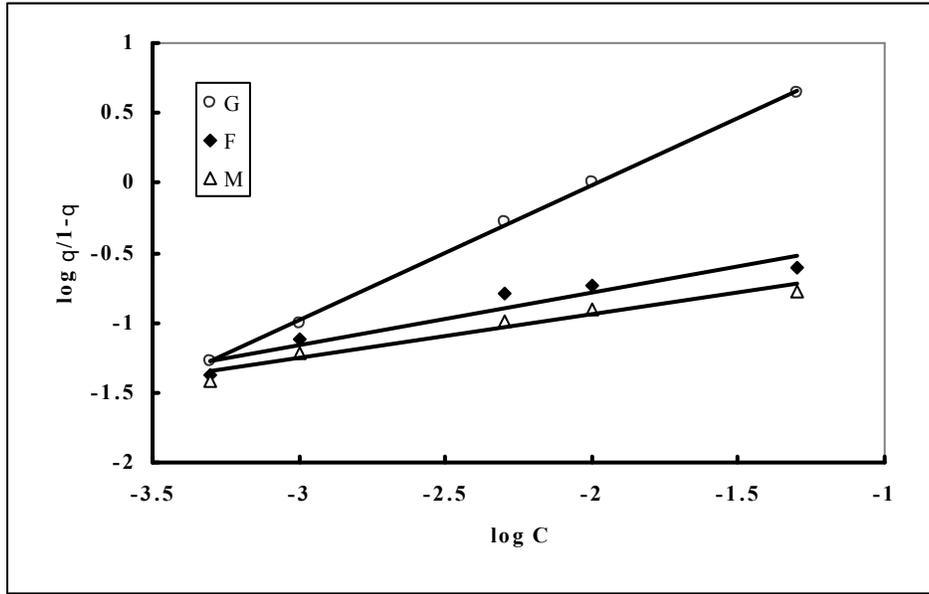


Fig (3): Adsorption isotherms of the sugars molecules on C-steel surface.

Inspection of Fig (3) reveals that, straight lines relationships were obtained with slopes of 0.97, 0.38 and 0.31 for glucose, fructose and maltose, respectively. This result suggests that the adsorption of glucose molecules on C-steel surface follows Langmuir adsorption isotherm, whereas the adsorption of fructose or maltose molecules deviate, largely, from Langmuir behavior. Therefore, these findings indicate that, there is no interaction force between the glucose molecules adsorbed on C-steel surface. On the other hand, the effect of such force is larger in case of adsorbed molecules of fructose or maltose. On the basis of these results, the standard free energy of adsorption (ΔG_{ad}^o) could be obtained only for glucose molecules using equations [14]:

$$\log \frac{\theta}{1-\theta} = \log C + \log K$$

$$\log K = -1.74 - \frac{\Delta G_{ad}^o}{2.303RT}$$

where K is the adsorption constant which obtained from the intercept of the relationship in Fig (3). It was found that the value of ΔG_{ad}^o for glucose molecules in alkaline solution is $-20.92 \text{ kJ.mole}^{-1}$. The negative sign indicates that the adsorption of glucose molecules on C-steel surface, in alkaline medium, is a spontaneous process, whereas the value suggests a chemo-sorption process.

3.2. Potentiostatic polarization

Fig (4) represents the anodic and cathodic potentiostatic polarization curves of C-steel electrode in solutions of 1.0 M NaOH devoid of and containing different concentrations of glucose. Similar curves were also obtained in presence of different concentrations of fructose and maltose, but not shown here.

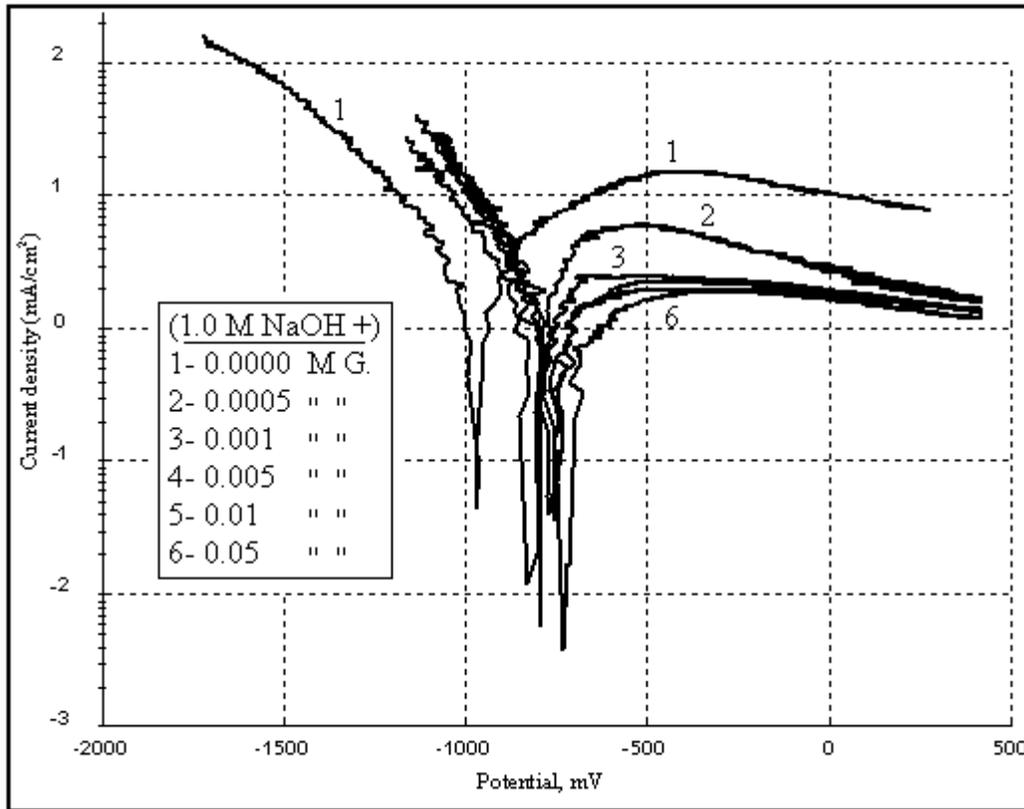


Fig (4): Anodic and cathodic polarization curves of C-steel in solutions of NaOH devoid of and containing different concentrations of glucose.

Inspection of Fig (4) reveals that the polarization curves are shifted toward less negative potentials and less current densities as the concentration of glucose is increased. This behavior indicates the inhibitive action of the added glucose on C-steel corrosion in alkaline solution. Moreover, the shape of the anodic branch, rather than the cathodic one is largely affected by presence of glucose. Therefore, as the concentration of glucose is increased the current corresponding to the passive state decreases. This behavior indicates that the adsorbed molecules form a surface layer which improves the protection action of the original passive oxide film.

The corrosion parameters of C-steel electrode in free and inhibited solutions of 1.0 M NaOH are given in Table (2). The data in Table (2) reveals that the corrosion potential shifts toward the less negative values as the concentration of every additive is increased. Moreover, the corrosion current density decreases with increasing of additive concentration. The inhibition efficiencies of the three sugars follow the same order obtained by weight loss measurements. It is of interest to note that the values of inhibition efficiencies calculated using polarization technique are relatively larger than those obtained by weight loss measurements. This discrepancy could be attributed to the difference in the nature of experimental procedure of every technique.

Further inspection of Table (2) reveals that the value of anodic Tafel constant is larger than that of the cathodic one, for the alkaline solution free from additives. This behavior could lead to the prediction that the corrosion process, of C-steel in alkaline solution, is cathodically controlled. The reduction of oxygen is the conceivably cathodic reaction which can take place in the used alkaline solution. Thus, the corrosion process is controlled by the reduction of oxygen dissolved in the corrosive medium. Upon addition of sugar compounds, the value of anodic Tafel constant decreases markedly. The magnitude of decrement increases as the additive concentration is increased. However, the value of cathodic Tafel constant also decreases, but in a smaller extent, due to the presence of sugars. The variation of the Tafel

constants values due to the presence of sugars indicates that the mechanism of C-steel corrosion has been changed. Furthermore, because that the change of the anodic constant value is higher than that of the cathodic one, it could be concluded that the major effect of sugars takes place on the oxidation process. Since all the used sugars are reducing compounds, it could be expected that the oxidation reactions of them interfere with the oxidation dissolution reaction of C-steel. It was reported that glucose undergoes electro-oxidation according to the following equation [15-17]:



Bearing in mind that the corrosion process is cathodically controlled, the presence of such interfering anodic reactions results in decreasing the rate of C-steel dissolution. Thus, it could be stated that the used sugars act as anodic inhibitors. It was reported that the reducing sugars, fructose and mannose, as well as reducing ascorbic acid, inhibited the corrosion reaction of aluminum pigment in the aqueous alkaline media, whereas the non-reducing sucrose did not inhibit it [6].

Table (2): Corrosion parameters of C-steel corrosion in free and inhibited NaOH solutions.

Additives	E_{corr} mV	I_{corr} mA/cm ²	a mV/decade	$-c$ mV/decade	IE%
0.0 M <i>glucose</i>	-1008	2.71	677	353	----
0.0005	-800	2.439	405	225	10.00
0.001	-800	2.26	396	206	16.60
0.005	-761	1.28	381	201	52.76
0.01	-706	0.774	269	192	71.44
0.05	-739	0.37	132	191	86.34
0.0 M <i>fructose</i>	-1008	2.71	677	353	----
0.0005	-998	2.32	612	331	14.39
0.001	-970	2.21	438	294	18.45
0.005	-893	1.95	375	288	28.04
0.01	-860	1.90	356	286	29.88
0.05	-780	1.84	349	267	32.10
0.0 M <i>Maltose</i>	-1008	2.71	677	353	----
0.0005	-993	2.61	613	376	3.69
0.001	-986	2.58	539	363	4.79
0.005	-958	2.4	498	360	11.44
0.01	-953	2.24	444	331	17.34
0.05	-904	2.1	416	313	22.50

According to this proposed inhibition mechanism, the compound which possesses the higher reducing power must have higher inhibition efficiency. Glucose is known to be more reducing compound than fructose due to the presence of aldehyde group in its structure which is more effective than the ketone group of fructose. On the other hand, in spite of the presence of aldehyde group in maltose, its reducing power may be affected by its complicated structure containing two molecules of glucose. It appears that such large structure hinders the adsorption process of maltose molecules on the metal surface. Moreover, for the same surface area of C-steel, the number of adsorbed fructose molecules will be double of that of maltose molecules. This situation renders the reducing power of fructose superior relative to that of maltose owing to the presence of one reducing group per one molecule of each. Therefore, the expected order of decreasing inhibition efficiencies of the three tested sugars will be; glucose > fructose > maltose. This order is consistent with the experimentally obtained results.

3.3. The uv-visible absorption spectra

The uv-visible absorption spectra of different test solutions were obtained to verify the formation of complex compounds as a result of combination between the added sugars and dissolved ferrous cations. Fig (5) represents the uv-visible spectra of 1.0 M NaOH solutions containing 0.05 M glucose, fructose or maltose. The blank solution used in every measurement was 1.0 M NaOH solution. All the three sugars are characterized by presence of absorption band in the region of uv spectra.

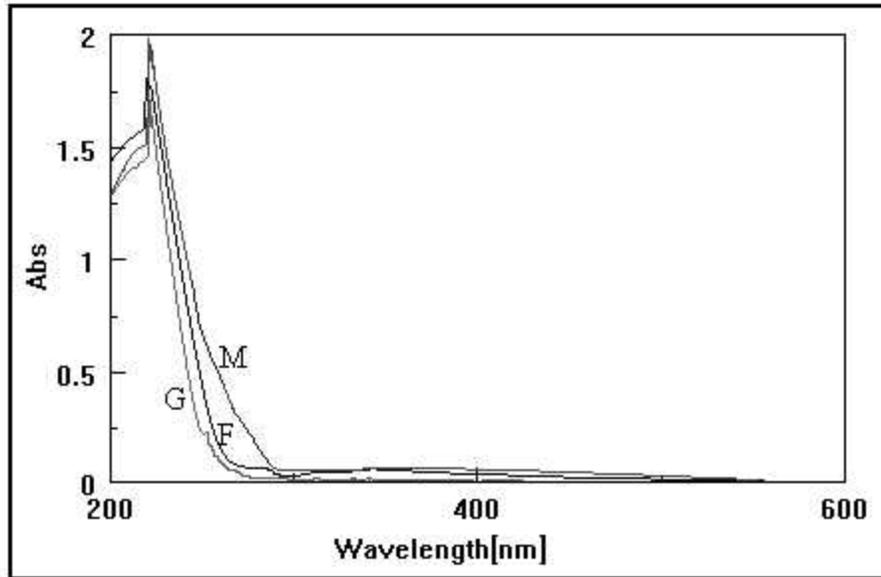


Fig (5): uv-visible spectra of glucose, fructose and maltose.

Fig (6) illustrates the uv-visible absorption spectra of the solutions taken after the performance of C- steel weight loss measurements for 15 days. The compositions of these solutions were 1.0 M NaOH containing additions of 0.05 M glucose, fructose or maltose. The freshly prepared alkaline solutions containing the corresponding sugar were used as blank for these spectra measurements. Inspection of Fig (6) reveals that there are three absorption bands located at the same wavelength in the visible region, for the three tested solutions. The appearance of such absorption bands in the visible region is a strong evidence for the formation of complex compounds in the tested solutions. The absorbance of solution containing maltose is the highest whereas that of glucose containing solution is the lowest. This behavior indicates that the solubility of maltose-ferrous complex is higher than that of fructose one, whereas the glucose complex have the lowest solubility.

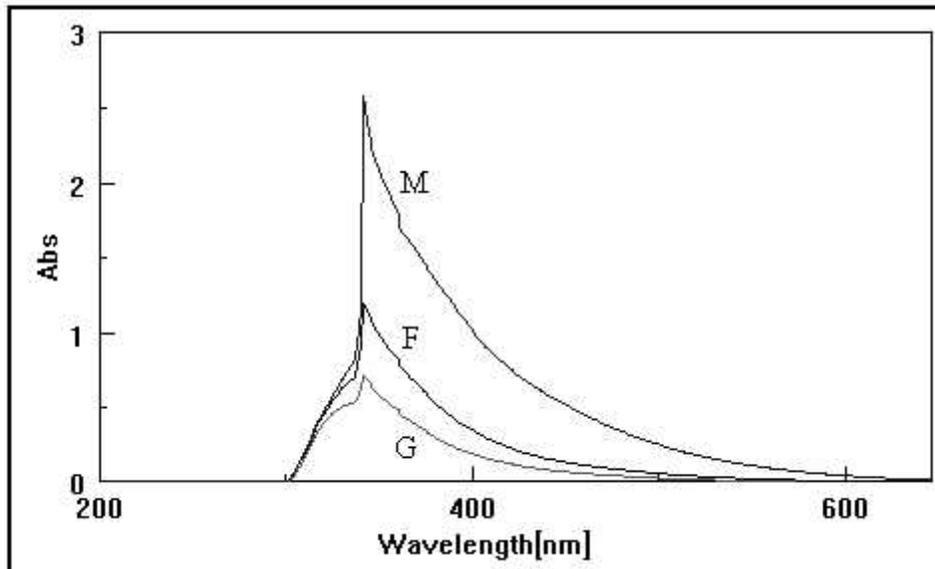


Fig (6): UV-visible spectra of the inhibited solutions resulted from weight loss tested.

According to the obtained results, it could be stated that the inhibition of C-steel corrosion by reducing sugars take places via the following mechanism. First of all, the sugar molecules are adsorbed on C-steel surface. Some of the adsorbed molecules are anodically oxidized parallel with the anodic corrosion

reaction of the metal. Because the corrosion reaction is cathodically controlled, the oxidation process of the sugar molecules leads to a decrease in C-steel corrosion rate. At the same time ferrous-sugar complex is formed in solution which soon precipitates, after exceeding its saturation limit, on C-steel surface. The precipitation of such complexes on the surface covered by passive film improves the protection action of the later leading to decrease the current of passive state as revealed from polarization curves of Fig (4). Thus, the degree of C-steel surface protection provided by the ferrous-sugar complexes depends on their solubility in the aqueous medium. Therefore, according to this argument, the expected order of protection ability of the three sugars will be glucose > fructose > maltose. Again, this order is consistent with that experimentally obtained.

4. Conclusions

- 1- The three tested reducing sugars; glucose, fructose and maltose inhibit the C-steel corrosion.
- 2- For monosaccharides, the aldose glucose is more effective than the ketose fructose while the two of them are more effective than the disaccharide maltose.
- 2- The corrosion of C-steel in alkaline solution is cathodically controlled while the used sugars are anodically inhibitors.
- 3- The adsorption of only glucose molecules follows Langmuir adsorption isotherm.
- 4- All the used sugars form complexes by combination with dissolved ferrous compounds.

References

- 1- Yi-Jiu Li, Bin Wu, Xin-Ping Zeng, Ya-Fei Liu, Ya-Ming Ni, Guo-Ding Zhou and Hong-HuaGe, Thin solid film, 2002, **405**,153
- 2- R. Cabrera-Sierra, E. Sosa, M. T. Oropeza and I. González, Electrochim. Acta, 2002, **47**, 2149.
- 3- Lin Wang, Corros. Sci., 2001, **43**, 1637.
- 4- T. Anh True, N. Pebere, T. T. Xuan Hang, Y. Hervaud and B. Boutevin, Corros. Sci., 2002, **44**, 2055.
- 5- S. Rajendran, B. V. Apparao and N. Palaniswamy, Anti-corros. Meth & Mater., 47 (2000) 147.
- 6- B. Muller, Corros. Sci., 2002, **44**, 1583.
- 7- A.Y. El-Etre, Corros. Sci., 1998, **40**, 1845.
- 8- A. Y. El-Etre and M.Abdallah, Corros. Sci., 2000, **42**, 738.
- 9- A. Y. El-Etre, Corros. Sci., 2001, **43**, 1031.
- 10- A.Y. El-Etre, Corros. Sci., 2003, **45**, 2485.
- 11- A. A. El Hosary, R. M. Saleh and A. M. Shams El Din, Corros. Sci., 1972, **12**, 897.
- 12- B. Muller and M. Kurfe , Werkst. Korros., 1993, **44**, 373.
- 13- B. Muller, M. Muller and I. Lohrke, Farbe Lack, 1994, **100**, 467.
- 14- T. P. Hoar and R. D. Haliday, J. Appl. Chem., 1953, **3**, 502.
- 15- T. Chen, S. C. Barton, G. Binyamin, Z. Gao, Y. Zhang, Hyug-Han Kim, and A. Heller, *J. Am. Chem. Soc.*, 2001, **123**, 8630.
- 16- E. Katz, I. Willner, A. Kotlyar, B. J. Electroanal. Chem. 1999, **64**, 479.
- 17- E. Katz, B. Filanovsky, I. Willner, New J. Chem. 1999, **23**, 481.