

INHIBITIVE ABILITY AND ADSORPTION CHARACTERISTICS OF WATER EXTRACT OF THAI NGUYEN GREEN TEA LEAVER FOR CORROSION OF MILD STEEL IN 1M HCL SOLUTION

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TÓM TẮT

KHẢ NĂNG ỨC CHẾ ĂN MÒN VÀ ĐẶC TRƯNG HẤP PHỤ CỦA DỊCH CHIẾT CHÈ XANH THÁI NGUYÊN ĐỐI VỚI THÉP THƯỜNG TRONG DUNG DỊCH HCL 1M

Trong công bố này, chúng tôi đã nghiên cứu khả năng ức chế ăn mòn cho thép thường trong dung dịch axit HCl của dịch chiết nước lá chè xanh bằng phương pháp điện hóa. Kết quả nghiên cứu cho thấy ở các nồng độ dịch chiết nước lá chè xanh khác nhau đều có khả năng ức chế ăn mòn thép thường. Hiệu quả ức chế ăn mòn nói chung tăng khi nồng độ dịch chiết tăng. Các nghiên cứu nhiệt động học đã chứng minh rằng sự hấp phụ của dịch chiết chè lên bề mặt thép trong dung dịch axit là tự xảy ra và tuân theo thuyết hấp phụ Langmuir. Các kết quả tính toán động học và nhiệt động học chứng minh sự hấp phụ xảy ra theo cơ chế hấp phụ vật lý.

Từ khóa: ức chế ăn mòn, thép thường, thuyết hấp phụ đẳng nhiệt Langmuir, hấp phụ vật lý, chè xanh

1. INTRODUCTION

A corrosion inhibitor, when added in minute quantity, decrease the rate of corrosion of a metal or a metal alloy. Due to their industrial importance, most corrosion inhibitors have been synthesized from cheap raw materials or chosen from compounds containing hetero atoms in their aromatic or long

carbon chain [1,2]. Green corrosion inhibitors are biodegradable and do not contain heavy metals or other toxic compounds. The successful uses of naturally occurring substances to inhibit the corrosion of metals in acidic and alkaline environment have been reported by some research groups [1-8] but the application of green tea for this purpose

has not been investigated much yet. Especially, green tea also contains polyphenol promising electrochemical performance as well as the ability to inhibit corrosion of metal. This research concentrates on the inhibitive and adsorptive characteristics of water extract of *green tea* for the corrosion of mild steel in 1M HCl solution.

2. EXPERIMENTAL

Extraction of plant

Leaves of *Green tea* were collected in Thai Nguyen city. The clean air-dried leaves were grounded and extracted 3 times with distilled water. After that, three parts of filtered water were further subjected to evaporation at 353 K. The obtained residue of the extract were washed with n-hexane, dichloromethane, ethylacetate, n-butanol, respectively. The final product called water extract W(G) is used to prepare solutions with its different concentrations by dissolving 0.1, 0.5, 1.0, 2.0, 5.0 and 10.0g in 1 L of 1M HCl solution.

Preparation of working electrode

Working electrode was made from CT38 Steel (produced in Thai Nguyen) specie (wt%: 0.154%C; 0.636%Mn; 0.141%Si; 0.019%P; 0.044%S and the rest Fe) with exposure area $S = 0.785\text{cm}^2$. Non-working area was isolated by using epoxy resin. Prior to the test, the electrodes were mechanically polished with successively finer grades of emery papers until their surfaces become smooth. Afterward, they were degreased with acetone, washed thoroughly with

distilled water, dried and immersed in study solution.

Chemicals and Apparatus

Chemicals used are analytical grade.

All electrochemical measurements were performed in the three-electrode mode using a homemade multifunctional potentiostat connected to a computer (Manufactured in Lab of Computer Application to Chemical Research, Institute of Chemistry, Viet Nam Academy of Science and Technology). A silver/silver chloride electrode and a piece of stainless steel with large area were employed as pseudo-reference and counter electrode, respectively. All experiments were done in unstirred and nondeaerated solutions at room temperature after immersion for 60 min in 1M solution with and without addition of inhibitor.

The linear polarization study was carried out from -20 to $+20\text{mV}$ versus corrosion potential (E_{corr}) at a scan rate of 0.1mV.s^{-1} to determine the polarization resistance (R_p), the inhibition efficiency has been calculated

from the equation: $H = \frac{R_t - R_o}{R_t} \cdot 100\%$

(1) where R_o and R_t are the polarization resistance in absence and in presence of inhibitor, respectively.

Tafel curves were obtained by changing the electrode potential automatically from -150 to $+150\text{mV}$ versus corrosion potential (E_{corr}) at a scan rate of 3mV.s^{-1} . The linear Tafel segments of anodic and cathodic curves were

extrapolated to corrosion potential to obtain corrosion current densities (I_{corr}).

3. RESULTS AND DISCUSSION

3.1. Effect of concentrations of W(G) extract and Effect of Acid Concentration

Polarization curves for mild steel in 1M HCl solution with various concentrations of W(G) are shown in Figure 1. The calculation of the corrosion rate and inhibition efficiency are given in Table 1.

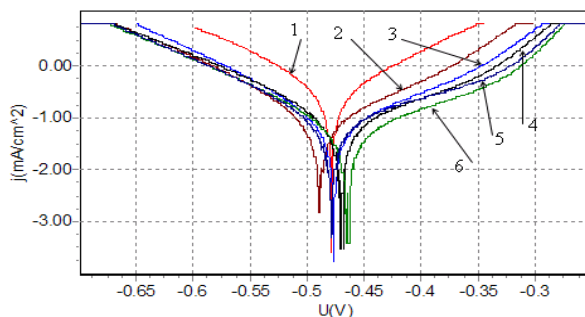


Figure 1. Polarization curves in absence and presence of different concentrations of W(G) in 1M solution of HCl

1 – 0,0g/l 2 – 0,1g/l 3 – 0,5g/l
4 – 1,0g/l 5 – 2,0g/l 6 – 5,0g/l
7 – 10,0g/l

Table 1. Potentiodynamic polarization parameters for mild steel without and with different concentrations of W(G) extract in HCl solution

solution	C(g/l)	$E_C(V)$	$R_P(\Omega)$	$E_R\%$	$E_S(V)$	$V_T(\text{mm/year})$
1MHCl		-0.468	77.71		-0.466	2.64
1M HCl + W(G)	0,1	-0.458	220.01	64.68	-0.457	9.19.10-1
	0,5	-0.465	322.63	76.97	-0.457	7.20.10-1
	1	-0.469	338.00	77.01	-0.469	6.94.10-1
	2	-0.465	347.41	77.63	-0,464	6,66.10-1
	5	-0.470	451.75	82.80	-0.467	5.98.10-1
	10	-0.461	615.84	87.38	-0.478	4.27.10-1

In general, inhibition efficiency increased with increasing in inhibitor concentrations. In the presence of W (G), although the small concentration (0.1 g/l), inhibition efficiency is approximately 65%, the maximum inhibition efficiency of extract is 87.38% at concentration of 10g/l. Anodic and cathodic current densities of

steel in acidic solution were reduced with the present W(G). It is clear that both cathodic and anodic reactions are inhibited and the inhibition increases as the inhibitor concentration rises. And, there was no definite trend in the shift of E_{corr} values, in the presence of various concentrations of water extract of green tea in 1M HCl solution. This result

indicated that water extract of green tea can be considered as mixed inhibitor in 1M HCl solution.

3.2. Scanning electron Microscope (SEM)

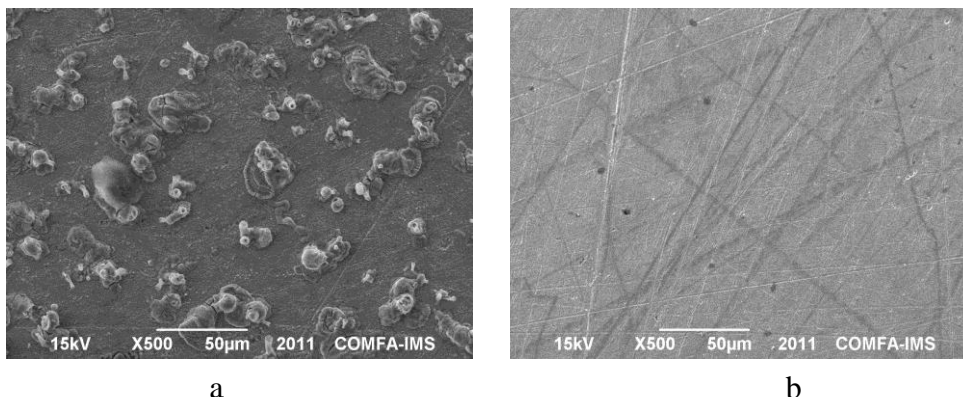


Figure 2. SEM micrographs of Thai Nguyen steel in (a) without inhibitor, (b) with W(G) 5g/l

Fig. 2 shows the SEM images of different slides of Thai Nguyen steel after immersed in the 1M HCl solution with the absence and presence of the inhibitor. Here, the micrograph exhibits a cocoon-like structure for solution with the presence of the inhibitor but there are many plots of corrosion on the surface of sample which is immersed in the solution with the absence of the inhibitor. It means that the W(G) is a good inhibitor for Thai Nguyen steel in the 1M HCl solution.

3.3. Adsorption Isotherm

If it is assumed that corrosion occurs only at the free sites, the covered sites have zero corrosion rates, and the degree of surface coverage θ for different concentration of W(G) extracts was evaluated from linear polarization method by using the following equation ($\theta = E(\%) / 100$).

It can be seen that the values of surface coverage increases with the rise in inhibitor concentration (Table 1) as a result of more inhibitor molecules adsorption on the steel surface. Now assuming that the adsorption of W(G) extracts belongs to monolayer adsorption and the lateral interaction between the inhibitor molecules is ignored, then the Langmuir adsorption isotherm applied to investigate the adsorption mechanism is [4.5]:

$$\theta = \frac{KC}{1 + KC} \quad (3)$$

Where C is the inhibitor concentration in the electrolyte, K is the equilibrium constant of the adsorption process. By plotting values of C/θ versus C , straight line graphs were obtained (Fig. 3) which proves that Langmuir adsorption isotherm is obeyed over the range of studied concentrations.

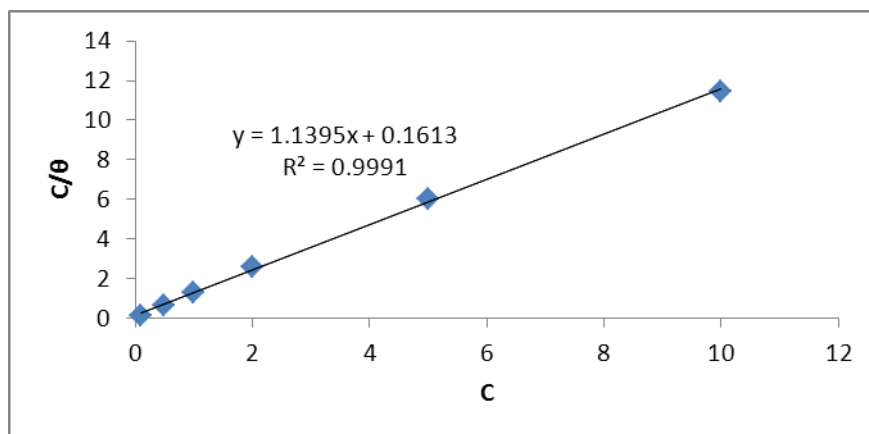


Figure 3. Langmuir Isotherm plot for CT38 Steel corrosion in 1M HCl solution.

The degree of linearity of Langmuir adsorption isotherm as measured by values of R^2 is nearly equal to 1 which indicates that the assumption and the deduction were correct. In other words, the adsorption of W(G) extracts on steel surface in 1 M HCl solution is well described by the Langmuir adsorption isotherm [4]. The considerable deviation of the slopes from unity shows that the isotherm cannot be strictly applied. This deviation is attributable to interaction between adsorbate species on the metal surface [4,5]. A modified Langmuir adsorption isotherm [5,6] could be applied to this phenomenon, which is given by the corrected equation:

$$\frac{C}{\theta} = nC + \frac{n}{K} \quad (5)$$

The relationship between the standard free energy of adsorption and The adsorption equilibrium constant according to the following equation [3]: $\Delta G^\circ = -2.303RT \log(55.5 \times K)$

Where R is the molar gas constant, T is the absolute temperature and 55.5 is the concentration of water in solution expressed in molar.

The result is : $K = 7.0745$ and $\Delta G^\circ = -14.800$ kJ/mol

The negative values of $\Delta G^\circ_{\text{ads}}$ suggest that the adsorption of W(G) extract onto steel surface is spontaneous. Furthermore, the obtained values of $\Delta G^\circ_{\text{ads}}$ indicate that adsorption of W(G) extracts occurs via physical adsorption mechanism. [5, 6].

4. CONCLUSIONS

1. *Green tea* extracts were found to be an efficient 'green' inhibitor for Thai Nguyen steel in 1M HCl solution.
2. Inhibition efficiency increases with the rise in W(G) concentration. The maximum inhibition efficiency of extract is 87.38% at concentration of 10g/l.
3. The corrosion process is inhibited by adsorption of the W(G) extracts onto the steel surface following the Langmuir adsorption isotherm.

4. The values of the free energy of adsorption calculated indicate strong, spontaneous and physical adsorption of the extracts on the CT38 steel surface.

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