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WATER EXTRACT OF GREEN TEA OLD LEAVES AS A METAL CORROSION INHIBITOR

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ABSTRACT

Corrosion inhibitors original from natural products have been considered preferential due to the environment friendly effect. Green tea is an especially tropical produce in Vietnam, which is very rich of the polyphenol compounds. In our study, water extracts of Thainguyen green tea old leaves were studied as a corrosion inhibitor in acid solutions. Firstly the old tea leaves were extracted in boiled water. The extract then was thermally boiled down to prepare tea glues. The tea leaf extracts and glues were then dissolved at different concentrations in 2 M H_2SO_4 solution. The corrosion inhibition of the extract and glues on the mild steel (construction steel) has been studied using electrochemical polarization and impedance technique. The obtained results of i_{cor} measurements, Tafel slopes and R_{ct} analyses, inhibition efficiency calculation… show that the water extract and glues of Thainguyen green tea old leaves manifest good corrosion inhibitors, with an efficiency up to more than 90%. The corrosion inhibitors affect both anodic and cathodic reactions. The mechanism of inhibition is an adsorption of the polyphenol compounds on the metal surface in both anodic and cathodic branches.

I - INTRODUCTION

Metal is one of the most popular materials even for long next time in 21st century. The largest industrial application of metal has been in construction with well known family of mild steel, or construction steel. This steel is also largely used in many other industrial branches. Unfortunately the steel is not resistant in acid solutions which are used widely in industry, mostly as acid pickling, industrial acid cleaning, acid descaling and oil well cleaning. In order to restrain the oxidation attack of the acid solution on metallic materials it is necessary to add different corrosion inhibitors to the acid solution. Traditionally, the widely used inhibitors have been $NaNO_2$, ion PO_4^{3-}, chromate… However those inorganic inhibitors, even manifesting as very high efficient inhibitors, are considered as not friendly for the environment. Some of them are interdicted in most European countries.

A lot of synthesized organic inhibitors have been studied, most of them containing nitrogen, oxygen and multiple bonds in the molecules, most of which can strongly adsorb on the metal surface forming a resistant inhibition layer and reducing an attack of the acid solutions.

Instead of the synthesized corrosion inhibitors, natural products, as tannin [1 - 4], have been investigated as promising green inhibitors. The natural inhibitors are non expensive, renewable, and in particular environment friendliness. Thus, anticorrosion effects of natural polyphenol have been studied [1, 5]. The well known polyphenol source is green tea leaves, one of the important tropical natural produce in Vietnam. The principal green tea products are very rich in polyphenol, strong antioxidants making the tea so valuable, consequently are very expensive and not suitable for the other application, excepting well known tea drinks. However there are secondary green tea products, such as old leaves, tea powders occurred during tea production, which are enough cheap for next treatment such as recuperating polyphenol and other products. In this paper, corrosion inhibition effects of water extracts of green tea secondary products, as old leaves, on mild steel in acid solution have been investigated.

II - EXPERIMENTAL TECHNIQUE

1. Tea leaf extracts and glues

The tea old leaves are gathered and freshly extracted in boiling water, mass ratio tea leaves/ water is 1:10. The extraction was repeated with recuperated water from previous concentration extract at the same ratio. The extracts were mixed and then boiled down to prepare tea glues with water ratio about 13% – 14%. The total extraction efficiency was about 20% - 23%. The glues then are well air hermetically packed and preserved in room temperature.

2. Electrochemical inhibition study procedure

Green tea glues have been freshly dissolved at 5 g/l in H_2SO_4 1 M solution to prepare inhibition solutions. The electrochemical experiments were carried out in H_2SO_4 1M solution, with different tea glues concentrations, which are marked as M0- 0ml of the inhibition solution, M1-5ml, M2-10ml and M3-20ml. The water extracts have been used in nearly the same proportional ratio.

Electrochemical potentiostat is AUTOLAB PGSTAT 30 (Eco Chemie B.V. Utrecht, the Netherlands) connect to a PC with Window XP. Two readily installed software GPES 4.9 and FRA 4.9 control the measurement system and also analyze the experimental data. Measurement system is three electrodes glass cell. Working electrode is a plate Pt of 1cm^2 effective surface. Coating electrode of larger surface was prepared from Pt wire. Electrochemical bridges were used for connecting a compartment of saturated calomel electrode (SCE) to the cell.

Steel sample was domestic Thainguyen product, TCVN 1656-75, with composition as follow:

Elements	C	Mn	Si	P	S	Fe	Cr	Cu
Weight %	0.34	0.51	0.19	0.017	0.035	98.7	0, 044	0.1

The steel samples, as a working electrode in the electrochemical cell, were cut in cylindrical form of nearly 1cm^2 profile, then polished around before being enclosed in epoxy resin with electric contact (figure 1). The electrodes surface then was polished using abrasive papers of grades 400, 600, 800, 1000, 1200, and then cleaned in distilled water following rinsing in technical alcohol and then drying in hot air current. The previously prepared electrodes then were protected in an air hermetic desiccator.

Inhibition effects of the glues have been investigated using 3 techniques: measurement of open circuit potential (E_{opc}), corrosion current

(i_{cor}) and electrochemical impedance [6, 9, 10]. The i_{cor} measurement has been realized in polarization range $\Delta E = E - Eoc = \pm 5$ mV with scan rate 0.1mV/s. Corrosion current i_{cor}, Tafel coefficients anodic β_a nd cathodic β_c, polarization resistance R_P have been determined using readily installed GPES program. B constant has been calculated according to relation $B = R_P.i_{corr}$ and re-examined using Tafel coefficients in following equation [6 - 8]:

$$B = \frac{1}{2.303}\left(\frac{\beta_a\beta_c}{\beta_a + \beta_c}\right)$$

III - RESULTS

1. Open circuit potential E_{opc} measurement

Variations of E_{oc} in the studying solution as a function of emerge time are presented in figure 1. It is clear that the potentials obtained in the all 4 solutions increase in general with time, and those measured in the inhibition solutions M1 – M3 are significantly more positive than that of solution sample M0. The E_{oc} values determined after 1800s emerge are shown in figure 2. Variation of the open circuit potentials due to the inhibition effects (M1 – M3) in comparison with that in solution M0 is not very large, about 20 mV, but the difference increases with the green tea glue concentration. It simple saturation of the green tea glue concentration for the solution M2 and M3 where E_{opc} is the same for both solutions (Fig. 2).

2. Corrosion current i_{cor} measurement

Linear polarization measurement was realized in potential interval 10 mV starting at 5mV more negative than Eoc, scan rate 0.1mV/s. The stability of the measured electrochemical system has been examined by cyclic polarization with the same potential interval and scan rate. The typical polarization curves in log scale Tafel plot) are represented in figure 3. From these linear polarization curves i_{corr}, R_P, Tafel coefficients β_a and β_c have been determined. Variation of corrosion current i_{corr} and of polarisation resistance R_P according to the samples is presented in figure 4.

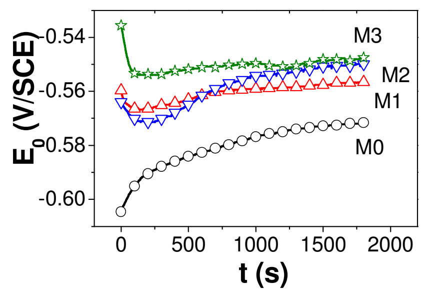

Figure 1: Variation of open circuit potentials as a function of emerge time, measured in solution M0, M1, M2, M3

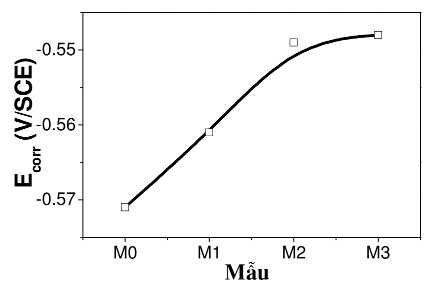

Figure 2: Variation of open circuit potentials as a function of glue concentration; $\Delta E = E_{ocMi} - E_{ocM0}$ where i = 1, 2, 3 are, respectively, 10, 20 and 23 mV

In general i_{corr} decreases and R_P increases with increasing inhibitor concentration. The inhibition efficiency calculated on i_{cor} for samples M1, M2 and M3 are 65.2, 87.3 and 92.0, respectively, and calculated on R_P for these samples are 59.2, 76.1 and 84.6, respectively. This high inhibition efficiency of the green tea glue is significant in practice [1, 9].

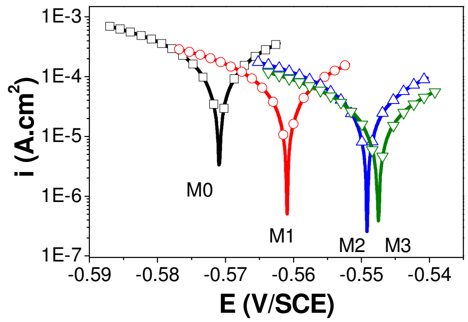

Figure 3: Linear polarization curves, Tafel plot, 4 samples M0 – M3

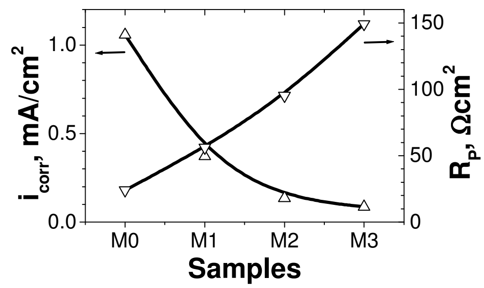

Figure 4: Variation of corrosion current as a function of the inhibitor quantities

3. Anodic polarisation measurement

It is interesting to examine anodic polarisation behaviour of the green tea glue inhibitor. Tea glue diminished remarkably anodic dissolving currents and prolonged passive region on the curve which was not occurred for the sample M0 (Fig. 5).

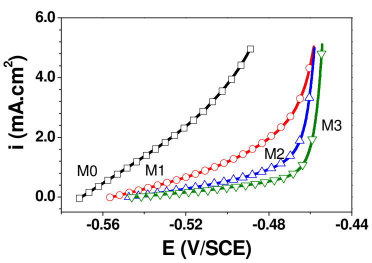

Fig. 5: Anodic polarisation curves obtained from 4 study solutions

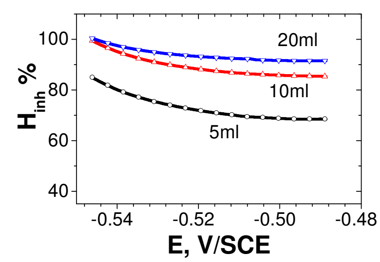

Fig. 6: Inhibition efficiency calculated at the same polarisation potential

Inhibition efficiency, calculated at the same polarisation potential for the all 3 samples, is strongly dependent on the tea glue concentration and polarisation potential (fig.6). For more negative potentials the efficiency reaches up to 100% (M2 and M3), but decreases remarkable according to increasing potential.

Anodic polarisation provokes brutal augments of dissolving currents and certain diminution of the inhibition efficacy (figures 5 and 6). At closed open circuit potential the efficiency arrives nearly 100%, and then gradually decreases. Sample M3 provides obviously highest, practically acceptable inhibition efficiency, even at high polarisation, and quantitatively more than 90% (figure 6).

3. Electrochemical impedance measurement

The impedance was measured at E_{oc}, and the obtained data are presented as Nyquist diagrams in figure 7. The tea glue inhibitors augment significantly the impedance of the steel electrodes. Variation of charges transfer resistance R_{ct} and double layer capacity C_{dl}, determined from obtained impedances using FRA program, as a function of the tea glue solution volumes, are presented in figure 8.

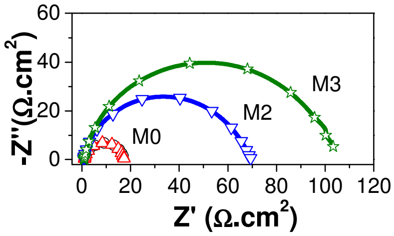

Figure 8: Nyquist diagram of EIS, samples M0, M2 and M3.

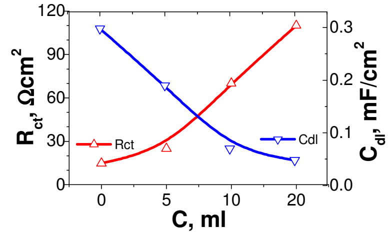

Figure 9: Variation of R_{ct} and C_{dl} of glues concentration, samples M0, M2 and M3.

4. Discussion

The obtained results from previous electrochemical investigation on corrosion inhibition of the tea glues provided good corrosion prevention of the green tea glues. The corrosion inhibition manifests not only at the open circuit potential region, but expending to large anodic region with still high efficiency up to more than 90% (figures 5 and 6).

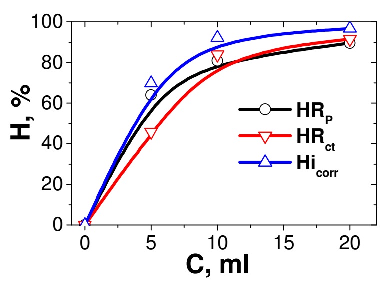

Figure 10: Variation of H (%) as a function of concentration, different experimental techniques: HR_P calculated from R_p,, HR_{ct} from R_{ct}, and Hi_{corr} from i_{corr} data

The obtained corrosion inhibition efficiency is well analysed with variable technique and calculation method. Thus Hi_{corr} is directly calculated, but HR_p and HR_{ct} are deduced using well known semi-experimental relation i_{corr} = B/R_P or = B'/R_{ct}. Namely, R_{ct} data are calculated from impedance measurement, considered as an accurate technique, additionally capable providing reaction mechanism [8, 9]. In fact, the decreasing of C_{dl} while tea glue concentration increases, indicating a strong adsorption into interface electrode / solution, in other word in the double layer [8]. The adsorption mechanism of the polyphenol inhibitors has been mentioned and discussed [1 – 5]. However in this study, using simplest model electric circuit R_{ct} in parallel with C_{dle}, and applying the characteristic relation for the maximum imaginary impedance (–Zi) of a parallel RC circuit $(RC\boldsymbol{\omega})^2 = 1$, where $\boldsymbol{\omega}$ is angular frequencies [8], we have tried to examine the variation of product $R_{ct}C_{dl}$ (figure 11), alternatively also the product $B = R_p i_{corr}$ [8, 9]. Variation of these products as a function of the concentration shows that adsorption of tea glues compounds on the steel sample surface increase strongly with concentration, and the increase of the product $R_{ct}C_{dl}$ indicates a state variation of the double layer providing a shift of the maximum characteristic frequency, from 25.1 Hz (M0) to 15.8 (M2) and finally to 12.6 (M3). Capacitance C_{dl} and characteristic frequency f_{max} diminish obviously indicate more solid absorption film, consequently preventing more efficiently metal dissolution.

Product $R_p i_{corr}$ is a constant charactering a given active electrochemical system, such as a corrosive electrode in an aggressive solution [8]. Consequently $B = R_p i_{corr}$ remains constant uniquely when the essence of the system has been conserved. However the R_P increase in this case is not proportionally with the i_{corr} decrease so, fortunately, the product $R_p i_{corr}$ diminishes, providing a remarkable increase of the inhibition efficiency. The system change can be explained by an adsorption of the tea glues compounds making a barrier film.

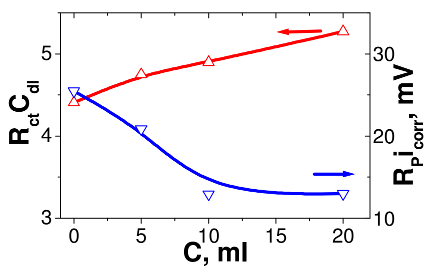

Figure 11: Variation of product $R_{ct}C_{dl}$ and $R_p i_{corr}$ with tea glues solution volumes C.

IV - CONCLUSION

Green tea old leaves can be gathered all to extract active compounds, such as polyphenol, a strong antioxidant providing values for green tea. One of the possible applications of the green tea old leaves extract is as construction steel corrosion inhibitors. In 1M H_2SO_4 solution, a small quantity of the concentrated water extract of these secondary tea products well presents acid attack up to nearly 100% efficiency at open circuit potential. The inhibition can remain at high anodic polarisation. The tea old leaves extract prevents acid corrosion on construction steel via adsorption mechanism, which modifies the nature of the interface metal surface/acid solution, probable due to create a barrier film with certain metal complex with tea polyphenol. The obtained results show a possible use of the tea secondary products presenting metal corrosion at industrial scale, as in acid pickling, cleaning, and descaling etc.

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