Use of Different Natural Extracts from Tropical Plants as Green Inhibitors for Metals

Walter Bogaerts, V.T. Thuy, Rauf Addul*, and Pham Hong Phong**

*University of Leuven (K.U.Leuven), Electrochemistry & Corrosion Engineering Lab.
Kasteelpark Arenberg 44, B-3001 Leuven, Belgium, walter.bogaerts@mtm.kuleuven.be, thuy.vuthi@mtm.kuleuven.be

**Vietnamese Academy of Science & Technology (VAST)
18 Hoang Quoc Viet, Cau Giay, Hanoi Vietnam.

ABSTRACT

The authors present an overview of the work & results obtained in the framework of a bilateral cooperation program between Belgium and Vietnam to discover new environmentally-friendly *corrosion inhibitors* or *"harmless corrosion inhibitors to nature"* based on components from naturally-occurring tropical plants. A few hundreds of tests/experiments of a dozen selected tropical plant-extracts as corrosion inhibitors have been performed employing electrochemical impedance spectroscopy (EIS), potentiostatic and potentiodynamic polarization techniques. The efficiency of these extracts, i.e. slow down or reduce corrosion of a metal/alloy when added to a given environment with different concentrations is presented and some of the most recent results are illustrated.

Keywords: green inhibitors, harmless environment, tropical plant-extracts, corrosion, metal

1 INTRODUCTION

The desire to reduce corrosion problems is a prime strategic objective for industry. Since decades ago man has succeeded in modifying the environments among other methods through the injection of substances that can reduce the rate of corrosion. These substances are generally called inhibitors[1-2]. They function through adsorption on metal surfaces to form an invisibly thin film, giving the surface a certain level of protection or a protective layer. The interest to use some tropical plant extracts[4], as inhibitor came to our minds after the fact that several countries have already introduced restrictions on the use of some of the most harmful heavy metal compounds & biocides and more strict regulations on their use are under completion both at the EU- and international level. We, in the framework of the "*Green Inhibitors*" project -a Belgian-Vietnamese joint research programme, want to examine and explore possibly the efficiency of 10 to 20 tropical plant extracts[4] as *corrosion inhibitors* for a metal/alloy in different environments. In addition to being environmentally friendly and ecologically acceptable, plant products are low-cost, readily available and renewable sources of materials.

2 OVERVIEW & TECHNIQUES

As result of Literature Data Search, a "long list" of 200 tropical plants was collected from which a "short-list" of more than 20 extracts was defined/screened as potential inhibitive candidates. Totally over 600 tests using 10 extracts such as Rhizophora, Glycine, Camellia sinesis, Nicotiana, Mimosa etc. on standardized metal surfaces (AISI 304, carbon steel, Brass), in static lab set-ups were performed, measured and evaluated at KULeuven lab in different environments (acidic, alkaline and saline) at room & heated temperature, at short-/long-term times. At this moment 2 more extracts (Artemicia, Ginger) are being tested in which the surface of metals/alloys is also being investigated using X-ray photoelectron spectroscopy (XPS) and scanning electron microscope (SEM).

2.1 Experimental/Materials

Experiments were performed on AISI 304 sheets having sickness of 1mm (with composition of 0.08% C; 19% Cr; 9.5 % Ni), Carbon Steel sheets of 3mm sickness (0.2% carbon; 0.045% phosphorous; 0.045% Sulfur) and Brass sheets of 3mm thickness (63% Cu; 35% Zn; 1% Pb).

All chemicals and reagents used were of analytical grade. The blank corrodents were, respectively, 1-5% HCl, 1-5% H_2SO_4, 1-5%NaOH and 3.5%NaCl solutions. Stock solutions of the plant extract were prepared by boiling weighed amounts of the dried & ground plant material or extracts were diluted in distilled water (Fig. 1) at 40–50^{o}C, with the concentration range from 0.5 g/L to 10gL.

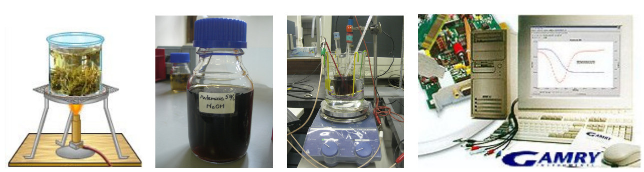


Figure 1: (Left to right) boiling plant, diluted extract, electrochemical measurement and Gamry CMS 100.

A three-electrodes with a conventional cell used for electrochemical methods consisting of linear polarization resistance (PR), electrochemical impedance spectroscopy

(EIS), electrochemical frequency modulation (EFM) and cyclic polarization (CP) were employed using potentiostat CMS 100. Potentiodynamic polarization curves were produced using the ACM AutoTafel software. A scan rate of 0.25 *mV*/s at potential range of ± 0.01 *V* vs. *Eoc*. EIS spectra were recorded in a wide frequency range of 5000 – 0.01 Hz with 10 points/decade using a logarithmic scale. A10 *mV*/ms amplitude was applied. CP curves were recorded at initial and final potential of -0.05 Vvs. *Eoc* with scan rate of 0.25 *mV*/s, and apex current was 3 *mA*/cm2.

2.2 Inhibitive Experiments & Efficiency

Experiments were conducted in acidic, alkaline and saline solutions *with/without* inhibitors at the concentration of 1-5% H2SO4, 1-5% NaOH, 1-3,5% NaCl (similar to seawater which encourages pitting of the substrates, due to the chloride ion) at room temperature and 50°C. After 30-60-90 days, the samples were visually inspected (zoom 4 to 40 times) and taken photographs to compare the rate of corrosion which was calculated from the weigh loss mills/year (mpy) as in Equation 1:

$$\underset{(\text{mpy})}{\text{Corrosion rate}} = \frac{\text{Weight lost (g)} * 3.45 \times 10^6}{\text{Alloydensity(g/cm}^3) * \text{Exposed area (cm}^2) * \text{Exposure time(hr)}}$$

Equation 1: Coupon evaluation after exposure.

The characterization of the free corrosion of metals/alloys in the different inhibitor/corrodent solutions was carried out by an assessment of the degree of surface coverage (θ) of the metal surface[3] by the inhibitor as well as the inhibition efficiency (*I%*) as follows (Equation 2):

$$\theta = 1 - \frac{\rho_{\text{inh}}}{\rho_{\text{blank}}} \qquad I\% = \left(1 - \frac{\rho_{\text{inh}}}{\rho_{\text{blank}}}\right) \times 100$$

Equation 2: Calculation of Plant Inhibition efficiency.

where ρ_{inh} and ρ_{blank} correspond to the corrosion rates in the presence and absence of inhibitor, respectively.

Lab Chemical inhibitors were 0.1% NaNO2; 0.1% C6H16N2; 0.1% Na3PO4.12.H2O.

2.3 Corrosion - Inhibitors & Toxicity

Corrosion of metals[5] leads not only to the loose of metals but it is often the case of ecological catastrophes which occur due to the destruction of metal constructions. It can be inhibited/reduced by certain types of chemicals. There is an increasing concern about its toxicity which affects not only living organisms but also poisons the earth. Therefore, it is necessary to discover new inhibitors which decrease metals corrosion rate and are not harmful for environmental situation. The latest results using "ecologically friendly" natural substances as inhibitor for metals are presented in this paper, earlier ones have been introduced elsewhere[5] by the present authors.

2.4 Tropical Plants as Materials Sources for New eco-friendly Protection Agents

These plants are very popular, available, daily used in Tropical countries as in Vietnam, China, Thailand… and cheap, easy to extract, and their chemical components[4] are rich enough to offer the ability to inhibit corrosion. The Tobacco is a virtual chemical factory with over 4,000 compounds being reported many of which inhibit metallic corrosion. In particular, tobacco extracts inhibit the galvanic corrosion of steel when coupled to copper in a sodium chloride solution, a solution known to rapidly corrode iron and steel. Green Tea contains high concentration of alkaloids, fatty acids and nitrogen-containing compounds. Glycine is primarily grown for oil production. However, technical uses of Glycine include anti-corrosion agents, disinfectants, dust control agents, epoxies and paints, printing inks, adhesives, particle board, plastics and polyesters, etc. Glycine provides excellent lubricity agents which function by displacing moisture from the surface of the metal. Rhizophora is well-known as a rich source of tannins, its bark contains about 1%-30% tannins. Anacardium Occidentale liquid is chiefly used in the preparation of synthetic resins. In addition to its main application in brake lining of motor vehicles, it is used for manufacturing heat and waterproof paints, corrosion-resistant varnishes, insulating enamels and different types of surface coatings. Mimosa contains alkaloid, its roots contain 10% tannin.

Figure 2: Inhibitive Plants (left to right): Green Tea, Tobacco, Rizophora, Mimosa

3 RESULTS AND ILLUSTRATION

3.1 Corrosion measurement methods

Corrosion measurement involves the application of various techniques to determine the corrosiveness of the environment and the rate of metal loss. After 2 years doing research, the results (corrosion rates and inhibitive effects) obtained are corroborated by different methods including PR (see Fig 3), weight loss measurement (see Table 1), EIS (Fig 4), potentiostatic polarization and impedance spectroscopy (Fig 5). Typical hydrogen evolution data for uninhibited and inhibited Carbon steel in 1% H_2SO_4 containing Rhizophora/Glycine extract at different concentrations (0g/L, 0.5g/L, 1.0g/L, 5g/L) is illustrated in Figure 4-5 and AISI 304, respectively in 3,5% NaCl containing Glycine extract (Fig 6).

Curves (Fig 3) displays the dependence of E_{oc} and I_{cor} for Carbon Steel with different Rhizophora concentrations in 1% H_2SO_4 solution at room temperature and 50°C respectively. Figures show an increase in *Eoc* with increasing the concentration of Rhizophora, meanwhile I_{cor} slightly decreases. These evidences prove that Rhizophora reduced corrosion of Carbon Steel in 1% H_2SO_4 solution.

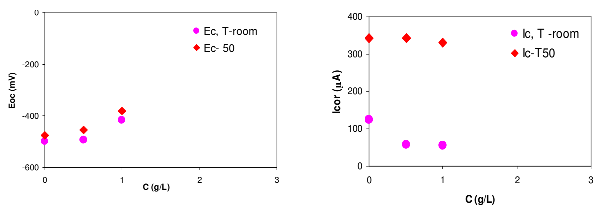


Figure 3: Variations of E_{oc} and I_{cor} values with Rizophora concentrations at T = room (●) and 50 °C (♦)

	Corrosion Rate mpy - After 1 mon		**Corrosion Rate** mpy - After 3 mons	
Solutions	**No-Extract**	**With Extract**	**No-Extract**	**With Extract**
3.5% NaCl	0.73	0.41	0.87	0.76
5% H2SO4	80.56	69.14	30.87	21.33
1% H2SO4	17.06	11.19	5.88	4.95

Table 1: Coupon evaluation of Carbon Steel in the presence and absence of Rhizophora Extract at room temperature.

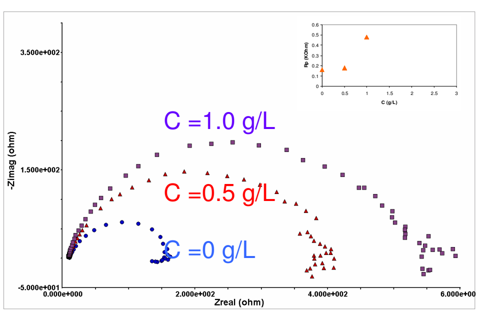


Figure 4: Nyquist plots for Carbon Steel in 1% H_2SO_4, with different Rhizophora concentrations, at T=room

The plots are characteristic semicircles which are of capacitive type whose size increases with increasing Rhizophora concentration. This is also consistent with the result obtained by R_p measurement as graphic shown in the inset on the right corner.

Potentiodynamic polarization curves for Carbon Steel in 1% H_2SO_4 solution in the presence/absence of Glycine extract at 50°C are recorded in Fig 5. As shown, the presence & increased amount of Glycine extract affect the corrosion potential: how higher in extract concentration, how more curve-shift to the positive potential direction or corrosion rates in the presence of the extract are markedly reduced, again indicating a corrosion inhibiting effect.

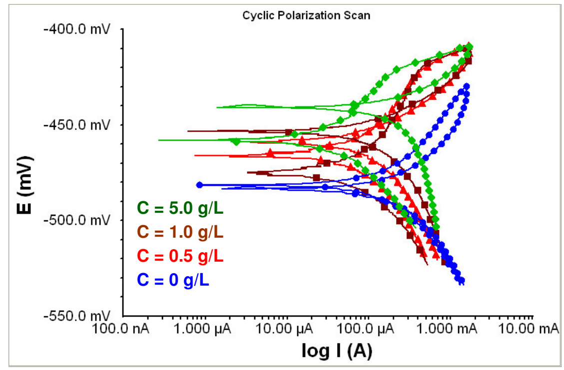


Figure 5: Potentiodynamic polarization curves for Carbon Steel in 1% H_2SO_4 solution in the absence and presence of Glycine extract with different concentrations, at 50°C.

Nyquist plots below show the increase in size of curves with increasing extract concentrations, suggesting that the inhibiting action was concentration dependent.

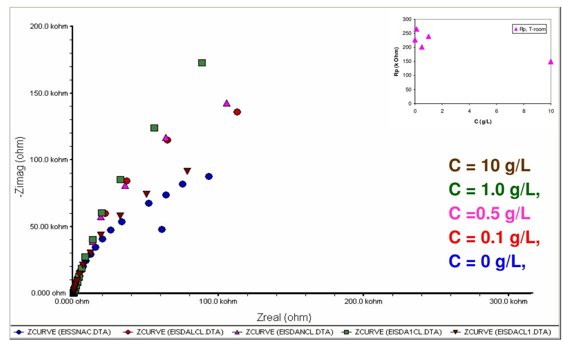
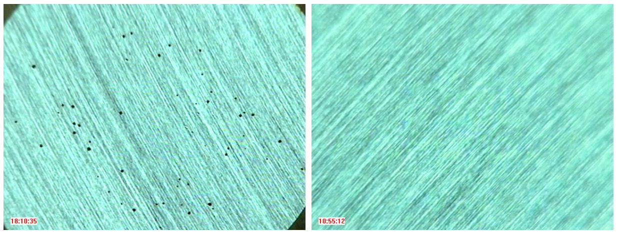


Figure 6: Nyquist plots for AISI304 in 3.5% NaCl *with/without* Glycine at different concentrations, T= room.

The obtained results indicate that these plant materials retard Carbon Steel, AISI 304 dissolution in the examined media by adsorption of the active components on the metal surface and efficiency of inhibition generally increased with concentration. In accounting for the observed protective effect, it should be noted that the extracts comprise a mixture of organic and resinous matter some of which are known to exhibit good corrosion inhibiting abilities. Their complex chemical compositions make it rather difficult to assign the inhibiting action to a particular/group of constituent(s). Nevertheless, the net adsorption of the extract organic matter on the metal surface creates a barrier to charge and mass transfer, thus protecting the metal surface from corrodent attack. The degree of protection varies for the different extracts/qualification, but generally increased with an increase in extract concentration due to higher degree of surface coverage resulting from enhanced adsorption of the extract organic matter

3.2 Illustrations &Comparison

Results (Fig 7) reveal that Rhizophora reduced corrosion of AISI 304, Carbon steel in studied solutions.



AISI ***without*** Rhizophora — A lot of pits are seen | *with* 0,5g/l Rhizophora — Almost no pit …

Figure 7: AISI 304 in 5%NaOH, after 30 days at 50°C.

Photos (Fig 8) indicate that plant materials retard Brass dissolution in the examined media by adsorption of the active components on the metal surface differently with different qualified inhibitors. The Chinese Green Tea was more inhibitive than the Vietnamese due to the facts that it consists of only buds and leaves, while the Vietnamese one of also stems and twigs, dust.

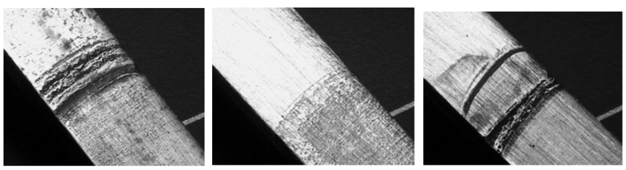


Figure 8: Brass in 1% H_2SO_4, 90days, T°C=Room. Photos (Left to right): w*ithout* inhibitor, *with* dried Chinese Green Tea, w*ith* dried Vietnamese Green Tea

Tobacco shows a very good inhibition behavior to Carbon Steel, Brass and Stainless Steel. Fig 9 compares Carbon Steel in 1% NaCl, at 50°C, after 90 days, *without* inhibitor (Upper) the metal was corroded, *with* chemical inhibitor (0.1% $NaNO_2$) partly corroded (Mid photo) and *with* Tobacco -almost no corrosion happened (Bottom).

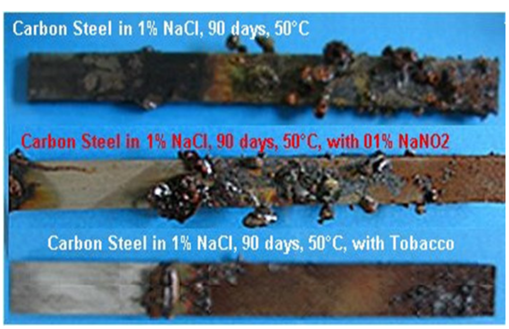


Figure 9: Carbon Steel *with/without* Tobacco

Data recorded of AISI 304, Carbon Steel and Brass (Table 2) is obvious that the plant compounds, Green Tea & Tobacco, display a remarkable protective ability in the examined media, even better than the lab inhibitor, mean while Mimosa could not protect Carbon Steel as good as other natural inhibitors, but Mimosa is *the best* inhibitive candidate for Carbon steel in *saline* solution (Fig 10)

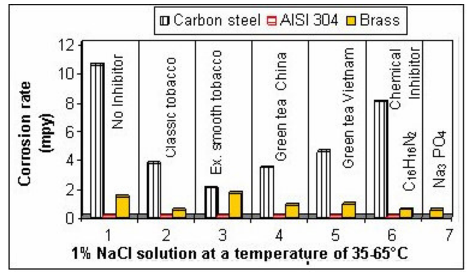
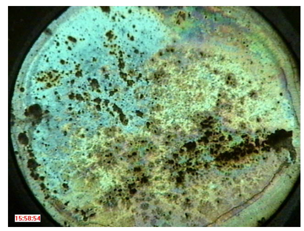
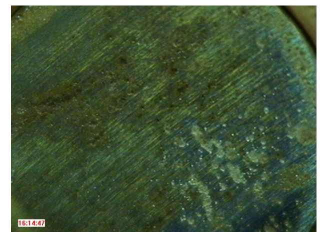


Table 2: Plant compounds retard corrosion rates in 1%NaCl solution, at 35-65°C.



Carbon Steel, 30 days, in 3,5% NaCl: heavily corroded, many pits…



Carbon Steel *with* Mimosa, 30 days, T=room, a few pits are seen….

Figure 10: Carbon Steel in 3.5%NaCl *without/with* Mimosa.

CONCLUSIONS

The inhibitive effects of Rhizophora, Glycine, Green Tea, Tobacco and Mimosa are not consistent. They appear to have inhibitive effects only for some selected metals. Though different extract concentrations and qualities showed different inhibitive effects on metals; generally these studied extracts have delivered very good inhibitive results in comparison with the chemical inhibitors. The corrosion process was inhibited by adsorption of the extract organic matter on the metal surface. Further investigation is required to assess the surface XPS analysis and ascertain the active species in the adsorption layer.

REFERENCES

[1] RL Martin, B.A. Alink, T.G. Braga, A.J. McMahon, R. Weare, "Environmentally acceptable water soluble corrosion inhibitors", Corrosion 95, Paper No.36, NACE, 1995.

[2] D J.I. Bregman, "Corrosion Inhibitors", Collier MacMillan Co., London (1963).

[3] Emeka E. Oguzie, "Evaluation of the inhibitive effect of some plant extracts on the acid corrosion of mild steel" Corrosion Science, Volume 50, Issue 11, November 2008

[4] BGCI Fact Sheet. 'Plants as medicine'. Botanic Gardens Conservation International/ British Airways/ International Centre for Conservation Education.

[5] L. Shreir (1976) "Corrosion and Corrosion Control", Vols 1-2, 2nd Edition, Butterworth, London.