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CHALLENGES IN CORROSION PROTECTION USING VEGETABLE EXTRACTS AS INHIBITORS - ELECTROCHEMICAL STUDIES

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ABSTRACT

Corrosion is an irreversible chemical or electrochemical reaction of a material with its surrounding environment or medium which results in consumption of the material or in dissolution into the material of a component of the environment. Corrosion can provoke severe and expensive destructions in any field of activity from transportation, home appliances, water and gas alimentary systems, energy production systems, chemistry, metallurgy, semi-finished production, bridges and public buildings, etc. The main important reasons of corrosion phenomena study are: economics, safety and conservation. The economic point of view includes the cost of material losses resulting from the above activity fields and may involve piping, tanks, ships, hulls, marine structures, etc. The corrosion costs also include the losses of energy and water reserves accompanying the production of metals and the need for expensive replacements for the corroded ones. Unexpected failures of equipment and devices because of weakening of structures induced by corrosion may reduce the safety criterion, which in the design of equipment for nuclear power plants and for disposal of nuclear wastes is critical. The effects of corrosion on the safe, reliable and efficient operation of equipment or structures are often more serious than the simple loss of a mass of metal. Finally, the third important consideration for which the corrosion phenomena must be studied is conservation of mineral and metal resources, whose world supply is limited. Several techniques have been applied to protect metallic structures against corrosion. One of the most important methods in that regard is the use of corrosion inhibitors. A corrosion inhibitor is a chemical substance that, when added in small concentration to an environment effectively prevents or decreases the corrosion rate. Inhibitors slow down the corrosion process by: increasing the anodic or cathodic polarization behavior, reducing the movement or diffusion of ions to the metallic surface and increasing the electrical resistance to the metallic surface. The paper presents some experimental results with vegetable extracts acting as corrosion inhibitors for carbon steel and copper in acidic and neutral environments.

KEYWORDS: corrosion, corrosion protection, green inhibitor, electrochemical methods, eco-friendly pickling process

1. Introduction

Technical and economic aspects of corrosion: Corrosion is one of the main causes of the accelerated degradation of metal constructions, a destructive process which tales place by modifying the surface geometry, through structural and chemical transformations of a metal material [1]. Corrosion phenomena occurr in various aspects and in various environments: in air, water, soil, industrial plants [2].

For the contemporary world economy, corrosion has become one of the acute problems to face. The high development rate of the modern industry involves high consumption of construction materials, among which the most important are ferrous metals and alloys; on the other hand, the crisis of raw materials occurring nowadays makes it imperative the restriction of metals use, their reasonable use, their saving.

Corrosion phenomena are significantly present not only in industry but also in other economic sectors and even in everyday life, especially under current pollution. The negative economic consequences of corrosion are briefly called ***corrosion cost***.

Apart from the losses of metal as such permanently unrecoverable, corrosion causes frequent interventions to ensure uninterrupted operation, for repairing or replacing parts or machinery along with production losses caused by these interventions.

The negative economic consequences of corrosion are briefly called ***corrosion cost***.

Estimation of the corrosion cost assumes clear and systematic records of both expenses and incurred losses caused by the corrosive degradation of the metal constructions.

Although in recent years there has been a high development of the protection methods such as the use of coatings, however, the rapidly developing method over the past 20 years has been the method of corrosion protection by means of inhibitors extending the area of application fields and the technical and variety of the products used. This method, in addition to being the most adequate method of protection of the plants in operation, has other advantages as well: simplicity of the solution in terms of its practical application (installations do not raise technical, maintaining or operating difficulty issues); it provides uniform protection of the whole surface in contact with the inhibitor; economy due to lower consumption of metallic materials, because in most cases use is made of conventional steel alloys, carbon steels, that are cheap, affordable and easy to process, etc.

To illustrate the advantage of the simplicity of the corrosion inhibitor treatment facilities on drilling and extraction equipment it should be noted that these inhibitors can be relatively easily introduced into wells (including old ones) and can get to any place on metal surfaces exposed to aggressive fluids, including depth machinery.

On the definition of corrosion inhibitors, experts in the field are unanimous that these are chemicals which added to the aggressive (corrosive) environment slow or stop the corrosion processes. The corrosion inhibitors are used in small amounts, calculated to the aggressive environment, namely at a concentration of 0.005 to 0.5%, which economically justifies the adoption of the solution of the corrosion protection of metallic materials by using corrosion inhibitors. Therefore, the corrosion inhibitors can not be mistaken for agents of stoichiometric deactivation of the corrosive environment, as a result of neutralization reaction, oxygen blocking, etc. although they finally have a positive effect on the protection of materials. It is obvious that in the latter case, consumption of chemicals is very high (maximum) as imposed by the chemical reaction that occurs to disable the aggressive agent.

Corrosion inhibitors act on a variety of metals but especially on alloys of iron and zinc, which are frequently used as materials in machinery manufacturing and industrial installations in recent years due to the development of metallurgy alloys of Cr, Ni Mo as imposed by certain conditions of temperature and environments under specific technological processes; as a result of all these, the issue of corrosion protection in the case of these types of alloys became necessary. It is obvious that in such conditions, the problems of the mechanism of inhibitors action and their types are different from the case of protection of carbon steel alloys.

With respect to aggressive environments the most often encountered in industrial practice to be inhibited are hydrochloric acid, sulfuric acid, nitric acid, hydrofluoric acid, citric acid, sulfanilic acid, or mixtures of them in various concentrations.

In the attempt to find the eco friendly corrosion inhibitors, there is a growing trend to use natural products such as plants, spices, vegetable peels, seeds etc, as corrosion inhibitors. This is because these natural products serve as a rich source of naturally synthesized chemical compounds which are environmentally acceptable, inexpensive, readily available and renewable sources of materials [5-11].

The objectives of this work are the followings: laboratory experiments to assess the effectiveness of the inhibitor Usinhib (from a vegetal extract) in a hydrochloric acid environment by electrochemical methods and Vegetal inhibitor efficiency calculation. The results will asses a **new eco-friendly anti-corrosion inhibitor.**

Electrochemical testing of inhibitors shows a major advantage, namely, short time of measurement while providing vital information on the mechanism of inhibition. Corrosion rate can be measured in minutes, while the weight loss methods can take days. Inhibitors protect by changing anode or cathode reactions thus forming a barrier between the metal and the electrolyte or a combination of both.

Corrosion inhibitors in acidic media are important in the pickling of metals covered with oxides. During pickling operations, oxide layers, thinner and slightly soluble, are removed before the thicker and poorly soluble layers. Consequently, part of the base metal is attacked before the pickling operations are completed. In order to reduce attack by acids, special adsorption organic inhibitors are used. Because the majority of organic compounds are toxic nowadays, the obtaining and testing of vegetal extract were approached in the work (USINHIB) as a green inhibitor.

2. Experimental procedures

2.1. Materials and methods

The tested material selected for study is mild steel, whose composition (wt.%) was 0.16 C, 0.53 Mn, 0.30 Si, <0.045 P, <0.055 S, and Fe balance.

The test solution was 0.5 M Hydrochloric acid (HCl) considering the importance of pickling of steel foils in this media.

The mild steel samples with a rectangular shape of 50 mm x 20 mm x 1.5 mm were connected with a protected copper fill in order to be used as working electrode in an electrochemical cell. Prior to the measurements, the samples were degreased ultrasonically in ethanol and acetone, and dried at room temperature. Insulation resin was used to separate well the active surface area.

As inhibitor it was used a vegetable extract called USINHIB in different concentration.

The electrochemical cell used is formed by: double-walled glass vessel to maintain a constant temperature, electrode connection system to the electrochemical equipment, the working electrode (WE), which is always the sample being analyzed, reference electrode against which all potentials (RE) are measured. The RE used was Ag/AgCl (saturated KCl) that has the stable potential value of +199 mV against normal hydrogen electrode (NHE).As auxiliary electrode (CE) it was used a platinum-rhodium mesh. Auxiliary electrode or counter - electrode should be inert in relation with the tested solution. The electrochemical measurements applied were: Free potential E (t), time variation of the electrode potential (WE) in open circuit, determination of the polarization resistance, Rp, and corrosion rate by linear polarization around OCP with ± 50 mV and potentiodynamic polarization curves with a potential sweep rate of 5 mV/sec.

3. Results and Discussion

3.1. Free potential (Open circuit potential – OCP)

When an electrically conductive material is immersed in an electrolyte, there is a potential difference E or U – at the **solution material interface** called **electrode potential**. This is not directly measurable; we only know how to measure the potential difference across an electrochemical cell formed by a complete electrochemical chain. If the electrode inserted to form the chain is well-defined and stable in time, it is a **reference** and it is then possible to compare different electrodes between them in relation to the adopted electrode reference [3]. **Analysis of the potential versus time** is useful information to track the **behavior of a material in contact with a wet corrosive environment**. Physico-chemical reactions present on the material surface change the solid-solution interface, which explains the evolution of the potential. This can be ensured by means of an acquisition device (interface millivoltmeter and micro computer) or simply by registering on a tracking board connected to the output which records an electronic millivoltmeter.

Figure 1 presents the evolution of the free potential (OCP) of mild steel since its immersion in the solution and monitored for 30 minutes, without inhibitor (blue curve) and with inhibitor (red curve).

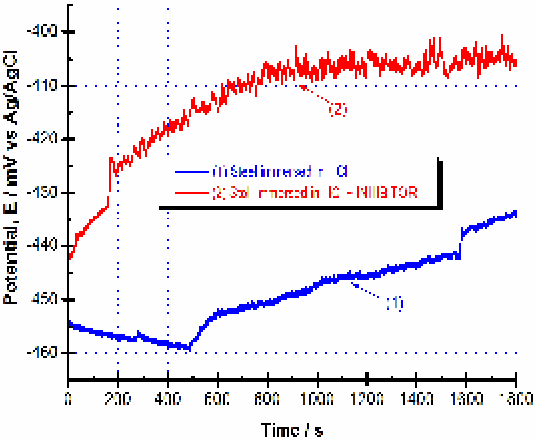


Fig. 1. *Open circuit evolution of steel immersed in 0.5 M HCl without and with inhibitor*

From Figure 1 it is observed that the open circuit potential of mild steel is shifted to more noble values in the presence of inhibitor. This means a more corrosion resistance of steel in HCl with inhibitor as compared to the behavior of steel immersed in HCl without inhibitor.

3.2. Measuring the polarization resistance (Rp) values during immersion time

Determination of polarization resistance (Rp) was performed by the method of linear polarization around the free potential with a very small potential difference (50 mV) to preserve the stady state balance of the surface relative to the solution. The results obtained after 1 hour without inhibitor and with inhibitor respectively are shown in Figure 2.

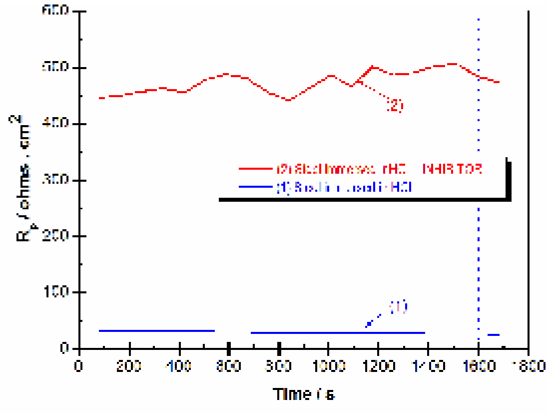


Fig. 2. *Evolution of polarization resistance values of mild steel immersed in HCl solution without inhibitor and in the presence of added vegetable inhibitor*

For simple corrosion systems, the corrosion reactions are strictly controlled by the charge transfer resistance and the corrosion current density, i_{cor} can be correlated with the polarization resistance R_p, by the relation [1], which represents the Equation Stern - Geary for the evaluation of the corrosion resistance:

$$i_{cor} = \frac{B}{R_p} \qquad (1)$$

The corrosion rate in this case is expressed in A/cm^2.

B is a constant specific to the material – environment system given by Equation [2]:

$$B = \frac{b_a |b_c|}{2.303(b_a + b_c)} \qquad (2)$$

Where: b_a and b_c are the Tafel slopes for anodic and respectively cathodic corrosion reactions. Increasing the polarization resistance means lower corrosion current density and thus lower rate of corrosion.

From Figure 2 it is observed that the polarization resistance value of steel immersed in HCl with vegetable inhibitor is about 10 times higher as compared to the value obtained for immersion in HCl without any inhibitor proving the increasing of corrosion resistance of steel 10 times compared to the behavior resulted from HCl solution without inhibitor.

Figure 3 illustrates the evolution of corrosion rate in time, corresponding to the polarization resistance in Figure 2, calculated as thickness loss.

Increasing polarization resistance in the hydrochloric acid with green inhibitor (Figure 2) means the lowering of the corrosion current density and hence lower corrosion rate (the loss of thickness), Figure 3.

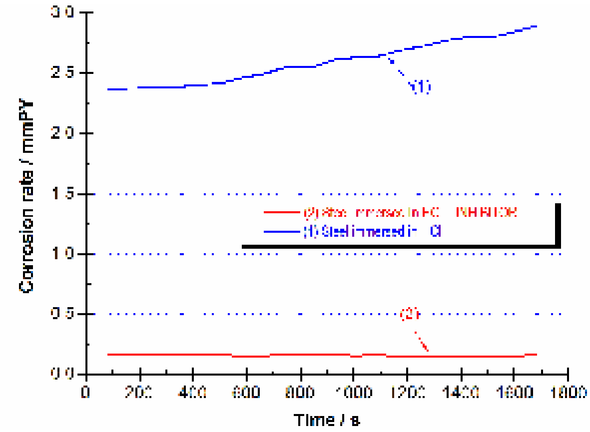


Fig. 3. *Evolution of corrosion rate values of mild steel immersed in HCl solution without inhibitor and in the presence of added vegetable inhibitor*

The steel immersed in HCl solution without inhibitor shows a corrosion rate at about 10 times higher compared to the corrosion rate of steel immersed in HCl solution in the presence of vegetable inhibitor.

3.3. Potentiodynamic polarization curves (PD)

Diagrams i = f (E) (intensity-potential curves) drawn in a wide range of cathodic potential to anodic potential with a constant scanning sweep of 5 mV/s allow us to make some predictions on the material and the environment as it is shown in Figure 4 (a, b).

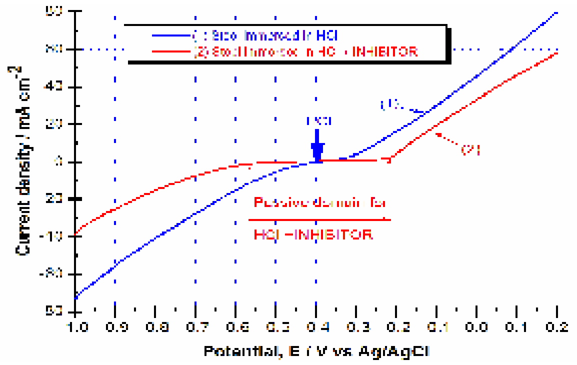


Fig. 4 (a). *Potentyodynamic diagrams for mild steel in HCl solution with and without inhibitor obtained at a scan rate of 5 mV/s for the entire potential domain (-1000 mV vs Ag/AgCl to + 200 mV vs Ag/ AgCl)*

In Figure 4 three distinct potential domains are shown as follow:

► Cathodic domain: the passive film is destroyed by hydrogen reduction reaction.

► The passive domain where the passive film is formed by oxidation or adsorbtion of inhibitor. The width of this field depends always on the material studied and the corrosive environment.

► Domain of trans-passivation where the passive film is dissolved and damaged.

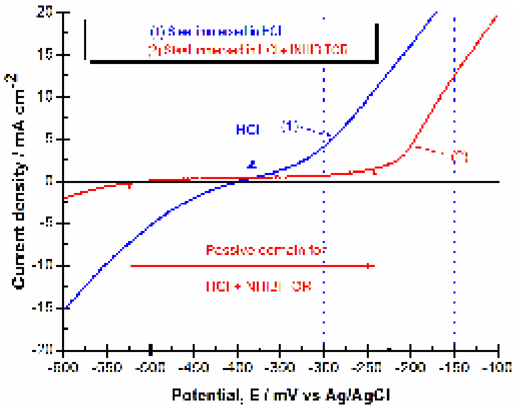


Fig. 4 (b). *Potentyodynamic diagrams for mild steel immersed in HCl solution with and without inhibitor obtained at a scan rate of 5 mV/s - zoom of diagrams from Fig. 4(a) in the passive domain of potentials*

The diagrams in Figure 4 show the different domains with the corresponding current densities and potentials. The status of "*cathodic*" is followed by those of "*passivity*" (stable domain) and "*transpassivity*". The potential domain for the passive state is indicated on specific diagrams with the passivation current density i_p. In the range of transpassivity, where the potential (E) becomes bigger than the passive potential (E_p), ($E>E_p$), the current density increases, since this is transpassive dissolution. In this domain the passive film loses its protective properties and even disappears at higher potentials [3].

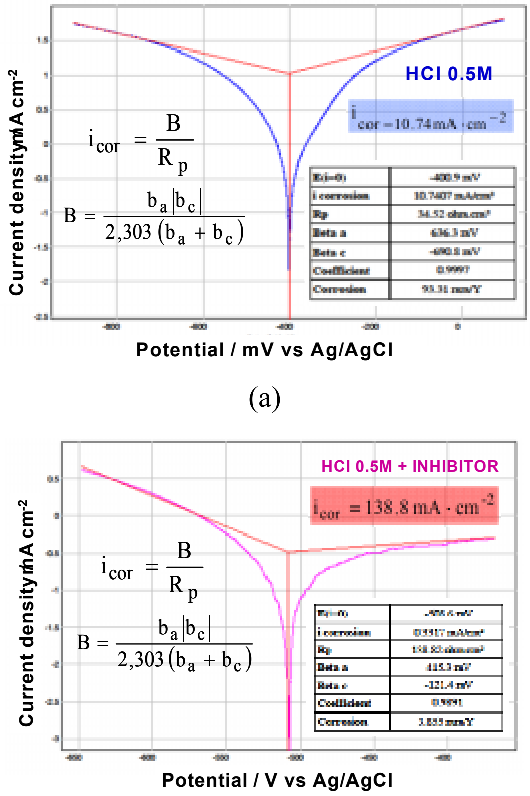
It is illustrated from the data plotted in the diagrams in Figure 4 (a,b) that both anodic metal dissolution of iron and cathodic hydrogen evolution reaction were inhibited after the addition of green inhibitor Usinhib to 0.5 M HCl solution. The inhibition of these reactions has the effect of lowering the corrosion process.

From a practical point of view, the relative width of each potential domain and the associated values depend directly on the material/environment system. The same material, the carbon steel in this study, behaves differently in the solutions of hydrochloric acid with and without inhibitor.

In the presence of vegetable extract as inhibitor the passive domain of steel is enlarged (red curve in Figure 4). By increasing the passive domain of mild steel indicating that the adsorption of vegetable extract on mild steel surface is consistent with the mechanism of physical adsorption and therefore acting as a passive film on the steel surface.

Corrosion inhibition is caused by the stabilization of the surface film formed on steel. The effect of chemically stable surface active inhibitors increases the energy of activation of iron dissolution reaction and leads to diminution of surface available for corrosion [12].

Calculation of the Tafel slopes and the corrosion current densities (as corrosion rates) from polarization potentiodynamic curves are presented in Figure 5 (a) for mild steel immersed in hydrochloric acid without inhibitor and Figure 5 (b) for mild steel immersed in hydrochloric acid with green inhibitor.



(a)

(b)

Fig. 5. *Application of Stern methods to evaluate the polarization resistance of carbon steel immersed in hydrochloric acid with and without green inhibitor: (a) the polarization resistance and corrosion rate of steel in HCl without vegetable inhibitor; (b) the polarization resistance and corrosion rate of steel in HCl with vegetable inhibitor*

As it is shown in Figure 5 (a, b) there is a good agreement between the values of corrosion rate and polarization resistance evaluated by the two methods like measurements of polarization resistance by linear polarization with a small amplitude around the free potential (Figures 2 and 3) and the last one by applying the Stern method and Tafel slopes.

3.4. Evaluation of Inhibitor’s efficiency

When expressing the corrosion rate in terms of current density relative to the surface area, the efficiency of the inhibitor can be expressed as follows:

$$\text{Inhibitorefficiency} = \frac{(i_0 - i_i)}{i_0} x100\% \qquad (3)$$

where: i_0 = corrosion current density in HCl 0.5M without inhibitor; i_i = corrosion current density in HCl 0.5M with inhibitor.

The result of inhibitor efficiency is about 97.2%, concluding that this vegetable extract as a green inhibitor could be utilised in the industrial applications for piclink of carbon steel in hydrocloric acid reducing in this way the material loss by dissolution during the technological process.

4. Conclusions

Using the green inhibitors from plant extracts as USINHIB in hydrochloric acid pickling operations of steel will have the following advantages:

- environmentally friendly, therefore pollution reduction.
- non-toxic, reducing the risk of manipulation.
- the process reduces the acid consumption by breaking the metal dissolution reaction, and also due to decreasing the process of carrying away the solution of H_2 gas evolved in the cathodic reaction of the corrosion process.
- it avoids the surface darkening due to the accumulation of fine particles of coal remaining after dissolution of iron in the case of carbon steel pickling.
- it prevents metal embitterment with H_2 of the metal being pickled, having serious consequences for its subsequent mechanical strength.
- the inhibitor reduces the rate of anodic dissolution of steel and reduces the rate of the corresponding cathodic reactions, with overall effect of slowing the corrosion process.
- by enlarging the potential domain of the passivation resulted from potentiodynamic polarization curves, it is clear that the green inhibitor USINHIB from vegetable extract is adsorbed on the steel surface to form further a protective layer.

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