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Corrosion Inhibition of Steel for Water Pipe Line by Adding a Non-Toxic Spearmint Extracts*

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Purpose: To investigate the corrosion inhibition effect of the natural spearmint oil extracted from Mentha Spicata plants on 304 stainless steel in different concentrations of hydrochloric acid.
Method: The anti-corrosive effect has been investigated in 0.5m, 1m and 2m HCl using weight loss test and electrochemical polarization method as a function of inhibitor concentration and immersion time in strong chloride environment. The surface morphology was analysed by scanning electron microscopy (SEM).
Results: The corrosion rate of steel decreased and inhibition efficiency increased with the increase in inhibitor concentration. Microscopic evaluation revealed significant corrosion in the specimens immersed in uninhibited conditions. Potentiodynamic polarization test results showed an increase in corrosion potential (Ecorr) and decrease in corrosion current (icorr) value with increasing concentration of inhibitor.
Conclusions: Immersion of steel in higher concentration of inhibitor resulted in greater surface coverage value and hence lesser number of surface corrosion sites/pores were formed; thus lowering the corrosion rate.

Keywords: Inhibition, Spearmint Oil, Corrosion Life, Reliability

1. Introduction

Stainless steels have been widely used for engineering and structural applications due to their high corrosion resistance and strength. The high corrosion resistance arises from the formation of a passive layer on their surface. However, the corrosion resistance of passivated stainless steel is often limited by its susceptibility to local breakdown and pit. Aggressive ions such as chloride ions produce local breakdown of the protective layers formed at the solid-solution interface, causing pitting corrosion [1].

Among the various methods to avoid and prevent destruction or degradation of metal surface, the corrosion inhibition is one of the best known methods for corrosion protection [2]. Inhibitors are substances or mixtures that prevent or minimize the corrosion in aggressive corrosive environment [3]. Organic inhibitors are used in the industrial processes to control the metal corrosion as

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well as dissolution. Inorganic compounds like chromates, phosphates, molybdates, etc. and a variety of organic compounds containing heteroatom like nitrogen, sulphur and oxygen have been investigated as corrosion inhibitors [4]. Efforts to stop or delay the corrosion attacks using synthetic inhibitors have been made from last couple of decades and proved to be very effective for corrosion inhibition. However, the applications of these inhibitors proved to be hazardous to the environment and also are very toxic for aquatic species and animal life [5].

To overcome these problems, researchers are struggling hard to find out the corrosion solutions using eco-friendly green inhibitors such as natural oils and plant extracts. V. Maria studied the effect of corrosion inhibition of mild steel using pectin-which is an ecofriendly inhibitor and found that the corrosion rate of mild steel decreased significantly with the addition of pectin in HCl solution. Moreover, it acted as a mixed-type inhibitor retarding both the hydrogen evolution and oxidation reactions by formation of a complex between pectin and Fe^{2+} ions released during the corrosion reaction [6]. Nasrin Sultani studied the corrosion inhibition characteristics of Salvia Officinalis leaves extract on 304 stainless steel and revealed that it act as a mixed-type inhibitor and reduce the overall corrosion rate significantly. The inhibition action was performed via adsorption of extract compounds onto the stainless steel surface [7]. Hazwan Hussin and Jain Kassim studied the inhibitive effect of extract on the acid corrosion of mild steel in 1m HCl solution [8]. Okafor studied the inhibitive action of leaves, seeds and a combination of leaves and seeds extract of on mild steel corrosion in HCl and H2SO4 solutions [9]. Corrosion inhibition effect of justicia gendarussa extract on mild steel in 1M HCl medium was also studied and inhibition efficiency up to 93% was achieved with 150 mg L^{-1} justicia gendarussa extract at 298K [10].

The objective of this paper is to study the anticorrosive effect of green-environment friendly organic spearmint oil extracted from Mentha Spicata plant on 304 stainless and to investigate the effect of acid concentration on the overall inhibition characteristics of the oil.

2. Experimental Procedure

Commercial 304 Stainless Steel (0.07% C, 0.55% Si, 2.00% Mn, 18.01% Cr, 9% Ni, 0.02% P and 0.03% S) was used in this work. The specimens were cut from 2 mm thick 304 stainless steel plate into a rectangular shape with the size of 15mm×20mm and then wet grounded up to No. 2000 sand paper, followed by polishing from 6 μm to 1 μm by diamond gel. For immersion test, the polished specimens were simply immersed into the solution for 7 days. For polarization experiments, the specimens were first mounted using epoxy and polymer hardener and then grinding and polishing was performed to get a mirror-like scratch-free surface. The exposed surface equal to 1×1㎠ was controlled by mounting with fast curing epoxy (Araldite Rapid, Huntsman Advanced Materials (Switzerland) GmbH. The corrosion test was implemented in 1m HCl solution which was prepared from de-ionized water and extra pure grade HCl (Duksan Pure Chemicals, Korea). The specific concentration of spearmint oil extracted from Mentha Spicata plant was added in to corrosion solution.

Immersion test was performed to measure the weight loss in the specimen as a function of inhibitor concentration and immersion time. The rectangular plates of 304 stainless steel were immersed in a hanging position in 150㎖ of solution of 0.5m, 1m and 2m HCl containing varying concentrations (0㎖, 5㎖, 10㎖, and 15㎖) of spearmint oil. Prior to immersion, the specimens were weighed to get initial weight (w_0) value. After a specific time interval, the specimens were taken out from the solution and carefully washed with distilled water and ethyl alcohol to remove the corrosion products from the surface. Care was taken to avoid the formation of any handling damages on the surface. The specimens were then dried using cold air and weighed again to get the weight (w_1) which were less than'w_0'values due to loss of material in the form of corrosion products.

The specimens were immersed in the test solution for one week and the weight changes were measured after every 24 hours throughout the week. Weight loss was then measured by taking the difference between the original weight value of the specimen taken before immersion and the weight after immersion for every 24 hours interval. The resulting weight loss data was plotted as a function of immersion time to get the changing trend of weight loss with increasing time. Based on weight loss measurements, corrosion rate and inhibition efficiency values were calculated and plotted as a function of immersion time and inhibitor concentration. The microstructures on corroded surface of the corroded specimen were analysed using scanning electron microscopy (SEM).

For electrochemical corrosion test, the open circuit potential was measured until the dynamic stability was achieved between working electrode (304 Stainless Steel) and HCl solution and recorded as a function of time up to one hour. The potentio-dynamic polarization measurement was performed by scanning the potential starting from -1,500mV to + 1,500mV with respect to open circuit potential at a scan rate of 1mV/s under the inhibited and uninhibited conditions.

3. Results and Discussion

3.1 Immersion Test

<Fig. 1> shows the charge of weight loss with immersion time 304 stainless steel at varying concentration of HCl and demonstrates that weight loss increases with the increase in HCl concentration. However, effect of inhibitor concentration on weight loss diminishes with the decrease in HCl concentration. At 0.5m HCl concentration, there is not a significant difference of weight loss among various inhibitor concentrations as compared to the 1m and 2m HCl (as shown in <Fig. 1(b) and 1(c)>). This means that at low concentration of HCl, even a very low conc. of inhibitor is able to cover the active corroding sites on specimen surface and give relatively good inhibition efficiency value.

The corrosion rate (C.R.) of 304 stainless steel in 0.5m, 1m and 2m HCl solution was determined after 7 days of immersion in different concentration of natural spearmint oil. <Fig. 2> show the change of corrosion rate with immersion time and inhibitor concentration, respectively. It is obvious that corrosion rate is rapid for the specimens immersed in the solution without inhibitor. The rate is decreasing with the increasing concentration of inhibitor.

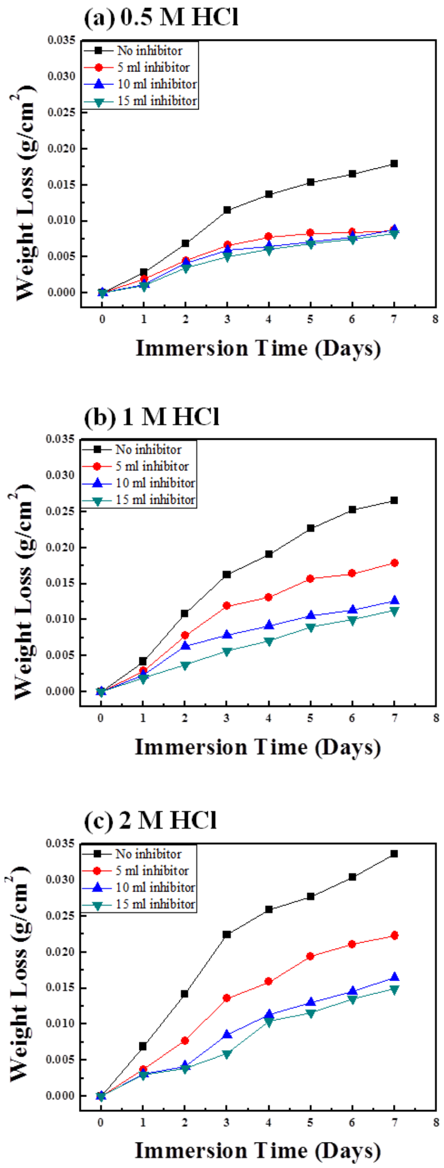

Fig. 1 Change of weight loss of the 304 stainless steel immersed in (a) 0.5m HCl, (b) 1m HCl, and (c) 2m HCl solution at different concentrations of spearmint oil

The decrease in corrosion rate can be attributed to the slowdown of the corrosion processes due to formation of adsorbed layer of inhibitor on the surface. The inhibitor suppresses the redox reactions, by forming complexes with the surface metallic ions. Hence, a reduction in oxidation-reduction process lowers the deterioration rate of steel in inhibited solution as compared to the specimens immersed in uninhibited conditions.

<Fig. 3> shows the change of inhibition efficiency (I.E) with immersion time and inhibitor concentration. The effect of inhibitor concentration on corrosion inhibition of metal is more prominent for the specimens

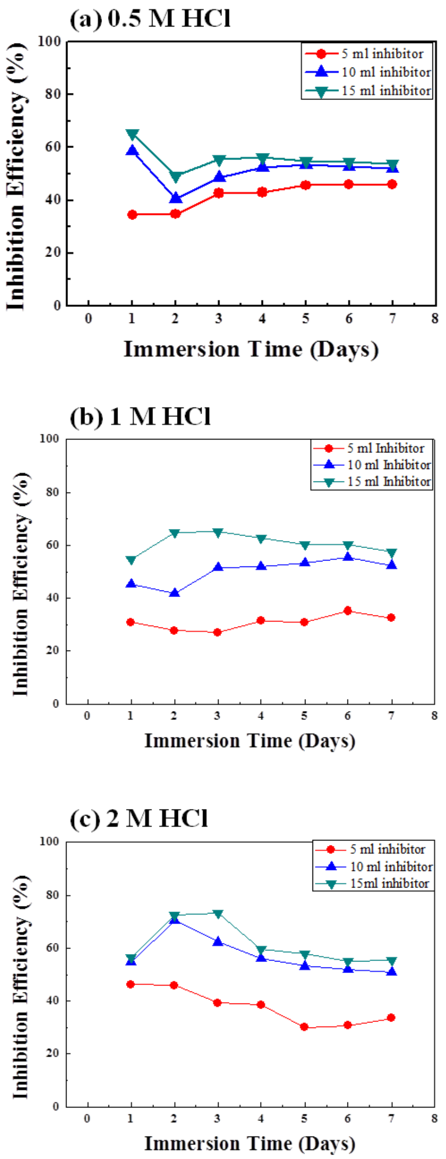

Fig. 3 Change of corrosion rate of the 304 stainless steel immersed in (a) 0.5m HCl, (b) 1m HCl, and (c) 2m HCl solution in the presence of various concentrations of spearmint oil

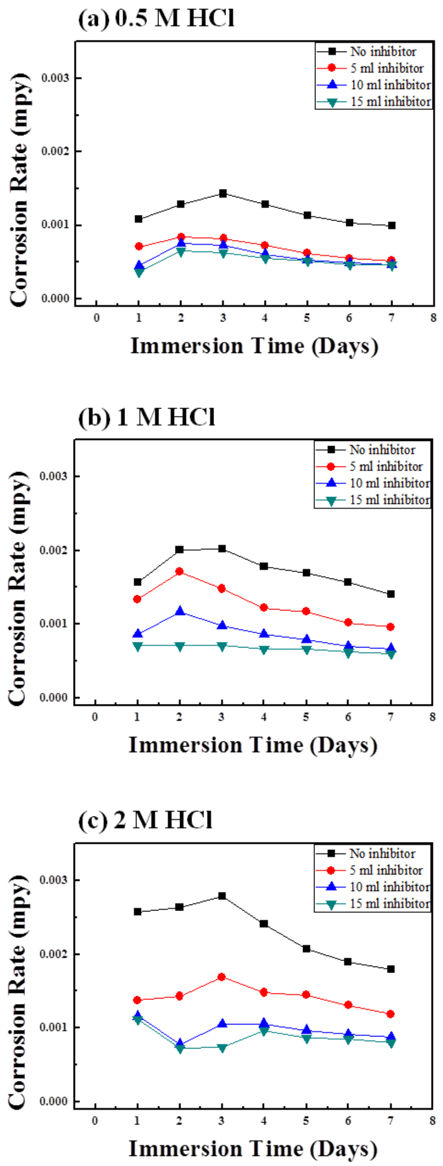

Fig. 2 Change of corrosion rate of the 304 stainless steel immersed in (a) 0.5m HCl, (b) 1m HCl, and (c) 2m HCl solution in the presence of various concentrations of spearmint oil

immersed in higher molar concentration of acid (1m and 2m HCl solution (<Fig. 3(b, c)>). A significant difference can be observed in the resultant corrosion rate values between specimens exposed to 5㎖ inhibitor solution as compared to solution containing 15㎖ inhibitor.

This is due to the fact that corrosion process is accelerated in higher molar concentration of acid and hence, the desired inhibition level cannot be achieved at lower concentration of inhibitor. Only few of the surface pores are covered and hence the reduction in corrosion rate is not remarkable. However, the surface coverage effect increases with the increase in inhibitor concentration and after reaching a certain extent, the effect of increase in inhibitor concentration on corrosion inhibition diminishes due to the increase in polar interactions between inhibitor-inhibitor radical ions instead of inhibitor-acid radical ions. At 0.5m HCl (<Fig. 2(a)>), corrosion rate is incredibly low and even a relatively lower concentration of inhibitor is capable to cover the corrosive sites on the surface and produce a surface coverage effect required for significant inhibition. Thus, the increase in inhibitor concentration does not induce notable difference on the corrosion rate values.

The increase in I.E. value in the presence of plant extracts can be attributed to the adsorption of phytochemicals present in the spearmint oil onto the specimen surface as organic compounds adsorption on the metal surface is characterized by a decrease in weight loss value, which in turn results in an increase in inhibition efficiency and surface coverage effect.

3.2 Microstructural Evaluation

<Fig. 4> reveals the surface morphology of the 304 stainless steel samples observed after 7 days of immersion in 2m HCl and varying concentration of spearmint oil.

The metal is attacked and grain boundary is revealed. However, as it is clear from the microstructures that the number of corrosion pits is more in the specimens immersed in uninhibited conditions and decreases significantly going from left <Fig. 4(a)> to right <Fig. 4(d)> with the increase in inhibitor concentration. In the absence of inhibitor (<Fig. 4(a)>), the surface is almost dissolved and the resulting morphology is facetted by the alternative presence of steps and terraces. Also, the surface is rough and the number of corrosion pits are remarkably high, indicating a severe corrosion attack by

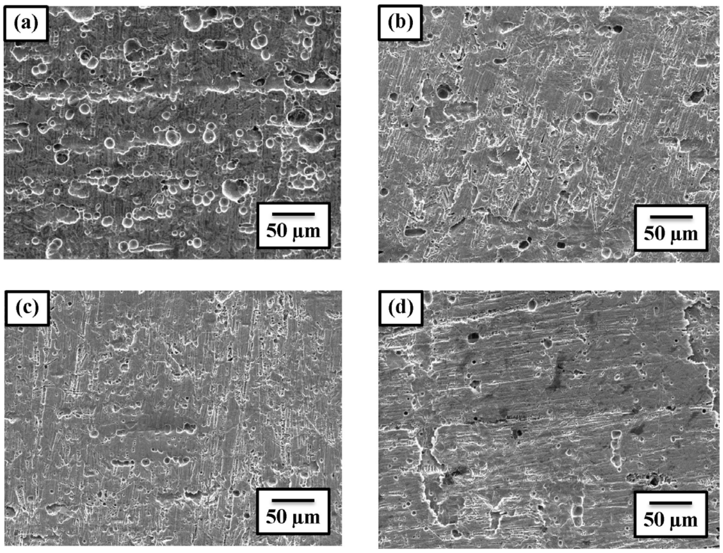

Fig. 4 SEM morphologies of the steel immersed for 7 days in 2m HCl solution; (a) without inhibitor, (b) 5㎖ inhibitor, (c) 10㎖ inhibitor, and (d) 15㎖ inhibitor [6]

the acidic media. In contrast, the surface of the specimens immersed in inhibited conditions is relatively smooth and corrosion attack is notably low, as obvious from <Fig. 4(b-d)>. As shown in <Fig. 4(d)>, at high concentration of spearmint oil, the surface contains significantly lower number of corrosion pits and shows a better inhibition. Hence, the extreme surface morphology resulting from the immersion of 304 stainless steel for 7 days in the corrosive electrolyte containing the Mentha Spicata extracts is quite different, and shows the presence of a totally covering organic film.

3.3 Polarization Results

<Fig. 5> shows the potentiodynamic polarization curves of 304 stainless steel in 1m HCl solution both in the absence and in the presence of inhibitor at room temperature. The potential was measured after almost 1 hour of immersion in the corresponding solution, thus allowing the samples to attain the stationary and stable open circuit potential (OCP) value. A significant decrease in the cathodic current density is observed in the specimen immersed in the inhibited conditions relative to the one immersed in the acidic medium only. It is evident that addition of inhibitor retards the hydrogen evolution reaction and precipitates the cathodic areas in order to increase impedance on the surface, thus limiting

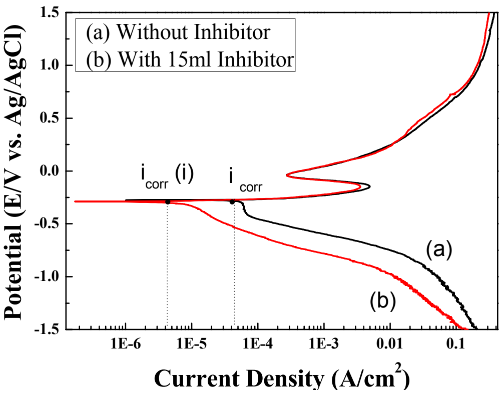

Fig. 5 Electrochemical polarization curves for the 304 stainless steel in 1M HCl solution; (a) without inhibitor, and (b) with 15㎖ inhibitor

the diffusion of reducible species. However, the inhibitor significantly affects neither the corrosion potentials nor the anodic current density. Hence, spearmint oil is classified as a cathodic inhibitor for 304 stainless steel.

The inhibition efficiency (I.E) is calculated for the steel specimen by taking into consideration the corrosion current density values in the inhibited (icorr(i)) and uninhibited conditions (icorr). As evident from the data drawn through the Tafel curves (see <Fig. 5>), spearmint oil inhibits the corrosion of 304 stainless steel up to a remarkably high value of about 87% and hence acts as an efficient eco-friendly inhibitor for stainless steel in a harsh acidic environment.

4. Conclusion

It can be concluded that Essential Spearmint oil from Mentha Spicata Extracts has the capability to control the corrosive attack on 304 stainless steel surface during acid cleaning operations by chemisorption of constituents of the oil onto the surface of specimen. Moreover, it can be classified as a cathodic inhibitor for stainless steel because of its ability to retard the hydrogen evolution reaction and thereby, reducing the overall corrosion processes. The addition of a certain concentration of spearmint oil during pickling, scaling and cleansing process of steel can protect the material by adsorbing onto the surface, thus inhibiting all the active corrosive sites exposed to acids resulting in a decrease in corrosion rate and a significant increase in surface coverage effect.

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