Study of Corrosion Efficiency of Mild Steel Using Commercial Liquid Additives for Fish in Natural Water

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This work is devoted to examine the effectiveness of the different commercial liquid additives for fish (sweet corn and molasses) on corrosion of mild steel in natural water by different methods (gravimetric and potentiostatic polarization) at room temperature. The corrosion tests were employed to evaluate corrosion rate (CR) and inhibition efficiency (IE %). The maximum inhibition efficiency was obtained for the inhibitor type molasses of 90.00% by gravimetric method for a period of 3 hours and over 31 % by potentiostatic polarization method. It was found that the commercial liquid additives acted as a good inhibitors for the tested environment. Furthermore, the corroded metal was observed by metallographic microscope.

Key words: corrosion, mild steel, natural water, inhibitors

Mild steel, also called plain-carbon steel, can be easy to shape and machine because it is very malleable. Considered the most common form of steel due to the low cost, mild steel is the perfect choice for construction materials, car manufacturing, motorcycle frames, construction of pipelines, is widely employed in large tonnages in marine applications, nuclear power, transportation, chemical processing, etc. [1, 2].

The corrosion of various metals (i.e mild steel, copper, boron steel, aluminum) is caused by the attack of the environment on the metal. The extent corrosion attack with expose time was called corrosion rate [3, 4].

In order to prevent the corrosive attack on metallic materials, various technologies and methods were applied such as: coatings [4], special steel bar (stainless steel bar, epoxy coated steel reinforcement) [5, 6], electrochemical protection (cathodic protection) [7], corrosion inhibitors [8-20].

Traditional corrosion inhibitors are classified into organic (i.e. pyridine, alkanolamine, urea, mercaptobenzothiazole, benzotriazole) and inorganic (i.e. phosphates, chromates, nitrites) substances [9].

Previous publications reveal that different organic compounds could be used as effective corrosion inhibitors due to their high tendency for adsorption [9-12]. Kern and Landolt [10] indicated that the organic inhibitors are adsorbed on the steel surface, forming a barrier layer to prevent corrosion steel. Violeta et al. [11] showed that the organic inhibitors can both stopped the anodic and cathodic reactions, reducing the corrosion rate of reinforcing steel. Fei-long Fei et al. [12] related that the imidazoline quaternary ammonium salt corrosion inhibitor can effectively increase the corrosion resistance of the steel reinforcement.

Today the traditional corrosion inhibitors due to high toxicity, to their carcinogenicity and biological toxicity were replaced with natural inhibitors. Many researchers [13-20] have applied the different extracts as natural inhibitors for preventing corrosion of metal due to their non-toxic, low-cost and high-efficiency features. Plant products are organic in nature, and contain certain photochemical including tannins, flavonoids, saponins, alkaloids, and polysaccharide which could be extracted by simple less expensive procedures. Extracts from different parts of plant (leaves, seeds, flowers, fruits, peel) have been widely reported as good metal corrosion inhibitors in various corrosive environments. These natural extracts get adsorbed on the metal surface and can decelerate the corrosion speed [13-32].

Inhibitors are widely used in the corrosion protection of metals in several environments due to its low cost, excellent inhibition performance, environment friendly, bio-degradability, non-toxic, natural, at low or without environmental impact [13-15].

The aim of this paper was to study the possibility of using different commercial liquid additives for fish (sweet corn and molasses) as safe inhibitors to prevent mild steel corrosion in natural water. In this study, these commercial liquid additives were chose because present many advantage such as: low cost, biodegradability, non-toxic, eco-friendly. The commercial liquid additive type sweet corn was obtained from cold pressing of corn, while commercial liquid additive type molasses is a syrupy residue resulting from sugar extraction of sugar beet (contains an important percentage of natural betaine). Another goal of this study was to minimization of adverse impact over the environment. The inhibition performance was examined by gravimetric method and potentiostatic polarization method. The corrosion rate and inhibition efficiency were also calculated. The experimental results were complemented with metallographic investigation.

Experimental part

The all corrosion tests were taken in natural water (Danube, disctrict Olt). Different commercial liquid additives for fish sweet corn (SC) and molasses (M) (Senzor Planet, Romania) were used in this study. The natural water was used without any purification or filtration.

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The mild steel sample with chemical composition of C (0.21%), P (0.29%), Si (0.35%), Cr (0.16%), Mn (0.51%) and the rest Fe, was used in this study.

The corrosion of mild steel was examined by gravimetric method at different times (3 h, 6 h, 12 h and 24 h), at room temperature (25°C), without stirred, and potentiodynamic polarization at room temperature (2 h). The test solution, for weight loss and for electrochemical measurement, contain: 70 ml of natural water and 2 mL of different commercial liquid additives, respectively.

Rectangular mild steel coupons (1.6 cm x 1.4 cm x 0.05 cm size) were mechanically cut with a small hole 1 mm diameter at the upper edge to facilitate suspension of the samples in the test solution for gravimetric method. For electrochemical studies, the electrodes size (two mild steel coupons - anode and cathode) was 2.5 cm x 1.6 cm x 0.05 cm.

The potentiostatic polarization test was conducted at values of current intensity betweeen 20 - 280μA/cm^2, using a DC power supply (AXIOMET AX-3005D, Germany). The potential of the electrode was measured from 5 to 5 minutes after setting the intensity value using a saturated calomel electrode (SCE) and a digital multimeter (AXIOMET AX-100, Germany). A standard corrosion cell was used for all the electrochemical measurements.

All coupons were mechanically polished with different grades (# 400 and 200) silicon carbide abrasive paper and then were cleaned with sodium carbonate (powder, Sigma-Aldrich) and washed with distilled water. Afterwards, the coupons were dried at room temperature and weighed accurately using the analytical balance (Precisa 390, Germany) (precision ± 0.1 mg) before and after all corrosion test.

For gravimetric experiments, weighed coupons were suspended in beakers, which contain the test solutions, using a support plexiglas with stainless steel hooks (fig. 1).

Fig. 1. The beaker with support plexiglas and stainless steel hooks

The morphology of the mild steel surface was carried out using a VHX optical metallographic microscope (magnification 10x). Images of the specimens were recorded after 24 h exposure time in corrosion medium without and with commercial liquid additive.

Result and discussions

Weight loss measurements

In order to investigate the inhibition performance of different commercial liquid additives, the gravimetric method was performed. The weight loss rate and protection degree of mild steel in natural water, in the absence and presence of different commercial liquid additives for fish, were evaluated.

Four mild steel samples were immersed in each prepared solution (figs. 2a-d). Afterwards, the mild steel samples have been removed from the corrosion medium at different times: 3 h (first sample), 6 h (second sample), 12 h (third sample) and 24 h (fourth sample), respectively.

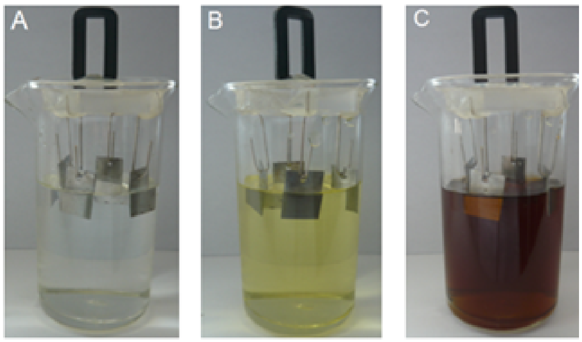

Fig. 2. The mild steel sample immersed in different corrosion medium: A) natural water (NW), B) natural water + sweet corn (SC), C) natural water + molasses (M)

Corrosion products have been removed using a solution of ammonium citrate (0.5 N), dried and then weighed. The corrosion surface of mild steel coupons was approximately 3.6 cm^2. The weight loss values were used for the calculations of corrosion rate.

Corrosion rate (CR) for the sample was calculated following equation (1) [16-28]:

$$CR = \frac{W_i - W_f}{A \cdot t} \quad (1)$$

where: CR - corrosion rate, g/m^{2}h; W_i - initial weight of mild steel coupon, g; W_f - final weight of mild steel coupon, g; A - area of the coupon exposed at corrosion test, m^2; t - the time of exposure (h).

The corrosion inhibition ability is expressed in terms of inhibitor efficiency (IE %) and is calculated following equation (2) [16-27]:

$$IE(\%) = \frac{CR_0 - CR_{inh}}{CR_0} \cdot 100 \quad (2)$$

where: CR_0 - corrosion rate in the absence of inhibitor and CR_{inh} - corrosion rate in the presence of inhibitor, respectively, g/m^2 h

The corrosion rate (CR) and inhibition efficiency (IE %) obtained by weight loss data, for each exposure time, are presented in table 1.

Table 1

THE VALUES OF CR AND IE FOR MILD STEEL AT DIFFERENT EXPOSURE TIME INTERVALS FOR DIFFERENT CORROSION MEDIUM

Corrosion medium	Time, h	CR, g/m^2 h	IE, %
NW	3	2.564	-
	6	3.968	-
	12	4.274	-
	24	4.895	-
NW+M	3	0.256	90.00
	6	0.649	83.64
	12	0.833	80.50
	24	1.082	77.89
NW+SC	3	0.541	78.90
	6	0.952	76.00
	12	1.082	74.68
	24	1.786	63.52

From table 1, it was found that the corrosion rates increases with immersion time. It can be observed that the corrosion rate of mild steel in natural water without inhibitors was much higher than when inhibitors were used. Analyzing the effect of immersion time for a period between of 3 h - 24 h, it can be observed that the commercial liquid additives present a maximum efficiency at immersion time of 3 h, being sufficient for corrosion protection process [21-23]. The maximum inhibition efficiency of 90.00% was obtained for molasses at immersion time of 3 h.

Potentiostatic polarization test

The corrosion behavior of mild steel electrode in natural water, without and with commercial liquid additives for fish, has been studied by polarization measurements. The recorded Tafel plots are shown in figure 3. From polarization curves, the corrosion potential (ε_{corr}) and corrosion current density (i_{corr}) values were obtained and shown in table 3. The corrosion current densities were calculated by extrapolation of linear parts of anodic and cathodic curves to the point of intersection of the corresponding corrosion potential [9, 10, 16-27].

The resistive corrosion and scale film formation on the mild steel surface were represented in the following equations (3) and (4) [24-27]:

$$\text{Anodic reaction: } Fe \rightarrow Fe^{2+} + 2e^- \quad (3)$$

$$\text{Cathodic reaction: } \frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^- \quad (4)$$

From Faraday's law, the corrosion rate was calculated by equation (5):

$$CR = \frac{AW}{z \cdot F} \cdot i_{corr} \quad (5)$$

where: CR is the corrosion rate, g/m^2 h; AW is the atomic weight of iron, g/mol; z is the number of electrons exchanged; F is Faraday's constant, Ah; i_{corr} is corrosion current density, A/m^2

The corrosion surface of mild steel coupons was approximately 4.2 cm^2.

The values for the corrosion potential (ε_{corr}), corrosion current density (i_{corr}) simulated from the plots, corrosion rate (CR) and inhibition efficiency (IE %) are listed in table 2.

Potentiostatic polarization curves reveals that the corrosion current density decreased with the addition of the commercial liquid additives and the corrosion potential shifts to less negative values upon addition of the commercial liquid additives. The anodic and cathodic curves indicated the reductions of the current density in the presence of commercial liquid additive type molasses. It is possible that the main constituents of molasses (sodium, calcium, boron, phosphorus, magnesium, zinc, iron) to be adsorbed onto the steel surface and made the retarded the corrosion process of mild steel. Molasses also contain organic compounds (glucose, fructose, betaine) that can be adsorbed on the mild steel surface by electrostatic interaction, but can also form a strong coordination bond with iron due to the existence of aromatic rings and heteroatoms [2, 9, 10, 16, 22-29]. The maximum inhibition efficiency of 31.61% was observed for natural water with commercial liquid additive type molasses.

Micrograph of the mild steel

The mild steel samples surfaces, before and after corrosion test through gravimetric method (24 h, commercial liquid additive type molasses), were evaluated using an optical metallographic microscope and shown in figure 4.

The micrograph image of the surface exposed to the natural water (fig. 4B) shows that the surface was damaged in the absence of the inhibitor in comparison with surface exposed to the natural water in presence of the inhibitor (fig. 4C). It can be observed that the surface of sample with molasses was protected against corrosion probable due to the formation of an adsorbed film of the inhibitor on the mild steel surface [2, 26].

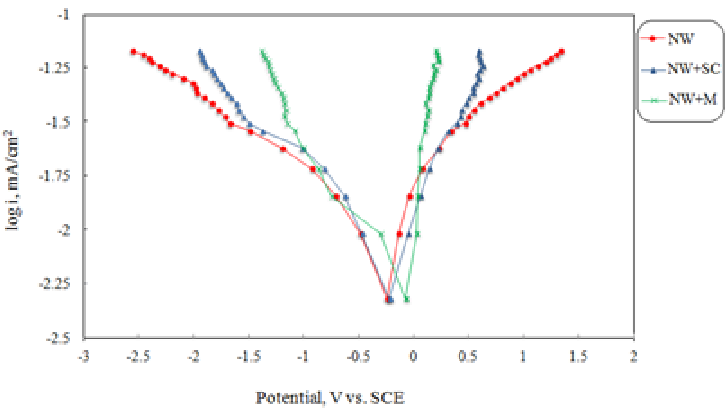

Fig. 3. Potentiostatic polarization curves for mild steel in different corrosion medium: natural water (NW), natural water + sweet corn (SC), natural water + molasses (M)

Table 2

POTENTIOSTATIC POLARIZATION PARAMETERS FOR MILD STEEL IN DIFFERENT CORROSION MEDIUM, AT ROOM TEMPERATURE, AFTER 2 h

Corrosion medium	i_{corr}, A/m^2	ε_{corr}, V	CR, g/m^{2}h	IE, %
NW	0.0977	-0.262	0.101	-
NW+SC	0.0809	-0.235	0.084	17.21
NW+M	0.0668	-0.102	0.069	31.61

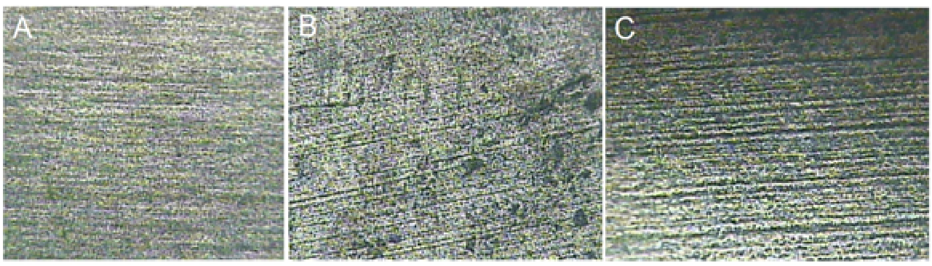

Fig. 4. Micrograph images (10X) of mild steel surfaces: (A) after polishing, (B) after 24 h of immersion in the corrosive medium without inhibitor, (C) after 24 h of immersion in the corrosive medium with inhibitor

Conclusions

The inhibiting impact of different commercial liquid additives for r the corrosion of mild carbon steel in natural water was examinted utilizing weight loss measurements and potentiostatic polarization method. The values of corrosion rate obtained from both methods (gravimetric and potentistatic polarization) decreases when the inhibitors were used. The best values for inhibition efficiency were obtained in case of inhibitor type molasses: 90.00% (gravimetric method) for immersion time of 3 h and 31.61% for immersion time of 2 hours (potentiostatic method). The micrograph image of the surface exposed to the natural water shows that the surface was damaged in the absence of the inhibitor in comparison with surface exposed to the natural water in presence of the inhibitor. In the absence of any surface films, the inhibitor are first adsorbed onto the metal surface.

The commercial liquid additives for fish proves that its good inhibitors against corrosions of mild steel in natural. Commercial liquid additives for fish can be used as green corrosion inhibitors due to multiple advantages such as: low cost, non-toxic, environmentally friendly, high-efficience and reduces the corrosion rate.

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References

1. KUMAR, R., CHOPRA, R., SINGH, G., J. Mol. Liq., **241**, 2017, p. 9
2. NNANNA, L., NNANNA, G., NNAKAIFE, J., EKEKWE, N., ETI, P., Int. J. Mater. Chem., **6**, no. 1, 2016, p. 12
3. YUAN, S. J., PEHKONEN, S. O., TING, Y. P., KANG, E. T., NEOH, K. G., Ind. Eng. Chem. Res., **47**, 9, 2008, p. 3008
4. SENEVIRATNE, A. M. G, SERGI, G., PAGE, C. L., Constr. Build. Mater., **14**, 2000, p. 55
5. ASSAADA, J. J., ISSA C. A., Constr. Build. Mater., **30**, 2012, p. 667
6. YEOMANS, S. R., Corrosion., **50**, 1994, p. 72
7. CANON, A., GARCES, P., CLIMENT, M. A., CARMONA, J., ZORNOZA E., Corros Sci., **77**, 2013, p. 128
8. SOYLEVA, T. A., RICHARDSON, M. G., Constr. Build. Mater., **22**, 2008, p. 609
9. DARIVA, G. C., GALIO, F. A., Corrosion Inhibitors-Principles, Mechanisms and Applications, Chapter **16**, p. 366
10. KERN, P., LANDOLT, D., Electrochim Acta., **47**, 2001, p. 589
11. VIOLETTA. F., MUNTEANU, F., KINNEY, F. D., Proceedings of the CANMET 2000. American Concrete Institute; 2000
12. FEI, F.-L., HU, J., WEI, J.-X., YU, Q.-J., CHEN, Z.-S., Constr. Build. Mater., **70**, 2014, p. 43
13. DEVI NITHYA, P., RAJENDRAN, S., SATHIYABAMA, J., RATHISH, J. R., SANTHANAPRABHA, S., JEYASUNDRAID, J., UMASANKARESWARI, T., Port. Electrochim. Acta, **33**, no. 3, 2015, p. 195
14. SHARMA, S. K. , SHARMA, A., Chapter 6 Green corrosion inhibitors: status in developing countries. In: Green corrosion chemistry and engineering. Wiley-VCH Publications, Germany, 2011, p. 157
15. SHARMA, S. K, PETER, A., OBOT, I. B., J. Anal. Sci. Technol., **6**, 2015, p. 26
16. YADAV, M., BEHERA, D., SHARMA, U., Arab. J. Chem., **9**, 2016, p. S1487
17. SUN, Z., SINGH, A., XU, X., CHEN, S., LIU, W., LIN, Y., Res. Chem. Intermed., **43**, no. 11, 2017, p. 6719
18. JI, G., SHUKLA, S. K., DWIVEDI, P., SUNDARAM, S., PRAKASH, R., Ind. Eng. Chem. Res., **50**, 2011, p. 11954
19. KRISHNEGOWDA, P.M., VENKATESHA, V.T., KRISHNEGOWDA, P. K. M., SHIVAYOGIRAJU, S. B., Ind. Eng. Chem. Res., **52**, 2013, p. 722
20. UMOREN, S. A., GASEM, Z. M., OBOT, I. B., Ind. Eng. Chem. Res., **52**, 2013, p. 14855
21. CARDOZO DA ROCHA, J., DA CUNHA PONCIANO GOMES, J. A., D'ELIA, E., Mater. Res., **17**, 2014, p. 1581
22. SHYAMALA, M., KASTHURI, P., Int. J. Corros. **2011**, 2011, p. 1
23. LI, X. L., NARENKUMAR, J., RAJASEKAR, A., TING, Y.-P., 3 Biotech., **8**, 2018, p. 178
24. ABDEL-GABER, A.M., ABD-EL-NABEY, B.A., SIDAHMED, I.M., EL-ZAYADY, A.M., SAADAWY, M., Corros. Sci., **48**, 2006, p. 2765
25. PAUL, S., PATTANAYAK, A., GUCHHAIT, S. K., Int. J. Met., **2014**, 2014, p. 1
26. ZAABAR, A., AITOUT, R., MAKHLOUFI, L., Pigm. Resin. Technol., **43**, no. 3, 2014, p. 127
27. ABDALLAH, M., ALTASS, M. HAL JAHDALY, B. A., SALEM, M. M., Green Chem. Lett. Rev., **11**, no. 3, 2018, p. 189
28. SAXENA, A., PRASAD, D., HALDHAR, R., SINGH, G., KUMAR, A., J. Mol. Liq., **258**, 2018, p. 89
29. BAMMOU, L., BELKHAOUDA, M., SALGHI, R., BENALI, O., ZARROUK, A., ZARROK, H., B. HAMMOUTI, B., J. Assoc. Arab. Univ. Basic Appl., **16**, no. 1, 2014, p. 83
30. GRIGORE, E., PANTEA, O., BOMBOS, D., CALIN, C., BONDAREV, A., GHEORGHE, C., Rev. Chim. (Bucharest), **66**, no. 5, 2015, p. 685
31. BOBINA, M., VASZILCSIN, N., MUNTEAN, C., Rev. Chim. (Bucharest), **64**, no. 1, 2013, p. 83
32. PATRASCU, B., TUGULEA, M.E., MEGHEA, A., Rev. Chim. (Bucharest), **60**, no. 1, 2009, p. 337

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