Surface analysis of mild steel protected from corrosion by a binary inhibitor formulation containing Zn^{2+} and citrate

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Abstract

Corrosion is a severe problem in drinking water supplies. Corrosion control refers to the action of controlling the corrosion of materials used in potable water. The present work aimed to develop a suitable corrosion inhibitor for minimizing the corrosion of potable water. Studies on surface analysis of mild steel protected from corrosion in potable water and eco-friendly inhibitor containing zinc ions and citrate ions are presented. FT-IR spectroscopy, atomic force microscopy (AFM), and water contact angle (WCA) measurements technique have been used to characterize the protective film on mild steel surface. All these studies showed that the protective film offers excellent protection against corrosion of mild steel.

Keywords: corrosion, surface modification, IR, AFM, WCA

INTRODUCTION

Corrosion is one of the most serious engineering problems and of great economic concern. The consequences of corrosion are many and varied and the effects of these on the safe, reliable and efficient operation of equipment and structures are often more serious in a corrosive environment. The understanding of corrosion mechanisms, prediction and controlling are the big challenges for safe operation of the components [1–6].

Mild steel pipes have been commonly used to supply potable water and corrosion of mild steel was one of the major problems in the supply network. Corrosion of potable water systems and release of contaminants into the conveyed water depend on both the material that is subject to corrosion and water comes in contact with the material. The corrosion product in water will influence the quality of water and also result in increased pipeline chocking [7-9]. Thus, it is important to understand the interaction of inhibitors in flow environment to retard the corrosion.

Wettability of a solid surface describes the ability of a liquid to maintain contact with the surface, which is important in the bonding or adherence of two materials [10]. Dependent on both roughness and chemical heterogeneity, wettability is a very important characteristic in nature as well as in our daily life. Hydrophobicity and hydrophilicity are two principal wettablility conditions. The surfaces of materials are hydrophilic if the water contact angle (WCA, θ) is in the range of $0° \le \theta < 90°$ and they are hydrophobic if the WCA is $90° < \theta \le 180°$. Hydrophobicity is observed in nonpolar substances, which tend to aggregate in aqueous solutions and exclude water molecules.

Application of inhibitors is a widely used method for corrosion control of mild steel, the primary material used in the construction of cooling water systems and other industrial water distribution systems. Due to environmental restrictions imposed on heavy metal ion based corrosion inhibitors, the focus has been shifted to environmentally friendly corrosion inhibitors [11]. The carboxylic acids have been used as a corrosion inhibitor. It is used to form a film on the surface of metal. The film formed on the metal surface was confirmed by FT-IR [12]. Inhibition phenomena are an important subject of worldwide investigation due to the large economic losses caused by the corrosion [13,14].

In this article, we report the development of hydrophobic protective film on mild steel surface in potable water and so that these surfaces are resistant to corrosion. The main objective of the present study is to investigate the inhibitory effects of the binary inhibitor formulation containing Zn^{2+} and trisodium citrate in corrosion protection of mild steel in potable water. Surface analytical techniques were also used to investigate the nature of the surface film.

EXPERIMENTAL

2.1. Materials

The specimens of size 1.0cm×4.0cm×0.2cm were press cut from the mild steel, were machined and abraded with a series of emery papers. This was followed by rinsing in acetone and bidistilled water and finally dried in air. Before any experiment, the substrates were treated as described and freshly used with no further storage. The inhibitors Zn^{2+} and TSC were used as received. A stock solution of 1000ppm of TSC was prepared in bidistilled water and the desired concentration was obtained by appropriate dilution. All solutions were using potable water (Perambalur, Tamil Nadu, India). The study was carried out at room temperature. The physico-chemical parameters are shown in Table 1 and structure of TSC is given in Fig 1.

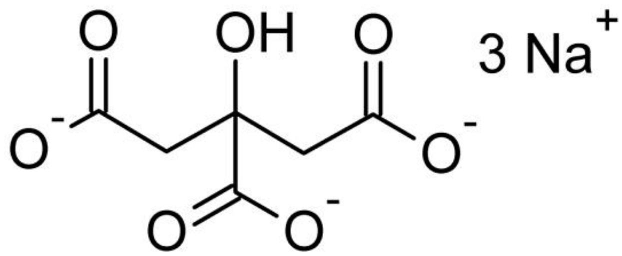

Figure 1. Structure of TSC

Table 1. Physico-chemical parameter of potable water

Parameters	**Values**
pH	7.84
TDS	251ppm
Chloride	30ppm
Alkalinity	113ppm
Total Hardness	102ppm
Conductivity	358µmhos/cm

2.2. Fourier Transform Infrared Spectroscopy

The polished mild steel specimens were completely immersed in potable water in the presence of the inhibitor. After 7 days of duration, the specimens were taken out, clean with distilled water and dried. From the dried specimens, the protective surface film was scratched carefully and the powder obtained was mixed thoroughly to make it uniform. Fourier transform infrared spectroscopy (FT-IR) was obtained with a resolution of 4 cm-1 over the range of 4000-400 cm^{-1} wave number using model Perkin – Elmer 1600 spectrometer. The spectra of pure inhibitor compounds and the protective surface film formed on the mild steel surface was done using KBr pellet method [15-23].

2.3 Atomic Force Microscopy (AFM)

Atomic force microscopy is a powerful method for the gathering of roughness statistics from a variety of surfaces. This exciting new technique, that allows surface to be imaged at higher resolutions and accuracies than ever before. The protective films are examined for a scanned area. AFM is becoming an accepted technique of roughness investigation [24-27]. AFM provided direct insight into the changes in the surface morphology takes place at several hundred nanometers when topographical changes owing to the initiation of corrosion and formation of protective film on to the metal surface in the with and without addition of inhibitors respectively. All the AFM images were recorded on a Pico SPM2100 AFM instrument operating in contact mode in air. The scan size of all the AFM images are 10 μm × 10μm areas at a scan rate of 0.20 H_z lines per second.

2.4 Water Contact Angle (WCA) Measurement technique

In order to evaluate the contact angle experimentally, the sessile droplet method was used. The sessile droplet rested on a horizontal substrate by a syringe. The substrate was illuminated by a light source, and then a picture was taken by using a high resolution camera (10.1 Mpixle SONY camera). The image was processed by computer by a software made for this reason.

The most widely used technique of contact angle measurement is a direct measurement of the tangent angle at the three-phase contact point on a sessile drop profile. Bigelow et al. [28] set up a simple and convenient instrument, which they referred to as a “telescope-goniometer” to measure contact angles of various liquids on polished surfaces. Later, the first commercial contact angle goniometer, designed by W.A. Zisman, was manufactured by ramé-hart instrument company in the early 1960s.

RESULTS AND DISCUSSION

3.1. Analyses of FT-IR Spectroscopic studies

FT-IR spectrum of pure TSC is shown in Figure 2. The C = O stretching frequency of the carboxyl group appears at 1620 cm^{-1}. The OH group stretching frequency appears at 3452 cm^{-1}. The FT-IR spectrum of film (KBr) formed on the surface of mild steel after immersion in the test solution containing 10ppm Zinc ions and 100ppm TSC is shown in the Figure 3.

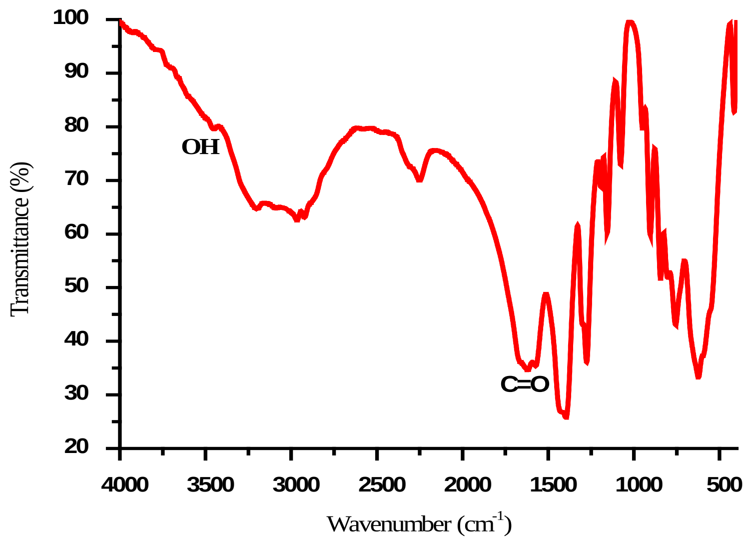

Figure 2. FT-IR spectrum of pure TSC

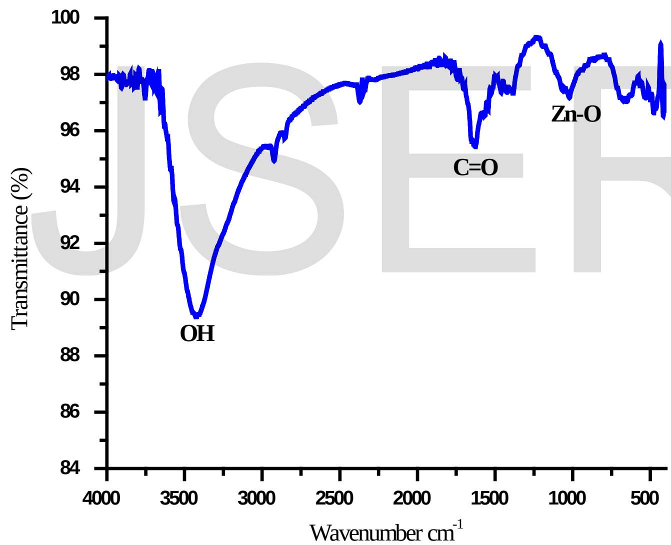

Figure 3. FT-IR spectrum of mild steel surface immersed in presence of inhibitor formulation containing 10ppm Zinc ions + 100ppm TSC

The C = O stretching frequency has shifted from 1620 cm^{-1} to1628 cm^{-1} [29]. The OH group stretching frequency shifted from 3452 cm^{-1} to 3434 cm^{-1}. There are many weak bands in the region between 1200-400 cm^{-1} and a peak observed at 420.19cm^{-1} in the spectrum of the surface film can be assigned to oxides of Fe. This indicates that oxygen atom of carboxyl group and OH group have co-ordinated with Fe^{2+} resulting in the formation of Fe^{2+}-TSC complex formed on the anodic sites of the metal surface. The peaks at 1383.68 cm^{-1} due to the formation of $Zn(OH)_2$ on the metal surface [30-33].

3.2 Analyses of Atomic Force Microscopic studies (AFM)

Atomic force microscopy **(**AFM) is a very high resolution type of scanning probe and it is considered to one of the most powerful techniques to investigate surface morphology. AFM is a powerful technique to investigate the surface morphology at nano to micro-scale and has become a new choice to study the influence of inhibitors on the generation and the progress of the corrosion at the metal/solution interface [34]. The topography of the surfaces recorded in 2D and 3D images was examined and surface roughness (R_{RMS}), average roughness (R_a), maximum peak to valley height were determined from the respective images. Table 2 shows various AFM parameters obtained for the mild steel surface immersed in different environments. Figure 4 is observed after immersion in the blank in the absence of the inhibitor, with an increased R_a value 104.5 nm, R_{RMS} value 118.6 nm and maximum peak to valley height value of 263.2 nm, indicating the formation of iron oxides. The root-mean-square R_{RMS} roughness is found to be 118.6 nm, which clearly indicates the high roughness of the corroded mild steel surface. The microstructure of the surface shows many smaller and larger corrosion product deposits. However, Figure 5 shows that the mild steel surface immersed in inhibitor formulation, 10ppm Zinc ions and 100ppm TSC showed a decreased Ra value 66.9 nm.

R_{RMS} value of 89.4 nm and maximum peak to valley height is 153.4 nm, which indicates the formation of a protective film on the metal surface. The decrease in R_{RMS} roughness from 118.6 nm in the case of the blank to 89.4 nm observed in the case of the inhibitor formulation, clearly infers the greater homogeneity and smoothness of the surface film produced by the inhibitor formulation and the absence of any corrosion product deposits. Further, these results are confirmed by the clearly visible differences among the optical cross section analysis. The metal surface was covered with a protective film, thereby, forming a barrier against attack by aggressive ions from the corrosive environment.

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Table 2. AFM parameters for mild steel surface immersed in the absence and presence of inhibitor systems

Samples	$R_{RMS}(R_q)$ Roughness (nm)	Average(R_a) Roughness (nm)	Maximum Peak – to – valley Height (nm)
Absence of inhibitor system (blank)	118.6	104.5	263.2
Presence of inhibitor system	89.4	66.9	153.4

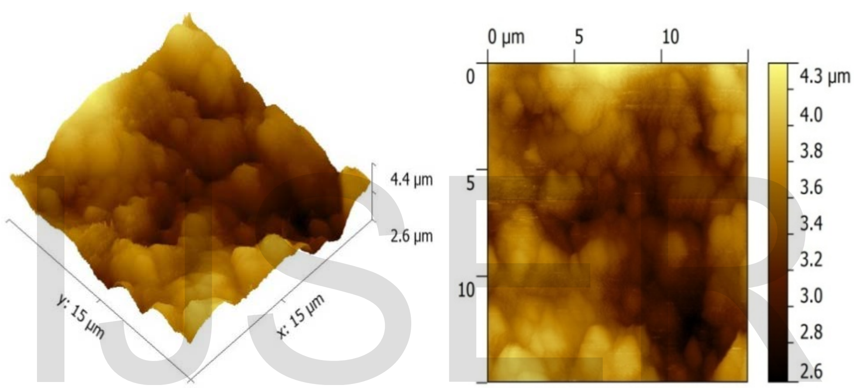

Figure 4. AFM images of mild steel surface immersed in potable water (blank)

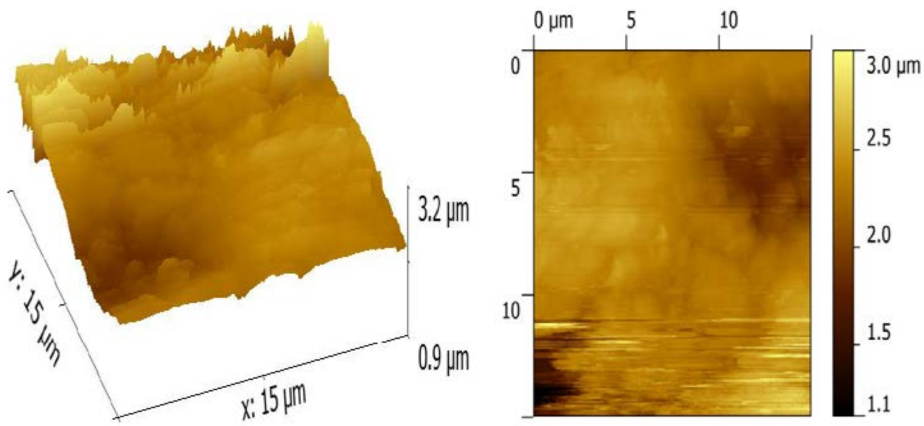

Figure 5. AFM images of mild steel surface immersed in presence of inhibitor formulations containing 10ppm Zinc ions + 100ppm TSC

3.3 Analyses of Water Contact Angle (WCA) measurement technique

The contact angle measurement were analyzed the nature of wettability, whether it is a hydrophobic or hydrophilic. Figure 6 shows mild steel surface immersed in potable water, surface highly porous, more roughness (WCA 55° ± 2°) due to mild steel surface get hydrophilic nature. Figure 7 shows mild steel surface immersed in the presence of inhibitor formulation 10ppm Zinc ions + 100ppm TSC smoother surface appear (WCA 102° ± 4°) beside the surface gets hydrophobic nature. This confirms the adsorption of a hydrophobic protective film adsorbed on the mild steel surface in the presence of inhibitor molecule.

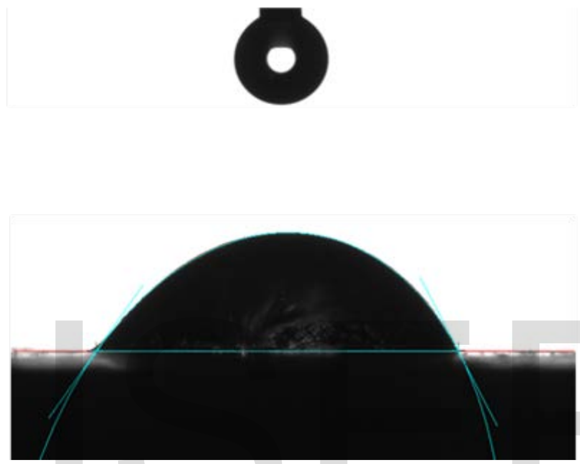

Figure 6. WCA image of mild steel surface immersed in presence of inhibitor formulations containing 10ppm Zinc ions + 100ppm TSC

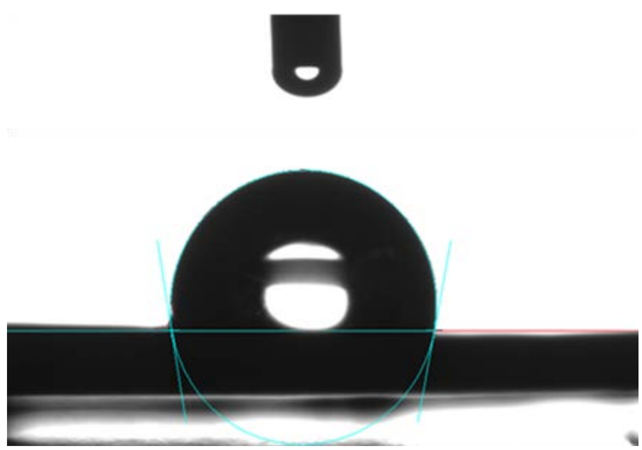

Figure 7. WCA image of mild steel surface immersed in presence of inhibitor formulations containing 10ppm Zinc ions + 100ppm TSC

3.4 Relationship between Atomic Force Microscope (AFM) and Water Contact Angle (WCA) values

These contact angle value could also be corroborated with the roughness value of the surfaces and the corresponding AFM images (Figures 4 and 5). This confirmed that the contact angle values were lower for smooth surfaces, while they were higher for rough surfaces. In the case of mild steel, the hydrophobic coating was thick and uniform when the sample was immersed in the solution containing 10ppm Zinc ions and 100ppm TSC (WCA 102° ± 4°), as shown in Figure 7.

CONCLUSIONS

- FT-IR spectral data appear to show that the protective film may consists of [$Fe^{3+/}Fe^{2+/}Zn^{2+}$-TSC] complex, $Zn(OH)_2$, hydroxides and oxides of iron.
- The protective film formation is also confirmed by atomic force microscopy (AFM) studies and Water Contact Angle (WCA) measurement technique.
- AFM images showed uniform coating and the surface was micro–nano rough with cluster-like projections.
- The hydrophilic surface has changed to hydrophobic in presence of inhibitor without any effect of flow.
- Thus, as a general conclusion, zinc ions and trisodium citrate shows good potential as an eco-friendly corrosion inhibitor for mild steel in potable water.

REFERENCE

1. K.R. Trethewey, J. Chamberlain, Corrosion for Science and Engineering, second ed., Longman, London, 1995.
2. A.H. Tuthill, Guidelines for the use of mild steel alloys in seawater, Mater. Per- form. 26 (1987) 12–22.
3. S.R. De Sanchez, D.J. Schiffrin, Flow corrosion mechanism of mild steel base alloys in seawater in the presence of sulphide contamination, Corros. Sci. 22 (1982) 585–607.
4. A. Neville, C. Wang, Erosion–corrosion mitigation by corrosion inhibitors-an assessment of mechanisms, Wear 267 (2009) 195–203.
5. R.C. Barik, J.A. Wharton, R.J.K. Wood, K.R. Stokes, Electro-mechanical inter- actions during erosion–corrosion, Wear 267 (2009) 1900–1908.

6. O. Hollander, R.C. May, The chemistry of azole mild steel corrosion inhibitors in cooling waters, Corrosion 41 (1985) 39–45.

7. J. Buchweishaija, G. S. Mhinzi, Portugaliae Electrochimica Acta, 26 (2008) 257.

8. Aiman El. Af-Rawajfeh, Enab,M. Al-Shamaileh Desalination, 206 (2007) 169 –178.

9. A.M. Shams El din, Desalination, 60 (1986) 75.

10. Qiao R, Zhang R, Zhu W, Gong P. Lab simulation of profile modification and enhanced oil recovery with a quaternary ammonium cationic polymer. J Ind Eng Chem, **18**, 111 (2012).

11. D.-J. Choi, S.-J. You and J.-G. Kim, "Development of an Environmentally Safe Corrosion, Scale, and Microorga- nism Inhibitor for Open Recirculating Cooling Systems," *Materials Science and Engineering*: *A*, Vol. 335, No.1-2, 2002, pp. 228-235.

12. S. Agnesia kanimozhi, S. Rajendran, The Arabian jour. for sci and engg, 2009, **34**, 39.

13. J.B. Cotton, I.R. Scholes, Benzotriazole and related compounds as corrosion inhibitors for mild steel, Br. Corros. J. 2 (1967) 1–5.

14. H. Gerengi, K. Darowicki, G. Bereket, P. Slepski, Evaluation of corrosion in-hibition of brass-118 in artificial seawater by benzotriazole using dynamic EIS, Corros. Sci. 51 (2009) 2573–2579.

15. R. Vera, H. Romero and Y.E. Ahumada, *Journal of Chilean Chemical Society,* 48, **(2003)**, 35.

16. R. Ravichandran, S. Nanjundan and N. Rajendran, *Applied Surface Science,* 236, **(2004)**, 241.

17. S. Ramesh and S. Rajeswari, *Corrosion Science,* 47, **(2005)**, 151.

18. N. Ohno, H. Nishihara and K. Aramaki, *Corrosion Science,* 36, **(1994)**, 583.

19. R. Tremont, H. Dejesuscardona, J. Garciaorozco, R.J. Castro and C.R. Cabrera, *Journal of Applied Electrochemistry,* 30, **(2000)**, 737.

20. A.Angamuthu, C.Thangavelu, S.Rajendran, T.Asokan, *Zastita Materijala,* 53, **(2012).**

21. C.Thangavelu, P.Patric Raymond, S.Rajendran and M. Sundaravadivelu, *Asian j. Research Chem.* 4(3), **(2011)**, 402-405.

22. C. Thangavelu and T. Kasilingam, *Chem. Sci. Rev. Lett.* 3(9), **(2014)**, 10-17.

23. T. Kasilingam and C.Thangavelu, *Inter. J. Inno. Tech. and Explo. Engin,* 3 (12), **2014**.

24. A.Duparre, N.Kaiser, H.Truckenbrodi, M.Berger and A.Kohler, *optical profilometry SPIE*, 1995, **(1993)**, 181-192.

25. C.Amra , C.Deumie, D.Torricini, P.Roche, R.Galindo, P.Dumas and Salvan.F Int. Symp. *On Optical Interference Coatings*, 6-10 June 1994. Grenoble, Proc. SPIE 2253, **(1994)**, 614-630.

26. R.N. Bhattacharyya, *Experiments with Micro Organisma (EMKAY) Publications*, **(1983)**, 80.

27. J. Micheal Pelczar, JREC Schan Noel R: Krieg; *Micro Biology*, Tata Magraw-Hill Edn., **(1988)**.

28. W.C. Bigelow, D.L. Pickett, W.A.J. Zisman, Coll. Sci. **1**, 513 (1946).

29. B. Balanaga Karthik, P. Selvakumar and C. Thangavelu, *Inter. J. of Sci. And Res*, 4, **(2014)**, 1 – 6.

30. Chinnayan Thangavelu and Thavan Kasilingam, *Chem. Sci. Rev. Lett.* 3(9), **(2014)** 10-17.

31. T. Kasilingam and Thangavelu, *Inter. J. of Inno.Tech. and Explo. Eng*, Volume-3, Issue-12, **(2014)**.

32. T. Kasilingam, C. Thangavelu and V. Palanivel, *Portugaliae electrochimica acta*, 32(4), **(2014)**, 259-270.

33. P. Selvakumar, B. Balanaga Karthik, and C. Thangavelu, *J. Chem. Bio. Phy. Sci. Sec. C*, 4, **(2014)**, 962-968.

34. A.K, Satapathy, G. Gunasekaran, S.C. Sahoo, K. Amit, P.V. Rodrigues, *Corros. Sci*, 51, **(2009)**, 2848.