



Surface Modification of Carbon Steel by Hexanesulphonic Acid- Ni²⁺ System and its Corrosion Study

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Abstract: Corrosion inhibition has become an important area of research because, corrosion cannot be prevented but it can be controlled. The topic corrosion is inter-disciplinary and it includes all the basic sciences, such as physics, chemistry, biology and all the disciplines of engineering, such as civil, mechanical, electrical and metallurgical engineering. The purpose of studying the process of corrosion is to find methods to control it. One approach is the use of corrosion inhibitors. This research is carried out to evaluate the corrosion inhibition behavior of hexanesulphonic acid (HS) along with nickel ion (Ni²⁺) on carbon steel in dam water using weight-loss method. Results of weight loss method indicated inhibition efficiency (IE) increased with increasing inhibitor concentration. Polarization study reveals that HS-Ni²⁺ system controls the anodic reaction predominantly. AC impedance spectra prove that a protective film is formed on the metal surface. The nature of the metal surface has been analyzed by Fourier transform infrared spectroscopy (FTIR), Scanning electron microscopy (SEM) and Energy dispersive x-ray detector (EDAX) measurements.

Keywords -Carbon steel; Corrosion; Electrochemical techniques; FTIR; SEM; EDAX.

Introduction

Corrosion, scale and fouling by microorganisms can be initiated when natural water is used as coolant. These effects can reduce the thermal efficiency of the cooling systems with significant economic problems. To eliminate or to reduce these impacts, corrosion inhibitors are added to water used in cooling systems. Inhibitors generally control metal dissolution. Organic compounds are accepted as effective inhibitors for the corrosion of many metals and alloys. The corrosion inhibition property of an organic compound is mainly associated with the chemical adsorption [1-5]. Most of these organic compounds contain nitrogen, sulphur, oxygen and multiple bonds in the molecules which are adsorbed on the metal surface [6,7].

A survey of the available literature reveals that a few sulphonic acids have been used as corrosion inhibitors [8-11].

For the present study, the medium used is dam water collected from Sothuparai dam in the state of Tamil Nadu, India, constructed across the Vaigai River. A few industries located in downstream uses the dam water as coolant.

Experimental Method

The chemicals used in this study, hexanesulphonic acid (inhibitor) and NiSO₄ 6H₂O (co inhibitor) were AR grade.

Preparation of the specimen

The dimension and chemical composition of carbon steel samples are 1.0 cm × 4.0 cm × 0.2 cm. 0.026 % sulphur, 0.06 % phosphorous, 0.4 % manganese, 0.1 % carbon and the rest iron. They were polished with emery wheel and degreased with acetone and then stored in desiccator. Then it is used for the weight loss method and surface examination studies.

Weight-loss method

Carbon steel samples in triplicate were suspended in 100 ml of the medium containing various concentrations of the inhibitor (HS) in the absence and presence of Ni²⁺ for 3 days. The weights of the samples before and after immersion were measured using a Digital Balance (Model AUY 220 SHIMADZU). The corrosion products were cleaned with Clarke's solution prepared by dissolving 20 gms of Sb₂O₃ and 50 gms of SnCl₂ in one litre of Conc. HCl of specific gravity 1.9 [12]. The corrosion IE was then calculated using the equation

$$IE = 100 [1 - (W_2/W_1)] \% \quad (1)$$

Where W₁ is the weight loss value in the absence of inhibitor and W₂ is the weight loss value in the presence of inhibitor. Corrosion rate was calculated using the formula [13] Mills penetration per year (mpy) = 534 W/DAT
(2)

W = weight loss in milligrams D = density of specimen in g/cm³

A = area of specimen in cm² T = exposure time in hours

Potentiodynamic Polarization

Potentiodynamic polarization accountings were done using computer - controlled potentiostat, CHI electrochemical work station with impedance mode 608E. A three- electrode cell assembly was used. Carbon steel was the working electrode. Saturated calomel electrode was the reference electrode. Platinum was the counter electrode.

AC impedance spectra

To record AC impedance spectra, the same instrument used for polarization study was used. The real part (Z') and imaginary part (Z'') of the cell impedance were measured in ohms at various frequencies. From the above data charge transfer resistance (R_t) and the double layer capacitance (C_{dl}) were calculated.

Surface examination study

For surface examination study, the carbon steel samples were immersed in various test solutions for a period of one day after which, they were taken out and dried. The film thus formed on the surface of the metal was subjected to various surface analysis techniques.

Fourier Transform Infrared spectra (FTIR)

A Perkin-Elmer-1600 spectrophotometer was used to record FTIR spectra using KBr pellet method. The FTIR spectrum of the protective film was recorded by carefully removing the film, mixing it with KBr, and making the pellet.

Scanning Electron Microscopy (SEM) and energy dispersive x-ray detector (EDAX)

The carbon steel samples after immersion in blank solution and in the inhibitor solution for a period of one day were removed, rinsed with double distilled water, dried and observed in a scanning electron microscope

to study the surface morphology. The surface morphology measurements of carbon steel were examined using JEOL MODEL6390 computer controlled scanning electron microscope. The elemental analysis of the carbon steel surface at the same condition was carried out using an energy dispersive X-ray analyzer unit attached to the SEM machine.

Results and Discussion

Analysis of Weight-loss study

The physicochemical parameters of dam water are given in Table 1.

Table1: Water Analysis

Parameters	Result
Appearance	Brownish
Total dissolved solids	45 ppm
Electrical conductivity	135 μ s/cm
pH	8.15
Total hardness	45 ppm
Calcium	10 ppm
Magnesium	0.6 ppm
Iron	1.2 ppm
Nitrate	10 ppm
Chloride	10 ppm
Sulphide	10 ppm

Table 2: Corrosion inhibition efficiencies (IE %) and the corresponding corrosion rates (CR) in (mpy) of HS- Ni²⁺ system

HS in ppm	Ni ²⁺					
	0 ppm		15 ppm		30 ppm	
	IE%	CR mpy	IE%	CR py	IE%	CR py
0	0	4.8032	25	3.6024	37	3.0260
50	10	4.3229	27	3.5063	48	2.4977
100	13	4.1787	32	3.2661	49	2.4496
150	19	3.8906	40	2.8819	51	2.3536
200	26	3.5544	44	2.6898	64	1.7292
250	31	3.3142	49	2.4496	85	0.7069

Inhibition efficiency (IE) and the corrosion rates (CR) in mills per year (mpy) of carbon steel in presence of HS–Ni²⁺ system for a period of 3 days, immersed in dam water are given in Table 2.

The IE of HS increases as its concentration increases. From the table it is clear that Ni²⁺ in the absence of inhibitor also has some IE. As the concentration of Ni²⁺ increases, IE also increases. A synergistic effect exists between HS and Ni²⁺. It is observed from the table 2, that 250 ppm of HS has 31% IE and 30 ppm of Ni²⁺ has 37% IE. However, their combination consisting of 250 ppm of HS and 30 ppm of Ni²⁺ has 85% IE. Therefore the mixture of inhibitors exhibits better IE than individual inhibitors [14-16]. In the presence of Ni²⁺, more amount of HS is transported towards the metal surface. On the metal surface, Fe²⁺–HS complex is formed on the anodic sites of the metal surface. Thus the anodic reaction is controlled. The cathodic reaction is the generation of OH⁻, which is controlled by the formation of Ni(OH)₂ on the cathodic sites of the metal surface. Thus the anodic and cathodic reactions are controlled effectively. This accounts for the synergistic effect existing between HS and Ni²⁺ [17, 18].

The corrosion rates (CR) of carbon steel with various concentrations of HS and Ni²⁺ systems immersed in dam water for the same period are given in table 2. From the table, it is observed that CR value decreases as the concentration of HS as well as Ni²⁺ increases. This behaviour is due to the increase in the adsorption amount of the inhibitor on carbon steel surface.

Analysis of Polarization curves

Polarization study has been carried out to know about the formation of protective film on the metal surface during corrosion inhibition process [19]. The potentiodynamic polarization curves of carbon steel immersed in blank (dam water) as well as in inhibitor Ni²⁺ (30 ppm), HS (250 ppm) solutions are shown in Figure 1. The electrochemical parameters such as corrosion potential (E_{corr}), corrosion current (I_{corr}), Tafel slopes (β_a and β_c), and linear polarization resistance (LPR) are given in table 3.

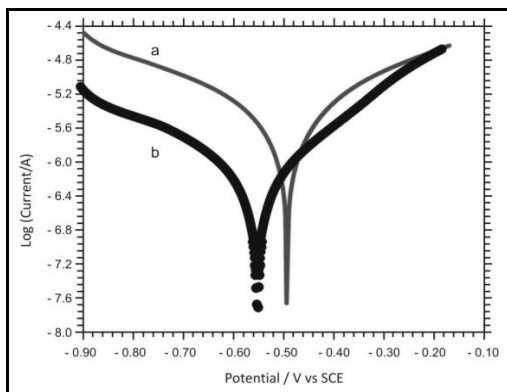


Figure 1. Polarisation curves of carbon steel immersed in various test solutions a) dam water b) dam water containing 250 ppm of HS and 30 ppm of Ni²⁺

Table 3: Corrosion parameters of carbon steel immersed in dam water in the presence and absence of inhibitor obtained by polarization method

HS ppm	Ni ²⁺ ppm	E_{corr} mV vs SCE	I_{corr} A/cm ²	β_a mV/dec	β_c mV/dec	LPR Ω cm ²
0	0	-494	2.66×10^{-6}	193	204	2.05×10^4
250	30	-554	5.83×10^{-7}	153	178	7.23×10^4

When carbon is immersed in dam water, the corresponding corrosion potential is -494 mV, and when it is immersed in the inhibitor solution, the corrosion potential is shifted to -552 mV, i.e., the corrosion potential is shifted to the cathodic side. From the Tafel slopes, it is observed that the shift in the anodic slope (from 193 to 153 mV/dec) is higher than the shift in the cathodic slope (from 204 to 178 mV/dec). Hence, it can be concluded that the same inhibitor system mainly controls the anodic reaction [20]. The corrosion current value and LPR value for dam water are 2.66×10^{-6} A/cm²ohm cm², 2.05×10^4 ohm cm².

In presence of the inhibitor system, the corrosion current value is declined to 5.75×10^{-7} A/cm² and the LPR value is raised to 7.53×10^4 ohm cm². The fact that the LPR value increases with decrease in corrosion current implies the absorption of the inhibitor on the metal surface to block the active sites and inhibit corrosion and reduce the corrosion rate [21].

Analysis of AC impedance spectra

The formation of film on the metal surface has been investigated using AC impedance spectra. When a protective film is formed, it enhances the charge transfer resistance (R_t) and decreases the double layer capacitance (C_{dl}) value [22]. Nyquist representations of carbon steel in dam water in the absence and presence of the inhibitor system are shown in Figure 2.

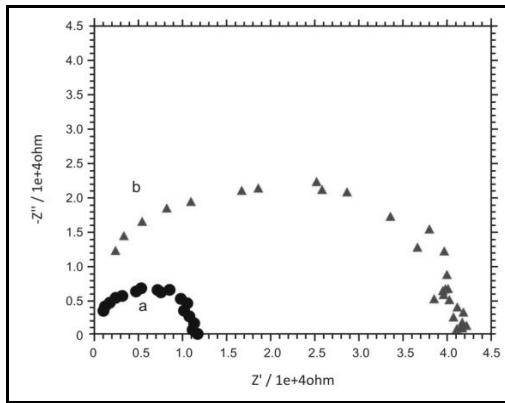


Figure 2. AC impedance spectra of carbon steel immersed in various test solutions a) dam water b) dam water containing 250 ppm of HS and 30 ppm of Ni²⁺

From the plots, it is clear that the impedance response of carbon steel was significantly altered after addition of the inhibitors. The impedance diagrams obtained have an almost semicircular appearance. This shows that the corrosion of carbon steel in aqueous solution is mostly controlled by a charge transfer process [23]. The deviation from the perfect semicircle shape (depression) is due to the frequency dispersion of interfacial impedance. This anomalous behavior is due to the inhomogeneity of the metal surface arising from surface roughness or interfacial phenomena [24]. The AC impedance parameters, namely charge transfer resistance (R_t) and double layer capacitance (C_{dl}) are given in table 4.

Table 4: Impedance parameters of carbon steel in dam water in the presence and absence of inhibitor obtained by AC impedance method

HS (ppm)	Ni ²⁺ (ppm)	R_t Ω cm ²	C_{dl} F/cm ² .
0	0	1.02×10^4	8.33×10^{-10}
250	30	4.02×10^4	1.76×10^{-10}

When carbon steel is immersed in dam water, R_t value is $1.02 \times 10^4 \Omega$ cm² and C_{dl} value is 8.33×10^{-10} F/cm². When 250 ppm of HS and 30 ppm of Ni²⁺ are added to dam water, R_t value increases from $1.02 \times 10^4 \Omega$ cm² to $4.20 \times 10^4 \Omega$ cm² and the C_{dl} decreases from 8.33×10^{-10} F/cm² to 1.96×10^{-10} F/cm². This confirms the formation of protective film on the surface of the metal.

Analysis of FTIR spectra

FTIR spectrometer is a powerful instrument used to analyze the type of bonding for organic inhibitors adsorbed on the metal surface [25]. FTIR spectrum (KBr) of pure HS is given in Figure 3a. The peak at 2932.02 cm^{-1} is due to C–H stretching frequency. The S=O stretching frequency occurs at 1193.21 cm^{-1} and S–O stretching frequency appears at 1066.16 cm^{-1} . The bands at 1466.15 cm^{-1} and 795.08 cm^{-1} are due to bending C–H of methyl and methylene groups [26]. The FTIR spectrum of the film scratched from the surface of the metal after immersion in the dam water, for one day, in presence of the inhibitor is shown in Figure 3b. The S=O and S–O stretching frequencies have decreased from 1193.21 cm^{-1} , 1066.16 cm^{-1} respectively to 1120.13 cm^{-1} , 1020.80 cm^{-1} respectively. These shifts indicate that the electron clouds of S=O and S–O are shifted towards Fe²⁺ resulting in the formation of Fe²⁺–HS complex on the anodic sites of the metal surface. The peak at 658.07 cm^{-1} is due to Ni–O stretching. The peak at 3463.57 cm^{-1} is due to –OH stretching.

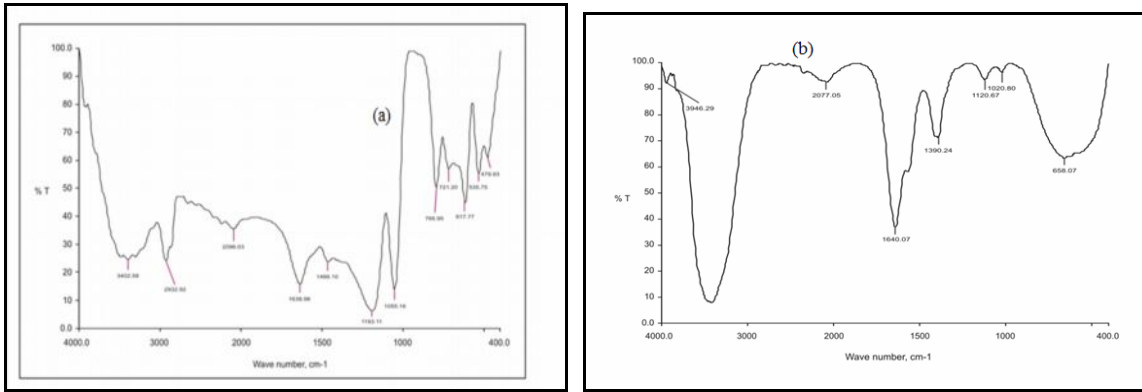


Figure 3 a). FTIR spectrum of pure HS. b) FTIR spectrum of film formed on metal surface after immersion in dam water containing 250 ppm of HS and 30 ppm of Ni²⁺

SEM Analysis of metal surfaces

SEM images of carbon steel after immersion in dam water for one day in the absence and presence of inhibitor system are given in figure 4(b) and 4(c) respectively. The SEM micrograph of the polished carbon steel surface (control) in figure 4(a) shows the smooth surface of the metal and this indicates the absence of any corrosion products on the metal surface. The SEM micrograph of the carbon steel surface immersed in dam water in figure 4(b) shows the roughness of the metal surface, which confirms the corrosion of carbon steel in dam water. Figure 4(c) indicates that in the presence of 50 ppm of Ni²⁺ and 250 ppm of HS mixture in dam water, the surface coverage increases, which in turn results in the formation of insoluble complex in the surface of the metal (Ni²⁺-HS inhibitor complex). The surface is covered by a thin layer of inhibitors that minimize the dissolution of carbon steel [27, 28].

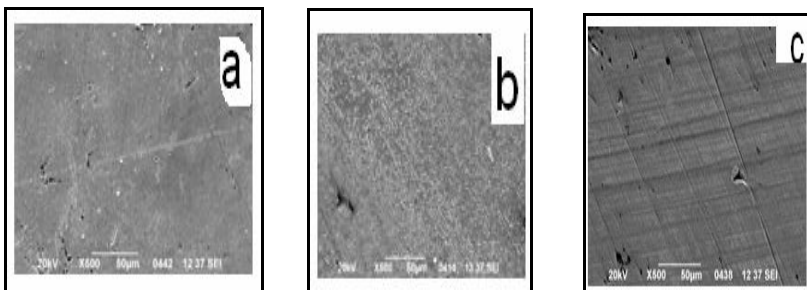


Figure 4. SEM micrographs of
a) Polished carbon steel (control)
b) Carbon steel immersed in dam water
c) Carbon steel immersed in dam water containing 250 ppm of HS and 30 ppm of Ni²⁺

Surface examination by EDAX

EDAX spectra were used to determine the elements present on the carbon steel surface before and after exposure to the inhibitor solution [29]. The objective of this section is to confirm, the results obtained from chemical and electrochemical measurements, when a protective surface film of inhibitor is formed on the metal surface. To achieve this goal, EDAX examinations of the metal surface were performed in the absence and presence of an inhibitor system. In Figure 5 spectrum (a) is the EDAX analysis of carbon steel surface immersed in dam water. The analysis indicates the presence of corrosion products elements (Fe, O and C). In Figure 5 spectrum (b) shows the EDAX analysis of carbon steel immersed in dam water containing 250 ppm of HS and 30 ppm of Ni²⁺. The analysis shows the presence of (Ni and S), which could be due to the presence of HS and Ni on the metal surface, resulting in the formation of a protective film.

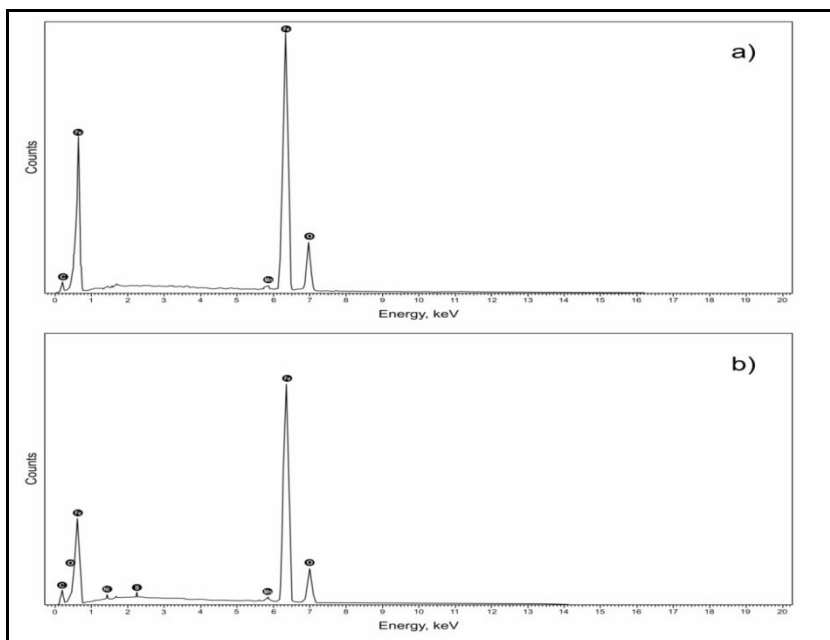


Figure 5. EDAX analysis of a) Carbon steel immersed in dam water b) Carbon steel immersed in dam water containing 250 ppm of HS and 30 ppm of Ni²⁺.

Conclusion

The present study leads to the following conclusions:

From the weight loss study, it is clear that this inhibitor system (concentration 250 ppm of HS and 30 ppm of Ni²⁺) has 85% IE in decreasing the corrosion of carbon steel in dam water. A synergistic effect exists between Ni²⁺ and HS. Polarization study reveals that HS–Ni²⁺ system functions as anodic inhibitor controlling the anodic reaction predominantly and to some extent controlling the cathodic reaction. AC impedance spectra confirm that a protective film is formed on the metal surface. FTIR spectra reveal that the protective film consists of Fe²⁺–HS complex and Ni(OH)₂. The SEM micrographs, and EDAX analysis corroborate the formation of protective layer on the metal surface.

References

1. Aditya Kumar Singh and Eno E. Ebenso, A New Corrosion Inhibitor for Corrosion of Mild Steel in Hydrochloric Acid Solution, *Int. J. Electrochem. Sci.*, 2013; 8: 10903 – 10909.
2. Singh A K and Quraishi M A, adsorption of isoniazid derivatives at mild steel, *Mater. Chem. Phys.*, 2010; 123: 666-677.
3. Singh AK and Quraishi MA, Inhibitive effects of 5- substituted isatin-based Mannich bases on the corrosion of mild steel in hydrochloric acid solution, *J. Appl. Electrochem.*, 2010; 40:1293-1306.
4. Oliver W X and Gonclaves R S, Electrochemical evidence of the protection efficiency of Furfural on the corrosion process of low carbon steel in ethanolic medium, *J. Braz. Chem. Soc.* 1992; 3:92-94.
5. Obot IB, Obi-Egbedi NO and Umoren SA, Adsorption Characteristics and Corrosion Inhibitive Properties of Clotrimazole for Aluminium Corrosion in Hydrochloric Acid, *Int. J. electrochem. Sci* 2009; 4: 863-877.
6. Lj M Vracar and Drazic D M, Adsorption and corrosion inhibitive properties of some organic molecules on iron electrode in sulfuric acid, *Corros. Sci.*, 2002;44: 1669-1680
7. Prakash Rajesh D, Kumar Singh and Ranju Kumar, Corrosion inhibition of mild steel in 20% HCl by some Organic compounds, *Indian J. chem.Technol.* 2006; 13: 555-560.
8. Manickavasagam R, Jeya Karthik K, Paramasivam M and Venkatakrishna Iyer S, Poly (Styrene sulphonic acid) - doped poly aniline on mild steel in acid Media, *Anti Corros. Methods. Mater.* 2002; 49: 19-26.

9. Aliev TA, Influence of salts of Alkyl phenol Sulphonic acid on the corrosion of ST3 steel in HCl-Kerosene systems, *Mat. Sci.*, 2008; 44: 69-74.
10. Shakkthivel P and Vasudevan T, Acrylic acid-diphenylamine sulphonic acid copolymer threshold inhibitor for sulphate and carbonate scales in cooling water systems, *Desalination*, 2006 ; 197: 179-189.
11. C. Mary Anbarasi and Susai Rajendran, , “Inhibition of corrosion of carbon steel by Heptane sulphonic acid–Zn²⁺ system”, *J. Electrochem. Sci. Engg.*, 2(1), (2012) 1-18.
12. G. Wranglen, Introduction to Corrosion and protection of Metals (Chapman & Hall, London), (1985) 236.
13. Mars G. Fontana, Corrosion Engineering, TATA McGraw-Hill publishing company Limited, New Delhi, Third edition, (2006) 171.
14. C. Mary Anbarasi and Susai Rajendran, “Surface protection of carbon steel by Hexanesulphonic acid–Zinc ion system”, *ISRN Corrosion*, (2014) 1-8.
15. K. Anuradha, R. Vimala, B. Narayanasamy, J. Arockia Selvi and Susai Rajendran, “Corrosion inhibition of carbon steel in low chloride media by an aqueous extract of hibiscus rosa-sinensis linn”, *Chem. Engg. Commn.*, vol. 195, (2008) 352-366.
16. C. Mary Anbarasi, Susai Rajendran, B. Narayanasamy and A. Krishnaveni, “Surface analysis of inhibitor film formed by Butane sulphonic acid –Zn²⁺ system on carbon steel in aqueous medium” *Asian J. Chem.*, Vol. 24, (2012) 5029-5034.
17. J. Sathiyabama, Susai Rajendran and J. Arockia Selvi, “Eriochrome Black T as corrosion inhibitor for carbon steel in well water”, *Bul. Electrochem*, vol. 22, (2006) 363-370.
18. J.Arockia Selvi, Susai Rajendran and J.Jeyasundari, “Analysis of nano film by atomic force microscopy”, *Zastita Materijala*, vol. 50, (2009) 91-98.
19. V. Johnsirani, J. Sathiyabama, Susai Rajendran, and A. Suriya Prabha, “Inhibitory Mechanism of Carbon Steel Corrosion in Sea Water by an Aqueous Extract of Henna Leaves”, *ISRN Corrosion*, (2012) 1-9.
20. F.N. Grosser and R.S. Gonclaves, “Electrochemical evidence of caffeine adsorption on zinc surface in ethanol”, *Corros. Sci.*, vol. 50, (2008) 2934 -2938.
21. S. Martinez and M. Mansfeld-Hukovic, “A nonlinear kinetic model introduced for the corrosion inhibitive properties of some organic inhibitors”, *J. Appl. Electrochem.*, vol. 33, (2003) 1137 -1142.
22. M. Elayyachy, A. El Idrissi and B. Hammouti, “New thio-compounds as corrosion inhibitor for steel in 1M HCl”, *Corros. Sci.*, vol. 48, (2006) 470-2479.
23. S.K. shukla and M.A. Quarishi, “4-Substituted anilinomethylpropionate: New and efficient corrosion inhibitors for mild steel in hydrochloric acid solution”, *Corros. Sci.*, vol. 51, (2009) 1990-1997.
24. C. Mary Anbarasi and Susai Rajendran, “Electrochemical and AFM Study of Corrosion inhibition of Carbon Steel by Octanesulphonic acid-Zinc Ion System “, *In. J. current Engg. Technol.*, (2013) 2088-2093.
25. A. Lalitha, S. Ramesh and S. Rajeswari, “Surface protection of copper in acid medium by azoles and surfactants”, *Electrochimica. Acta, Electrochimica. Acta*, vol. **51**, (2005) 47–55.
26. Robert M Silverstein and X. Francis, Webster Spectrometric Identification of Organic Compounds, VI Edition, Wiley Student Editon, (2007) 108.
27. C. Mary Anbarasi and Susai Rajendran, “Investigation of the inhibitive effect of octanesulfonic acid-zinc ion system on corrosion of carbon steel”, *Chem. Engg. Commn.*, vol. 199, (2012) 1596-1609.
28. Benita Sherine, A. Jamal Abdul Nasser and S.Rajendran, “Inhibitive action of hydroquinone-Zn²⁺ System in controlling the corrosion of carbon steel in well water”, *In. J. Eng. Sci. Technol.*, vol. 2 (2010) 341-357.
29. H.Amar, J.Benzakair, A. Derja, D.Vilemin, B.Moreau and T.Tounsi, “Synergistic corrosion inhibition study of Armco iron in sodium chloride by piperidin-1-yl- phosphonic acid–Zn²⁺ system”, *Corros.Sci.*,50, (2008) 124-129.
