

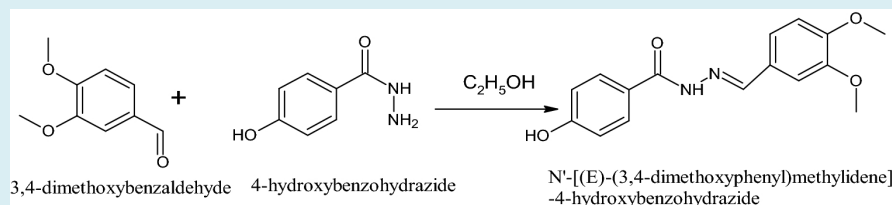
Thermodynamic and Electrochemical Aspects of Green Corrosion Inhibitors in Acidic Media at Mild Steel Surfaces

Dr. Rakesh Kumar Dubey

Assistant Professor, Government College, Gangapur City, Rajasthan, India

ABSTRACT

Mild steel (a low carbon steel) is an affordable engineering material used for many purposes in various environments including mild acidic environment with some precautions. The corrosion behaviour of mild steel (MS) in 0.5 M H₂SO₄ and 0.5 M HCl, in the temperature range (303–323 K) without and with the inhibitor N-[(3,4-dimethoxyphenyl)methyleneamino]-4-hydroxy-benzamide (DMHB), was investigated using Potentiodynamic polarization and Electrochemical impedance spectroscopy (EIS) techniques supplementing with surface characterization study using scanning electron microscope (SEM) and atomic force spectroscopy (AFM). Experimental observations were found to be in agreement with Density functional theory (DFT) calculations. The inhibition efficiency increases with increase in DMHB concentration and showed maximum inhibition efficiency of 86% in 0.5 M H₂SO₄ and 81% in 0.5 M HCl, respectively, at concentration of 3×10^{-3} M at 303 K. The inhibition efficiency of DMHB obtained relatively at its lower concentration (3×10^{-3} M) compared to other reported related compounds confirms its potential towards corrosion inhibition.



The variation in the kinetic and thermodynamic parameters indicated physisorption of DMHB on MS and its mixed type inhibitive action followed Langmuir's isotherm model. DFT calculations go along with the experimental results, signifying the potential corrosion inhibition behaviour of DMHB for MS in both the acid media.

KEYWORDS: mild steel, thermodynamic, electrochemical, green corrosion, inhibitors, acidic media

INTRODUCTION

Corrosion is metal degradation as a result of contact with aqueous corrosive surroundings (air, moisture, or soil; through direct chemical or electrochemical reaction to form noble compounds. As defined by the International Union of Pure and Applied Chemistry, corrosion is an interfacial material (polymer, metal, concrete, wood, and ceramic) reaction (irreversible) with its environment, which results in material consumption or in dissolution into the material of an environmental component. Corrosion is an environmental threat with economic, conservation, and safety impacts in various engineering applications

such as building construction, chemical, automobile, mechatronics, metallurgical, and medical. Various forms of material corrosion under different environments have been discussed. Thus, there is a need to develop novel techniques and methods of tackling this dangerous phenomenon from existing prominent ones, which are protective coatings and linings, cathodic/anodic protection, and corrosion inhibitors. However, the results of numerous research conducted in anticorrosion material applications in previously mentioned engineering fields revealed using corrosion inhibitors as the most effective and

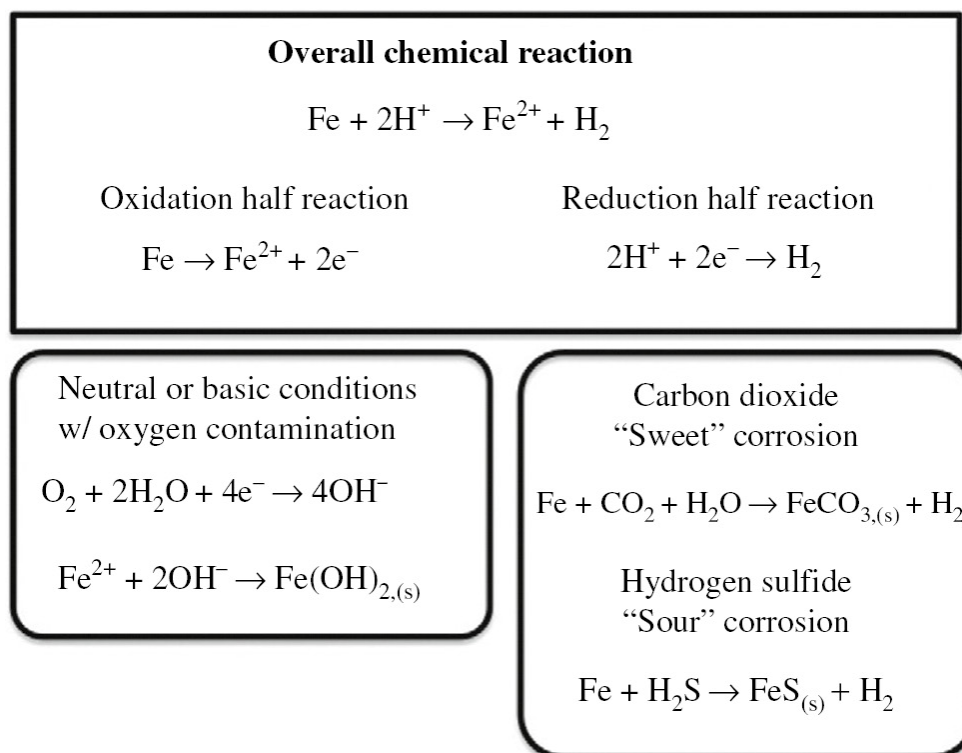
How to cite this paper: Dr. Rakesh Kumar Dubey "Thermodynamic and Electrochemical Aspects of Green Corrosion Inhibitors in Acidic Media at Mild Steel Surfaces" Published in International Journal of Trend in Scientific Research and Development (ijtsrd), ISSN: 2456-6470, Volume-6 | Issue-4, June 2022, pp.519-524, URL: www.ijtsrd.com/papers/ijtsrd50128.pdf



Copyright © 2022 by author(s) and International Journal of Trend in Scientific Research and Development Journal. This is an Open Access article distributed under the terms of the Creative Commons Attribution License (CC BY 4.0) (<http://creativecommons.org/licenses/by/4.0>)



simple approach of preventing deleterious [1,2]
degradation of metals and alloys in corrosive media.



Chemical reactions of the corrosion process

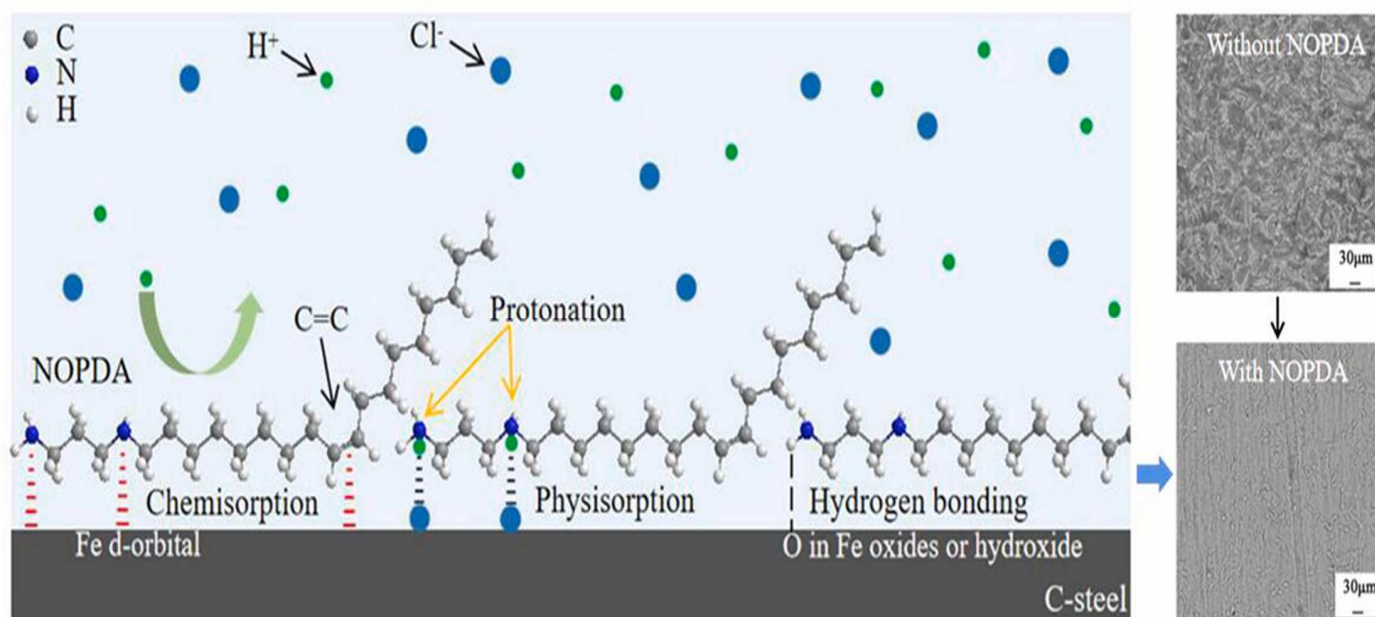
One of the most widely used methods of protecting metals against corrosion is the use of inhibitors. [3,4] They act by adsorption on the metal surface. The effectiveness of the corrosion inhibitor has been evaluated by several methods; polarization technique (Tafel line); electrochemical impedance and mass loss spectroscopy (immersion test) in acidic media. Green corrosion inhibitors are of interest because there has been an increase in environmental awareness and a change in regulations that restrict regular corrosion inhibitors due to their toxicity. [5,6] Natural products are a good source of green corrosion inhibitors, where most of their extracts containing the necessary elements such as O, C, N, and S, which are active in organic compounds, assist in adsorption of these compounds on metals or alloys to form a film that protects the surface and hinders corrosion. Numerous natural products and their application in different processes, especially in steel reinforcement embedded in concrete, are discussed. Development of green chemistry and green chemical technologies offers novel synthetic methods for ionic liquids, which are considered as new corrosion green inhibitors, and their mechanism of adsorption, how these green inhibitors act in different media, and their protective role for different metals and alloys.[7,8]

Discussion

Mild steel is also used in numerous applications as flow lines, constructions of tanks, and petroleum refinery equipment owing to its simple fabrication process and low cost. Yet, both metals are susceptible to corrosion and degradation, particularly in acidic media. HCl is the most widely used acid in metal pickling and descaling processes. Organic inhibitors, whose molecules appear to adsorb on the metal surface, are among the best methods to protect metals from corrosion. Although their application seems an effective, easy technique, most of them are non-biodegradable and vastly poisonous for human beings and the environment. So far, for environmental and safety reasons, much consideration has been focused on finding low-priced non-toxic green inhibitors. Many research studies have attempted to evaluate naturally occurring plant extracts as corrosion inhibitors for different metals. Their efficiencies were estimated to be around 55-90% in acidic media.[9,10]

DEAE (diethyl-aminoethanol) could promote the emulsification and dissolution of NOPDA in aqueous solution and therefore facilitate its adsorption onto carbon steel surface. The weight loss experimental results showed that the adsorption of the FFA inhibitor onto metal surface was endothermic and conformed to Langmuir isotherm model.[11,12] Electrochemical impedance spectroscopy (EIS) analysis proved that a protective film was formed on the surface of carbon steel to prevent the transfer of charge. Contact angle measurements indicated that the film formed on the surface of the carbon steel was hydrophobic. According to X-ray photoelectron spectroscopy

(XPS) analyses and thermodynamic calculation, it is inferred that the adsorption mechanisms mainly involved chemisorption, electrostatic attraction and hydrogen bonding. [13,14]



Corrosion is metal dissolution caused by interaction with acidic corrosive environments by direct chemical reactions resulting from the formation of noble compounds. As described by the International Union of Pure and Applied Chemistry, corrosion is the irreversible reaction of an interlayer (polymer, metal, concrete, wood, or ceramic) with the environment leading to ingestion or dissolution of the environmental component material. Corrosion is an environmental hazard with economic, preservation and safety consequences in many areas such as manufacturing, chemicals, automobiles, mechatronics, metallurgy, and medical applications. Different forms of material degradation have been addressed in different environments. [15,16] There is also a need to create new approaches and methods to counter these hazardous phenomena from the known factors, such as coatings, defensive bushings, cathodic/anodic protection, and sealants. However, the results of studies conducted on anti-corrosion textile applications in the above engineering fields showed the use of corrosion inhibitors to be the most gentle and easy way to prevent the degradation of metals and alloys in corrosive media. The corrosion inhibition efficiency of untested organic corrosion inhibitors has been linked to the availability of nitrogen, oxygen, phosphorous and sulfur atoms in organic compounds that have both protective effects and corrosion inhibiting potential. The high-ranking corrosion inhibitors were cited to be green oxygen corrosion inhibitors that display their inhibitory effect via hydrolysis or chemical absorption at the mineral solution interface by removing surface water molecules to form a dense barrier film. The incidence of a coordinate covalent bond is subject to the interaction between the lone pair and the electrons available in untested organic corrosion inhibitor molecules with vacant steel orbitals. However, the combined adsorption on the metal surface using the pi-bond formation is outperformed as a final result of the interference of the p electron with the three-dimensional vacant orbital of the iron atom due to the availability of N, O, and S atoms and the double bonds in an organic compound. [17,18]

Results

During the acidizing procedure a number of organic compounds serve as CIs for steels, including acetylenic alcohols, aldehyde-containing aromatic compounds, imminium salts, nitriles, triazoles, thiocyanates, pyridine and its derivatives or salts, quinoline derivatives, thiourea derivatives, quaternary salts, thiosemicarbazide, quinoline derivatives, thiourea derivatives, thiosemicarbazide derivatives, nitriles, imminium-based salts, and nitrogen heterocycles. Nitrogen and acetylenic alcohol molecules appear to form a film on metal surfaces and to be able to delay the metal breakdown (anodic response) and production of hydrogen (a cathodic reaction). Propargyl alcohol is soluble in acidic liquids, however, with an ever larger length of carbon chain, the solubility of other acetylenic alcohols reduces. In conjunction with quaternary ammonium surfactants, the solubility of these acetylenic alcohols can be improved. The industrial supply and cost efficiency of acetylenic alcohols was commonly used. The normal CI for acidification is generally propargyl alcohol, with the synergistic influence of other compounds often substantial. Propargyl alcohol, its salts, cinnamaldehyde, and aromatic compounds such as quaternary pyridinium chloride are the most widely encountered CIs in the natural resource industry. In 1984 an outline of the use of CIs for acid media. [19]

The effects of Alhagi Maurorum, Morusnigra and Apricot leaves extracts on the corrosion of steel in aqueous 0.5M H₂SO₄ were investigated by weight loss, thermometric, potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) techniques. The corrosion rate of steel was measured in absence and presence of different concentrations of the three extracts, and the percentage inhibition of the different solutions were determined using the four techniques. Effects of solvent of extraction on the inhibition efficiencies of the three extracts were discussed. Theoretical Kinetic-Thermodynamic model of adsorption of the inhibitors on the metal surface was tested to fit the experimental data of the three extracts. The activation parameters of the corrosion reaction of steel with H₂SO₄ in the absence and the presence of the three extracts were determined.

The corrosion inhibition properties of a synthesized hydrazone derivative namely, 1 - (4 -isopropyl phenyl) - 2 - (2,4 -dinitrophenyl) (HYD (iso)) on API 5L -X60 carbon steel (CS) in 1.0 M HCl solution were evaluated by chemical, electrochemical, X -ray photoelectron spectroscopy (XPS) and theoretical studies. The obtained results revealed that the tested compound acted as a good corrosion inhibitor with inhibition efficiency of 96.32% at a concentration of 5×10⁻³ M. The polarization technique indicated that the HYD (iso) belonged to mixed -type inhibitors, preventing simultaneously anodic and cathodic reactions. The binding between the HYD (iso)'s molecule and CS surface follows a Langmuir adsorption type model and its inhibition mechanism is assisted by physical and chemical interactions. Scanning electron microscope (SEM) and contact angle analyses were performed to examine the surface morphology of inhibited and uninhibited samples. Additionally, theoretical studies using Density Functional Theory (DFT) and molecular dynamics (MD) simulation were performed to explore the most reactive sites of the hydrazone molecule and its adsorption mechanism.

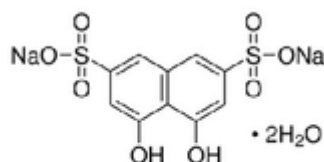
Conclusions

HYD (iso) acted as a good corrosion inhibitor and its effectiveness increases by concentration. The adsorption mode of HYD (iso) on the CS surface obeys to Langmuir adsorption isotherm. The spontaneity of adsorption was justified by negative values, and their value reveals a combination of physical and chemical interactions. Electrochemical results indicated that the hydrazone derivative acted as a mixed -type inhibitor, also, the increment in the values of R_p with increasing concentration showed the effective adsorption of inhibitor on the surface. SEM, contact angle and XPS analysis explained well enough why the investigated compound is an efficient corrosion inhibitor and how it exerts its corrosion inhibition effect. Computational calculations supported experimental findings by providing useful theoretical insights. The results indicated that the presence of nitro groups makes the tested compound an excellent corrosion inhibitor, thereby providing a highest inhibition efficiency compared to previously studied hydrazone derivatives.

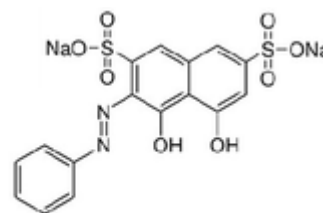
Also,

- DMHB (N-[(3,4-Dimethoxyphenyl)Methyleneamino]-4-Hydroxy-Benzamide) acts as a mixed inhibitor.
- Percentage inhibition efficiency increased with the increase in DMHB concentration and decreased with temperature increase.
- The maximum inhibition efficiency shown by DMHB at its optimum concentration (3 × 10⁻³ M) was about 90%.
- The corrosion rates obtained by Tafel extrapolation technique are in agreement with EIS results.
- Adsorption of DMHB on MS surface in acid media follows Langmuir adsorption isotherm.

CA (chromotropic acid) and CR (chromotrope 2R) dyes act as proficient inhibitors for the corrosion of mild steel in 1.0 M H₂SO₄ solution. Under similar conditions, the %IE of CR was found to be slightly higher than that of CA. The %IEs were increased with the inhibitor concentrations, while they decreased with rising temperature.



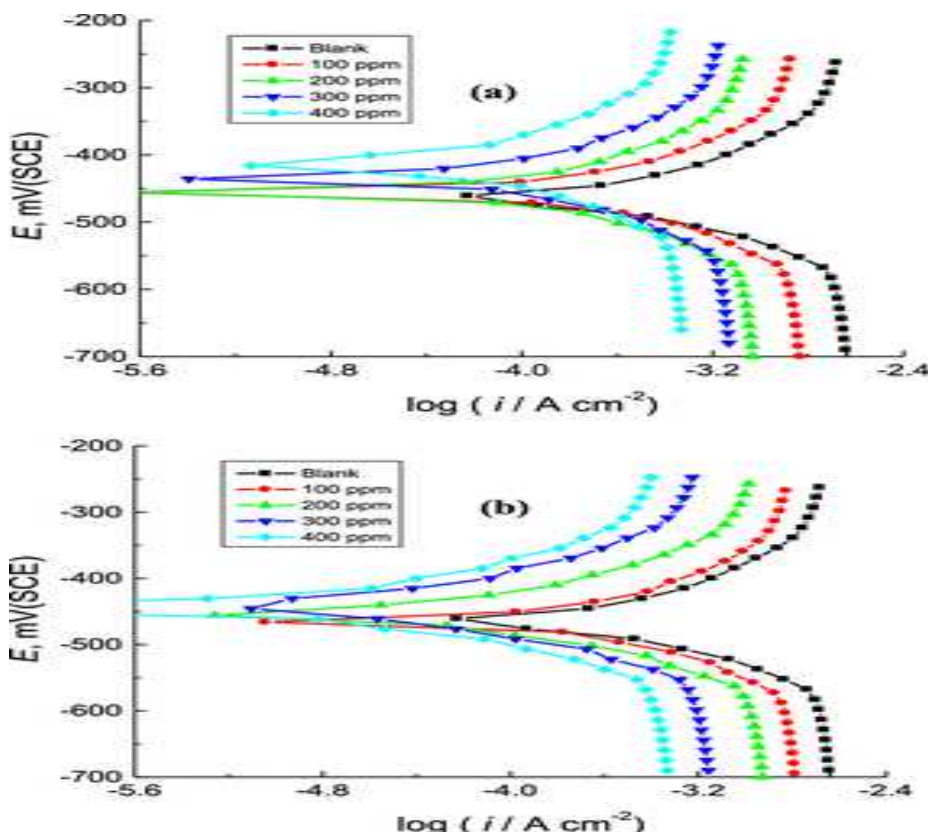
Chromotropic acid disodium salt dihydrate (CA)



Chromotrope 2R disodium salt (CR)

The examined inhibitors acted as mixed-type inhibitors with anodic prevalence. The obtained impedance spectra signified that the mild steel corrosion in sulfuric acid was managed by the charge transfer process. The SEM images (scanning electron microscopy) revealed a wide coverage of the examined inhibitor molecules on the steel surfaces. Thus, the acquired high %IEs of the examined inhibitors were interpreted by strong adsorption of

the organic molecules on the mild steel surfaces. This adsorption was found to follow the Langmuir adsorption isotherm. The evaluated thermodynamic and kinetic parameters supported that the nature of such adsorption was mainly physical.



PDP curves for the corrosion of mild steel in 1.0 M H_2SO_4 solution without and with various concentrations of: (a) CA and (b) CR

Results obtained from all employed techniques were set to accord with each other. The mechanisms of both corrosion of mild steel in sulfuric acid solutions and its inhibition by the tested organic dyes were also discussed. Finally, from the literature it was found that the examined organic dyes exhibited higher %IEs (inhibition efficiencies) than other reported organic dyes for the corrosion of mild steel in sulfuric acid solutions.

The influence of *Hyssopus officinalis* (L), (Hyssop), or (Zoufa) on the corrosion of mild steel in 0.5 M HCl solution was tested through open circuit potential-time measurements (OCP), potentiodynamic polarization, as well as electrochemical impedance spectroscopy (EIS) techniques. Hyssop leaf extract exhibited good inhibition efficiency in HCl solutions for steel surfaces. [20]

References

- [1] Vasantha Jothi R, Maheshwari P, Saratha R, Senthil Vadivu D. A study on Inhibitive action of *Bauhinia racemosa* Lam. Extract as Green Corrosion inhibitor for Mild steel in Hydrochloric acid medium. *Asian J. Research Chem.* 2017; 10(5): 611-615.
- [2] Agrawal R, Namboodhiri TKG. The inhibition of sulphuric acid corrosion of 410 stainless

steel by thioureas. *Corrosion Science.* 1990; 30 (1): 37–52.

- [3] Quraishi MA, Ahmad S, Ansari MA. Inhibition of Steel Corrosion by Some New Triazole Derivatives in Boiling Hydrochloric Acid, *British Corrosion journal.* 1997; 32 (4), 297-300.
- [4] Kertit S, Hammouti B. Corrosion inhibition of iron in 1M HCl by 1-phenyl-5-mercapto-1,2,3,4-tetrazole. *Applied Surface Science.* 1996; 93(1): 59-66.
- [5] Zucchi F, Trabaneli G, Fonsati M. Tetrazole derivatives as corrosion inhibitors for copper in chloride solutions. *Corrosion Science.* 1996; 38(11): 2019-2029.
- [6] Kertit S, Hammouti B, Taleb M, Brighli M. Peptidic compounds as corrosion inhibitors of iron in acid chloride solution. *Bull. Electrochem.* 1997; 13 (6): 241-244.
- [7] Fatiha C, Noureddine B, Mokhtar S, Amira O, Adel T, Souhila B, Hanane L, Abdellatif M, Noura M. Effects of Temperature on Microstructure and Corrosion behavior of API N80 Carbon Steel. *Asian J. Research Chem.* 2021; 14(1):61-66.

- [8] Quraishi MA. Thioamidines A novel class of corrosion inhibitors. *British corrosion Journal*. 1999;34: 220-24.
- [9] Bentiss F, Bouanis M, Mernari B, Traisnel M, Lagrenee M. Effect of iodide ions on corrosion inhibition of mild steel by 3,5-bis(4-methylthiophenyl)-4H-1,2,4-triazole in sulfuric acid solution. *Journal Of Applied Electrochemistry*. 2002; 32 (6): 671-678
- [10] Benmessaoud Left D, Zertoubi M, Irhzo A, Azzi M. Revue:Huiles et Extraits de plantes comme inhibiteurs de corrosion pour différents métaux et alliages dans le milieu acide chlorhydrique. (Review: oils and extracts plants as corrosion inhibitors for different metals and alloys in hydrochloric acid medium). *Journal of Materials and Environmental Science*. 2013; 4 (6) :855-866.
- [11] Idenyi NE, Nwofe PA, Idu HK. Influence of Moringa Oleifera and Psidium Quajava Leaves Extract on the Corrosion Susceptibility of Mild Steel in an Alkaline Medium, *Journal Of Applied Sciences Research*. 2015; 11(22): 158-163.
- [12] Lamoureux JJ. Précis de corrosion. 2e édition Editions MASSON, Laval (Québec): Beauchemin; Paris: Masson, (Impr. au Canada) Mention d'édition. 1994.
- [13] Thangavelu C, Patric Raymond P, Rajendran S, Sundaravadivelu M. Influence of Chloride Ion on the Corrosion Inhibition Efficiency of the ATMP - Zn²⁺ System. *Asian J. Research Chem*. 4(3): 2011; 4(3): 402-405
- [14] Kelly R G, Scully J R, Shoemith D, Buchheit R G. *Electrochemical Techniques in Corrosion Science and Engineering*. New York :Marcel Dekker Inc. 2003.
- [15] Deepa T, Thangavelu C, Sekar M, Sudhakaran R. Corrosion Inhibition of Carbon Steel in RO water Using Trisodium Citrate - Zn²⁺ System. *Asian J. Research Chem*. 2015; 8(10): 613-617.
- [16] Arockiasamy P, Thenmozhi G, Jaya Santhi R. Evaluation of Corrosion Resistance of Electroless Ni-P/Ni-W-P Double Layer Coatings on 6061 Aluminium Alloy. *Asian J. Research Chem*. 2014; 7(6): 551-557.
- [17] Perumal S, Sayee Kannan R, Muthumanickam S, Elangovan A, Muniyappan N. Comparative study of green corrosion inhibition effect on mild steel in different acid medium by Laburnum waterier Vossileaves extract. *Asian J. Research Chem*. 2018; 11(2):253-261.
- [18] Gyorik GL, Mészros G, Lengyel B, Lendvay G. Electrochemical and quantum chemical studies on the formation of protective films by alkynols on iron. *Corrosion Science*. 2003; 45(8):1685-1702.
- [19] Subha R, Saratha R. Corrosion Inhibition and Adsorption Properties of African marigold for the Corrosion of Mild Steel in Hydrochloric acid. *Asian J. Research Chem*. 2012; 5(3): 390-396.
- [20] Rakesh J, Karan S, Nayana B. Corrosion Inhibition of Zinc in Hydrochloric Acid by Vanillin, Phenyl Thiourea and N-Allyl Thiourea. *Asian J. Research Chem*. 2014; 7(12): 1062-1064.