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Synthesis of a novel polymeric corrosion inhibitor and investigation of its improvement by the addition of a ceramic powder extracted from corn cob

ABSTRACT

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A new anti-corrosion compound, Melamine Formaldehyde (MF), was formulated by the addition of proper amount of formaldehyde to melamine under specific conditions. This compound was mixed with a novel nano powder, which was extracted from corn cob ash containing SiO_2 particles, in order to improve its corrosion inhibition efficiency. This inhibitor provides a high level of protection for steel subjected to saline environments. The synthesized inhibitor works immediately with forming a dense protective layer and after adding the nano powder, its inhibition efficiency is improved. The electrochemical standard corrosion tests and the surface examination, using Scanning Electron Microscope (SEM) of steel specimen immersed in 3.5%Wt NaCl solutions with and without any inhibitor at room temperature, were carried out to investigate the inhibition behavior of the synthesized inhibitor. All of the results, which include the corrosion and electrochemical testing data, show that the tested corrosion inhibitor is generally effective and its efficiency gets better by adding the ceramic powder.

Keywords: *Corrosion inhibitors; Electrolyte; Concentration; Chemical nature; Film forming corrosion inhibitor; Corn cob ash.*

INTRODUCTION

In today's industrial world there is a focus on cost saving and there is a continuous effort for finding new innovative technologies and solutions to extend the working life of existing assets while lowering environmental impact. One of the biggest cost effective problems in industry is corrosion .As a large number of metallic materials continue to mature and maintain the operating costs continue to rise. So there has been an increased focus on finding environmentally friendly and innovative solutions to repel this problem.

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Among the several methods of corrosion control such as cathodic protection [1,2], anodic protection [3], coating [4] and alloying, the use of chemical inhibitors is often considered as the most effective and practical method of corrosion prevention. Corrosion inhibitors are widely employed in the petroleum industry to protect iron and steel equipment used in drilling, production, transport, and refining hydrocarbons [5, 6].

A corrosion inhibitor is a chemical additive which when added to a corrosive aqueous environment reduces the rate of metal wastage [7, 8]. It is widely accepted that most inhibitors, especially the organic ones, work by an adsorption mechanism. The resultant film of chemisorbed inhibitor is then responsible for protection either by physically blocking the surface from the corrosion environment, or by retarding the electrochemical processes [9-15]. The use of chemical inhibitors, to decrease the rate of corrosion processes, is quite varied. In the oil production and processing industries inhibitors have always been considered to be the first line of defense against corrosion [16-18].

Over the years, considerable efforts have been deployed to find suitable corrosion inhibitors of organic origins in various corrosive medias especially in petroleum industry; both in production and refining there are either oil soluble-water insoluble types or oil soluble-water dispersible compounds [19]. Most used additives are organic molecules however, inorganic molecules or polymeric material are also used. In spite of the highest efficiency of many organic molecules as corrosion inhibitors, the limitation of their solubility in water exhibits the main disadvantage for their uses. Therefore, water-soluble organic compounds have recently been considered and shown considerable inhibition behavior and are found to be a good replacement for oil based corrosion inhibitors [20]. Today with the advancement of science, methods of corrosion inhibition has also been much improved. Nano technology is the science that has made dramatic evolutionary in all areas of science. Innovative synthesis of materials using biological world as a source has sparked considerable interest among the material scientist all over the globe [21]. Corn cob waste is an important agricultural by-product mainly composed of cellulose, hemicelluloses and lignin [22]. It is a renewable source and a low-cost

material [23]. Nanotechnology holds great promise of revolutionizing materials use in the 21st century. Nanotechnology can be used to tap the enormous undeveloped potential that trees possess- as photochemical 'factories' that produce rich sources of raw materials using sunlight and water [24,25]. Therefore in this study the ameliorating role of a melamine formaldehyde resin in saline environment was investigated, and furthermore the improving effect of the ceramic nano powder on its corrosion inhibition was studied.

EXPERIMENTAL

Synthesis of resin

The MF resin is formed by the reaction of melamine and formaldehyde. The synthesis of MF resin comprises two stages. In the first stage formaldehyde and water were put in the reaction container and PH was adapted with formic acid or sodium hydroxide. Melamine was added and to commence the reaction, the mixture was heated and maintained at 80 °C to boost the formation of MF polymer. In order to intercept the solution from polymerizing too swiftly the pH was adjusted to between 8.0 – 8.5 by adding a few drops of sodium hydroxide at 48% concentration. The reaction was ended by rapidly cooling the mixture to 25 °C. The reaction kettle is shown schematically in Figure 1.
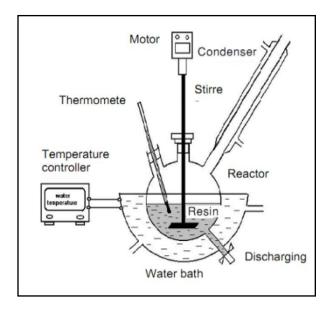

Fig.1. Schematic form of reaction kettle

In the next step the nano powder was prepared by calcifying the corn cob ash (CCA) in 650 °C for 2 hours in an electronic furnace, the chemical composition of CCA is presented in Table 1 [24].

In the next step the resin was mixed by 0.5 wt% of the nano powder. The powder was dispersed in the resin via ultrasonic homogenizer, for about 1 hour.

Table 1. Chemical composition of corn cob ash

Chemical constituents	composition(%)			Average
	sample1	sample2	sample3	
SiO_2	67.33	65.39	66.41	66.38
Al_2O_3	7.34	9.14	5.97	7.48
Fe_2O_3	3.74	5.61	3.97	4.44
CaO	10.29	12.89	11.53	11.57
MgO	1.82	2.33	2.02	2.06
SO_3	1.11	1.1	1.01	1.07
Na_2O	0.39	0.48	0.36	0.41
K_2O	4.2	4.92	5.64	4.92
$Total\ SiO_2 + Al_2O_3$	74.67	74.53	72.38	73.86

Sample and solutions preparation

3.5%Wt NaCl solution was prepared as test medium according to the ASTM-G44. In addition, two solutions of 3.5%wt NaCl with 500 ppm concentration of MF and MF with the nano powder resins were prepared as well. The mild steel specimen was used as the test sample; its chemical composition is mentioned in Table 2. All surfaces of the specimens for the electrochemical measurements were mounted except for one area. The exposed area was about $0.5 \times 0.5 cm^2$. The exposed area was polished by increasing grades of emery papers (400, 600, 800, 1000 and 2000 grit size), then was degreased with acetone and washed with distilled water. The specimens were dried and kept in a desiccator before exposed to the test solutions.

Table 2. The chemical composition of the specimen resulted from quantometer analysis

Fe	Mo	Cr	S
Base	0.01	0.106	0.01
Co	Cu	Nb	Al
0.017	0.083	0.005>	0.005>
Ni	Pb	W	V
0.075	0.05>	0.025>	0.005>
C	Si	Mn	P
0.211	0.335	1.27	0.013

Electrochemical measurements

The open circuit potential was measured in all solutions. AC impedance and potentiostatic polarization measurements were done in a three electrode electrochemical cell. All measurements were performed in 3.5%Wt NaCl solution at room temperature, in the absence and presence of 500 ppm MF and MF with the nano powder as well, against the saturated calomel electrode (SCE) and Pt electrode as the standard and counter electrode respectively. Potentiostatic polarization studies were carried out using potentiostat at a scan rate of 0.01Vs−1 under static condition. All these electrochemical measurements were done according to ASTM G59.

Electrochemical impedance tests were carried out at room temperature for all solutions by using the electrochemical impedance analyzer. Impedance tests were recorded with a 5 mV sinusoidal perturbation at frequencies between 100 kHz and 10 mHz at room temperature. The measurements were automatically controlled using Frequency Response Analyzer (FRA) software-Version 4.9.006. The impedance diagrams are presented as Nyquist plots.

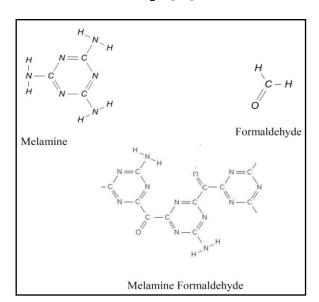***Scanning Electron Microscopy (SEM)***

The Scanning Electron Microscope was used to study the specimen surface morphology after immersion in blank and inhibitor containing solutions for about 24 hours.

RESULTS AND DISCUSSION

Chemical point of view

Corrosion phenomenon in the petroleum industry occurs in a two phase medium of water and hydrocarbon. It is the presence of a thin layer of water which leads to corrosion. Therefore rigorous elimination of water reduces the corrosion rate to a negligible value [19]. We should consider some treatments to omit this water phase or prevent its contact by metal parts, inhibitors do this for us. One class of inhibitors forms a film on the metallic surfaces and prevents corrosions.

MF resin is formed by blending melamine and formaldehyde, chemical structures of MF and its ingredients is shown in Figure 2. Melamine with a chemical formula of $C_3H_6N_6$ is an organic compound that consists of 66% nitrogen. It is produced in a large amount primarily for the manufacture of laminates, plastics, coatings, commercial filters, glues or adhesives, and dishware, and kitchenware [26]. The uniqueness of melamine lies on its three reactive amino groups, symmetrically positioned on an extremely stable triazine ring. And formaldehyde is the most simple, yet most reactive of all aldehydes, with the chemical formula of CH_2O [27].

Fig. 2. Chemical structure of melamine formaldehyde and its components

Heterocyclic compounds through owning heteroatoms such as nitrogen, sulfur and oxygen, and also because of their multiple bonds in their structure facilitate the molecule's adsorption on the metallic surfaces (Fe, Zn, Al, Mg, etc.)[28-33]. In this study a cyclic organic compound was synthesized as a corrosion inhibitor, which is bearing the heteroatom of N in its construction. The compound is being adsorbed over these heteroatoms by the metal surface and prevents the destructive effect of the aggressive saline medium. Besides of these atoms, aromatic ring systems, which are available in the structure of the compound, can also increase adsorption and consequently enhance inhibition efficiency of this compound with their π electrons. Furthermore, π electrons which are available in the various functional groups can also facilitate adsorption of corrosion inhibitors to the metal surface and increase their inhibition efficiency [34-35]. It has been proved that for most organic compounds the more the concentration increases the more the inhibit ability improves. This can be attributed to more molecules presented between the metal–water interfaces.

In this research we synthesized melamine formaldehyde (MF) from melamine and formaldehyde by polymerization. All compound's chemical structures are presented Figure 1. It is clear from the picture that MF resin has longer links than Melamine and Formaldehyde alone. Consequently, it can cover the surface better. To prove this claim the electrochemical corrosion tests were carried out and the results were recorded.

In today's industrial world there is a considerable effort to decrease the costs as much as possible. In order to gain this aim the scientific researchers have changed their approach to use the huge amount of agricultural wastages. By this explanation in this research we studied the improving effect of the nano powder, which was extracted from corn cob ash, on corrosion inhibition behavior of MF resin. By the addition of this nano powder to MF resin a very high improvement occurred. This powder already contains about 66.38 %SiO_2, and this amount of SiO_2 can cause the corrosion to be decreased. SiO_2 is a polar molecule, which has two oxygen atoms in its structure. This molecule can bond on the metal surfaces from its oxygen end. The cooperation between SiO_2 molecules and MF molecules can lead to the creation of more dense films on the

surface, which is the reason of corrosion inhibition of MF after the addition of the nano powder.

Polarization measurements

The OCP curves are shown in Figure 3. Clearly show that the OCP values changed to more noble values after adding 500ppm of MF inhibitor and this change was intensified after the addition of ceramic powder. It can be seen that after a specific time the potential started to get more positive and this can be a sign of film formation on the metal surface [36]. Figure 4 shows potentiostatic curves for carbon steel electrode in 3.5%wt NaCl solution with and without 500 ppm of MF and MF plus the nano powder. It is clear that the current density decreased both in the presence of MF and MF plus the nano powder.
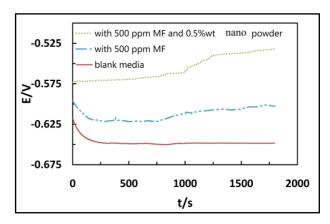

Fig. 3. Open circuit potential of carbon steel specimen in blank 3.5%wt NaCl solution, and in presence of 500 ppm MF and 500 ppm MF with 0.5%wt nano powder solution
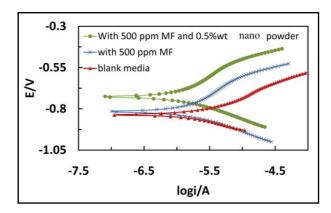

Fig. 4. Tafel polarization of carbon steel specimen in blank 3.5%wt NaCl solution, and in 500 ppm MF and 500 ppm MF with 0.5%wt nano powder solution

Values of free corrosion potential (E_{corr}), corrosion current density (i_{corr}), cathodic Tafel slope (b_c), anodic Tafel slope (b_a), surface coverage (θ), corrosion rate (CR) and inhibition efficiency *(%E)* for MF and MF with the nano powder in test solution are given in Table 3. The surface coverage (θ) was calculated from the following equation:

$$\theta = \frac{I^0{}_{corr} - I_{corr}}{I^0{}_{corr}} \qquad (1)$$

Where I_{corr} is the inhibited and $I^0{}_{corr}$ is the uninhibited corrosion current densities determined by the extrapolation of cathodic and anodic Tafel lines. The protection efficiency E% of this inhibitor was obtained from the following equation [37]:

$$E\% = \theta \times 100 \qquad (2)$$

According to Figure 4; A decrease in corrosion density with a slight shift of corrosion potential towards positive values was noted when MF resin was added. These changes were also arisen for MF, which contained the nano powder. Due to the decrease of corrosion current density there is a considerable decrease in corrosion rate, from 0.5 mm/y to 0.06 mm/y. The anodic and cathodic slopes didn't change so incredibly, which indicates that the mechanism of inhibition didn't change in the absence and the presence of corrosion inhibitor. In other words, the inhibitor decreases the exposed surface area for corrosion as well as not having an effect on the mechanism of carbon steel dissolution or hydrogen revolution reaction [38]. The increased value of R_p, with the presence of the inhibitors, indicates the adsorption of inhibitor molecules on the metallic surface.

Impedance spectroscopic measurements

To obtain a better understanding of the mechanism of the interactions between inhibitor molecules and metal surface, galvanostatic impedance measurements were carried out. Nyquist plots obtained at the interface in the absence and presence of MF resin and ceramic powder are given in Figure 5. The impedance diagrams obtained show only one capacitive loop. The major

parameters inferred from the analysis of Nyquist diagram are:

- The resistance of charge transfer(R_p is the diameter of high frequency loop)
- The capacity of the double layer, which is defined as

$$C = \frac{1}{\left(2\pi R_p f_c\right)} \qquad (3)$$

Where R_p and f_c represent respectively the resistance of charge transfer of the capacitive loop and the associated characteristic frequency corresponding to the maximum of capacitive arc [39]. The increase in the circle's diameter after the addition of MF resin and ceramic powder as well, corroborates this claim that the corrosion resistance has increased. The inhibition efficiency of the inhibitor compound in both absence and presence of the ceramic powder was evaluated by impedance measurements using the following equation [40]:

$$E\% = \frac{(1/R_p)_0 - (1/R_p)}{(1/R_p)_0} \times 100 \qquad (4)$$

Where $(R_p)_0$ and (R_p) are the uninhibited and inhibited charge transfer resistance. Values of charge transfer resistance (R_p), capacity of double layer (C_{dl}) and inhibition efficiency are given in Table 3. There is a good adjustment between polarization and impedance results.
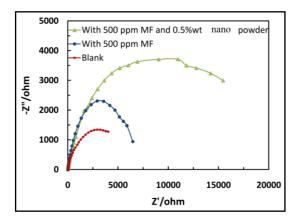

Fig. 5. Nyquest plots for carbon steel specimens in blank 3.5%wt NaCl, 500 ppm of MF and 500 ppm of MF with 0.5%wt nano powder solutions

Table 3. Data from potentiostatic polarization and electrochemical impedance measurements for carbon steel in defferent concentrations of the inhibitor

Technique	Media	Parameters	Inhibitor concentrations		
			Blank	500 ppm MF	500 ppm MF with 0.5%wt nano powder
Polarization parameters	3.5%wt NaCl solution	E_{corr} (V)	-0.84	-0.81	-0.72
		I_{corr} (A/cm^2)	20.14	11.05	2.5
		β_a (V/dec)	0.11	0.147	0.087
		β_c (V/dec)	0.13	0.258	0.139
		%E	-	%45	%88
		θ	-	45	88
EIS parameters		R_p (Ohm)	4427.64	7141.6	16926.6
		C_{dl} (μ)	261.63	246.78	124.10
		%E	-	%38	%74

SEM investigation

The SEM images of the specimen surface are given in Figure 6. It is clear from SEM images, Figure 6a, that the specimen surface was strongly damaged in the absence of the inhibitor. Fig. 6b shows the SEM image of the specimen exposed to the MF resin, which contained the nano powder in the concentration of 500 ppm. As it can be seen, there is a considerable increase in corrosion inhibition after adding the inhibitor into the aggressive solution. These photographs clearly show the inhibition behavior of new inhibitor compound in the presence of the nano powder. In comparison by the metal surface which was kept in blank solution, the amounts of deterioration of the metal surface were retarded in the presence of MF and the nano powder.
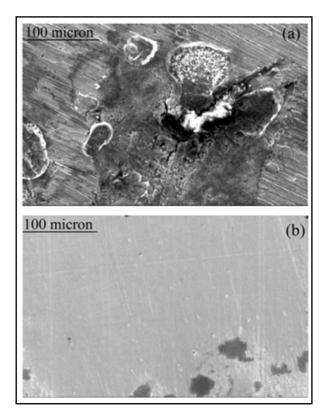

Fig. 6. SEM morphology of carbon steel surface after 24 immersion in (a) 3.5%wt NaCl solution (b) 3.5%wt NaCl solution of MF with 0.5%wt ceramic powder

CONCLUSIONS

To the best of our knowledge, the corrosion inhibition effect of this compound was studied for the first time. In the above results and discussion the following main conclusions are drawn:

- The water soluble MF resin acts as a novel good corrosion inhibitor for carbon steel in 3.5%wt NaCl solution at room temperature.
- The corrosion inhibition efficiency of MF resin increases extremely to 88% by the addition of the nano powder, which was extracted from corn cob ash.
- The reciprocal cooperation of two heterocyclic compounds like MF and SiO2 molecules can improve film formation procedure, and consequently can increase the cover ability furthermore the corrosion inhibition efficiency.
- By increasing the surface reactivity, which is caused by decreasing the dimension of the particles to the nano scale, the cover ability of the polymeric compound improves.

REFERENCES

[1] Schmit. G., (2000), A widely neglected property of corrosion inhibitors, In Proceedings of 9th European Symposium of Corrosion and Scale Inhibitors.

[2] Xueming. S. & Jianzhong. L. Experimental research on drag reduction by polymer additives,http://fluid.power.net/techbriefs/hanghzau/5_2_5.pf.

[3] Miksic. B. M, Kharshan. M. A. & Furman. A. Y, (2005), Proceeding of 10th European Symposium of Corrosion and scale inhibitors.

[4] Praveen. B. M, Venkatesha. T.V, Arthoba. Y, Naik. Y. A. & Prashantha. K., (2007), Corrosion studies of carbon nanotubes – Zn composite coating, *Surf. Coating. Tech*, 201:5836-42.

[5] Osman. M. M. & Shalaby. M. N., (2002), Some ethoxylated fatty acids as corrosion inhibitors for low carbon steel in formation water, *Mater.Chem.Phys*.77:261–269.

[6] Quraishi. M. A. & Sardar. R.,(2002), Corrosion inhibition of mild steel in acid solutions by some aromatic oxadiazoles , *Mater. Chem. Phys*.78:425–431.

[7] Yıldırım. A. & Cetin. M., (2008), Synthesis and evaluation of new long alkyl side chain acetamide, isoxazolidine and isoxazoline

derivatives as corrosion inhibitors, *Corros. Sci.*50:155–165.

[8] Winston Revie. R.,(2000), Uhlig's Corrosion Handbook, Second ed, Canmet Materials Technology Laboratory Ottawa, Ontario, Canada, John Wiley & Sons, INC.

[9] Sanyal. B. ,(1981) Organic compounds as corrosion inhibitors in different environments-a review , *Prog. Org. Coating*.9:165-236.

[10] Abd-El-Maksoud. S. A. ,(2008), Effect of organic compounds on the electrochemical behavior of steel in acidic media- A review , *Int.J.Electrochem.Sci.* 3:528-533.

[11] Raja. P. B. & Sethuraman. M. G.,(2008), Natural products as corrosion inhibitors for metals in acid media – A review, *Mater. Lett.*63:113-6.

[12] Giacomelli. F. C, Giacomelli. C, Amadori. M. F. & Schmidt. V.,(2004), Inhibitor effect of succinic acid on the corrosion resistance of mild steel electrochemical, gravimetric and optical microscopic studies, *Mater. Chem. Phys.* 83:124–128.

[13] Foad El-Sherbini. E. E, Abdel Wahaab. S. M. & Deyab. M.,(2005), Ethoxylated fatty acids as inhibitors for the corrosion of zinc in acid media, *Mater.Chem.Phys*. 89: 183–191.

[14] Düdükcü. M, Yazici. B. & Erbil. M.,(2004), The effect of indole on the corrosion behaviour of stainless steel, *Mater. Chem. Phys.* 44:138–141.

[15] Migahed. M. A.,(2005), Electrochemical investigation of the corrosion behavior of mild steel in 2M HCl solution in presence of 1-dodecyl-4-methoxy pyridinium bromide, *Mater. Chem. Phys*.93:48–53.

[16] Roberge. P. R.,(2000), Handbook of Corrosion Engineering, McGraw-Hill, New York.

[17] Osman. M. M & Shalaby. M. N.,(2001), Synergistic inhibition of anionic and nonionic surfactants on corrosion of mild steel in acidic solution, *Anti corros. Meth.Mater.*48:309–318.

[18] Finsgar. M, Fassbender. S, Nicolini. F & Milosev. I.,(2008), Polyethyleneimine as a corrosion inhibitor for ASTM 420 stainless steel in near-neutral saline media, *Corros. Sci.* 50:1245-1250.

[19] Ahmad. Z.,(2006), Principles of Corrosion Engineering and Corrosion Control, Elsevier Science & Technology Books.

[20] Moussa. M. N. H, El-Far. A. A. & El-Shafei. A. A.,(2007), The use of water-soluble hydrazones as inhibitors for the corrosion of C-steel in acidic medium, *Mater.Chem. Phys*.105:105–113.

[21] Maity. A, Kalita. D, Kumar Kayal. T, Goswami. T, Chakrabarti. O, Sekhar Mait. H. & Gangadhar Rao. P.,(2010), Synthesis of SiC ceramics from processed cellulosic bio-precursor, *Ceram. Intl*.36:323–331.

[22] Van Eylen. D, Van Dongen. F, Kabel. M & Bont. J.,(2011), Corn fiber, cobs and stover: Enzyme-aided saccharification and co-fermentation after dilute acid pretreatment, *Biores.Technol*.102:5995–6004.

[23] Bagheri. N & Abedi. J.,(2011), Adsorption of methane on corn cobs based activated carbon, *Chem.Eng.Resear.Desig.* 89:2038–2043.

[24] Lucia. L. A. & Rojas. O. J.,(2009), The nanoscience and technology of renewable biomaterials, John Wiley and Sons, Ltd, publication.

[25] Adesanya. D. A & Reheem. A. A.,(2009), A study of the workability and compressive strength characteristics of corn cob ash blended cement concrete, *Constr. Build. Mater*.23:347-352.

[26] WU. Y. N, Zhao. Y. F & Li. J. G.,(2009), A Survey on Occurrence of Melamine and Its Analogues, *China. Biomed. Environ. Sci.* 22:95-99.

[27] Olivares-Xometl. O,Likhanova. N.V, Dominguez-Aguilar. M. A, Arce. E, Dorantes. H. & Arellanes-Lozada. P.,(2008),Synthesis and corrosion inhibition of -amino acids alkylamides for mild steel in acidic environment, *Mater. Chem. Phys*.110:344-351.

[28] Elayyachy.M, Elkodadi. M, Aouniti. A , Ramdanib. A, Hammoutia. B, Malek. F & Elidrissi. A., (2005), New bipyrazole derivatives as corrosion inhibitors for steel in hydrochloric acid solutions, *Mater. Chem. Phys*.93:281–285.

[29] Bentiss. F, Lebrini. M , Vezin. H & Lagrenée. M.,(2004), Experimental and

theoretical study of 3-pyridyl-substituted 1,2,4-thiadiazole and 1,3,4-thiadiazole as corrosion inhibitors of mild steel in acidic media, *Mater. Chem. Phys*. 87:18–23.

[30] Sherif. El-Sayed M, El Shamya. A. M, Ramlab. Mostafa M & El Nazhawyb. Ahmed O.H.,(2007), 5-(Phenyl)-4H-1,2,4-triazole-3-thiol as a corrosion inhibitor for copper in 3.5% NaCl solutions, *Mater. Chem. Phys.* 102:231–239.

[31] Avci. G.,(2008), Inhibitor effect of N,N-methylenediacrylamide on corrosion behavior of mild steel in 0.5M HCl, *Mater. Chem. Phys.*112: 234–238.

[32] Khaleda. K. F, Fadl-Allahb. Sahar A. & Hammoutic. B.,(2009), Some benzotriazole derivatives as corrosion inhibitors for copper in acidic medium: Experimental and quantum chemical molecular dynamics approach, *Mater. Chem. Phys*.117:148–155.

[33] Shukla. S. K, Quraishi. M. A., (2010), A new and efficient corrosion inhibitor for mild steel in hydrochloric acid solution, *Mater. Chem. Phys*.120:142–147.

[34] Obota. I. B. & Obi-Egbedib. N. O.,(2010), Indeno-1-one [2,3-b] quinoxaline as an effective inhibitor for the corrosion of mild steel in 0.5M H2SO4 solution, *Mater. Chem. Phys*.122:325–328.

[35] Sherif. E. M.,(2011),Effects of 5-(3-aminophenyl)-tetrazole on the inhibition of unalloyed iron corrosion in aerated 3.5% sodium chloride solutions as a corrosion inhibitor, *Mater. Chem. Phys*.129:961–967.

[36] Foad El Sherbini. E. E.,(1999), Sulphamethoxazole as an effective inhibitor for the corrosion of mild steel in 1.0 M HCl solution, *Mater. Chem. Phys*. 61:223-228

[37] Musa. A. Y, Kadhum. A. A. H, Mohamad. A. B. & Takriff. M. S.,(2011), Molecular dynamics and quantum chemical calculation studies on 4,4-dimethyl-3-thiosemicarbazide as corrosion inhibitor in

2.5 M H 2SO 4, *Mater. Chem. Phys*. 129:660-665

[38] Achouri. M. E, Infante. M. R, Izquierdo. F Kertit. Gouttaya. S. H. M. & Nciri. B. ,(2001), Synthesis of some cationic gemini surfactants and their inhibitive effect on iron corrosion in hydrochloric acid medium Corros. *Sci.* 43:19-35.

[39] Ramesh. S. V. & Adhikari. A. V.,(2009), N-[4-(diethylamino)benzylidine]-3-{[8-(trifluoromethyl) quinolin-4-yl]thio}propano hydrazide) as an effective inhibitor of mild steel corrosion in acid media, *Mater*. *Chem. Phys*.115:618–627.

[40] Ehteram. A. N. ,(2009), Evaluation of inhibitive action of some quaternary N-heterocyclic compoundson the corrosion of Al–Cu alloy in hydrochloric acid, *Mater. Chem. Phys*.114:533–541