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Synthesis and Evaluation of modified Chitosan – Gluteraldehyde as corrosion inhibitor for mild steel in acidic medium

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Abstract

A new inhibitor derived from Chitosan and gluteraldehyde was synthesized and the efficiency of the synthesized inhibitor was screened out by electrochemical and surface scanning analysis in 0.24 M HCl. The Chitosan derivative was identified by Fourier-transformed infrared (FTIR) and the steel surface examinations were carried out via scanning electron microscope (SEM) and energy dispersive X-ray. The results of efficiency tests show very good performance as corrosion inhibitor. The corrosion rate lowered with the concentration increase of the new synthesized inhibitor. About 98.4% inhibition efficiency was measured by using 1000 ppm of the new synthesized derivative. The polarization results showed that the new synthesized derivatives have mixed inhibition effect. Langmuir isotherm was found to be the most fitted to represent the adsorption nature of the inhibitor. SEM analysis proved the presence of protective film formed by new synthesized Chitosan derivative (CH-gluteraldehyde) on the metal surface.

Keywords: Chitosan; Gluteraldehyde; HCl; Steel; Potentiodynamic polarization.

1. Introduction

Corrosion which could be identified as wearing out of a material duo to its reaction with its environment. It is the invisible enemy of the industry and that is not overstatement as the recent studies measured that the losses of corrosion for the United States only about $276 billion per year So, the use of corrosion inhibitor sounds to be very economical beneficial. [1]

Mild steel is one of the common materials used in industry and it is also highly affected by corrosion. There are many new chemically synthesized corrosion inhibitors. Unfortunately, most of these chemicals are expensive as well as hazard for human and environment so the usage of green inhibitors will provide the equilibrium of the equation to use safe and efficient inhibitor.[2-12]

In this work, a new corrosion inhibitor by using green polymer (chitosan) by making a multi layers through using of glutaraldehyde as a cross-linker. Glutaraldehyde in addition to its role to make a Schiff base cross-link, it also decreases the intramolecular hydrogen bonds of chitosan leaving more groups of hydroxyl and amines available to form linkage to metal surface. [13]

2. Methodology

2.1. Instrumentation

Polarization and potentiostatic instruments were applied for the preliminary experiments of anticorrosive characters. These tests were done by a three compartment with mild steel rod as a working electrode, platinum counter electrode and saturated calomel electrode as a reference electrode.

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The potential was scanned from -0.6 to 0.6 Volts by scan rate of 10 mVS-1 and the mild steel which used as working electrode was made with exposure area of 1 cm2 and then immersed in a different sample of hydrochloric acid.

Table 1. Chemical composition of mild steel

Element	C	Mn	P	Si	S	Cr	Ni	Fe
Weight%	0.158	0.495	0.060	0.157	0.062	0.047	0.006	rest

According to the experiments, the metal surfaces were abraded by different grades of papers (1200 – 2000) then degreased with AR-grade acetone then rinsed with deionized water and inserted in the test solution.

Parameters including corrosion potential (Ecorr), Corrosion current density (Icorr) were identified by Tafel curves extrapolation.

FTIR Nicolet Magna 5PC spectrophotometer (Thermo Fisher Scientific) was used to measure IR spectrum to identify the functional groups in the new synthesized resins and compounds.

2.2. Chemicals

Chitosan with average molecular weight of 160000 g. Mol-1 and glutaraldehyde, were purchased from Sigma Aldrich Co. Hydrochloric acid (30 – 34) % was purchased from El-NASR Co.

2.3. Synthesis of Gluteraldehyde modified Chitosan resin

Two gram of Chitosan was dissolved in 100 ml of acetic acid solution (1%) on cold for about half hour, then the addition of 20 ml drop by drop of gluteraldehyde solution (1gm of gluteraldehyde dissolved in 20 ml methanol) then stirring for about 2 hours on cold by using a magnetic stirrer.

Then reflux in water bath (60°C - 70°C) for 12 hours. After complete precipitation of CH-gluteraldehyde, we performed addition steps of washing and filtration to maintain the purity of the compound.

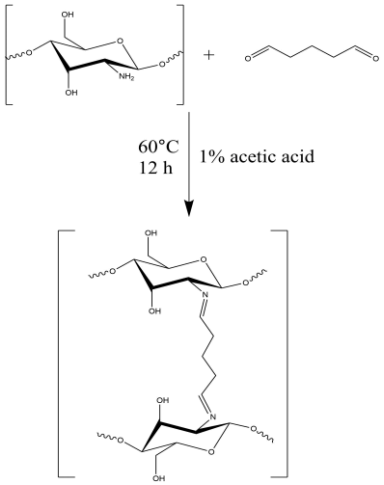


Figure 1. Synthesis of gluteraldehyde chitosan

3. Results and Discussion

3.1. FTIR Spectrum explanation

The FTIR spectrum of chitosan shows broad band at [3428-3440] cm-1 related to the OH functional group, the cyclic C-O-C group appears at [810-950] cm-1, the bands of [1070-1080] are related to C-O vibration and the new synthesized compounds as shown in fig. 2 clarifies the successful formation of Schiff base in stretching bands of C=N at 1615-1650 cm-1 in addition to disappearance of any aldehydic group.

FTIR Spectrum of glutaraldehyde Chitosan: The schiff base stretching peak vibration appears at 1629.55 cm-1 with low transmittance in comparison to other synthesized derivatives duo to the high availability (two groups).

3.2. Potentiodynamic polarization

Potentiodynamic polarization curves of mild steel in 0.24 M HCl in the absence and presence of different concentration polymers are given in Figure (3). The potentiodynamic polarization parameters were studied. Corrosion potential (Ecorr), anodic Tafel slopes (βa), cathodic Tafel slopes (βc) corrosion current density (Icorr) and inhibition efficiency (%IE).

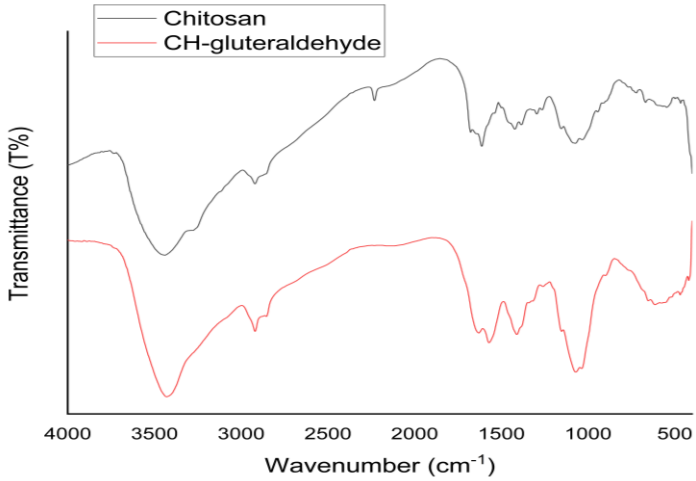


Figure 2. FTIR spectrum of chitosan and CH-gluteraldehyde

The inhibition efficiency was calculated using the following equation:

$$IE\ \% = \left(1 - (Iinh/Ifree)\right) * 100$$

Where Iinh and Ifree are the corrosion current of steel electrode in the presence and in the absence of inhibitors, respectively. The IE% increases with the increase of concentration as shown in table 2.

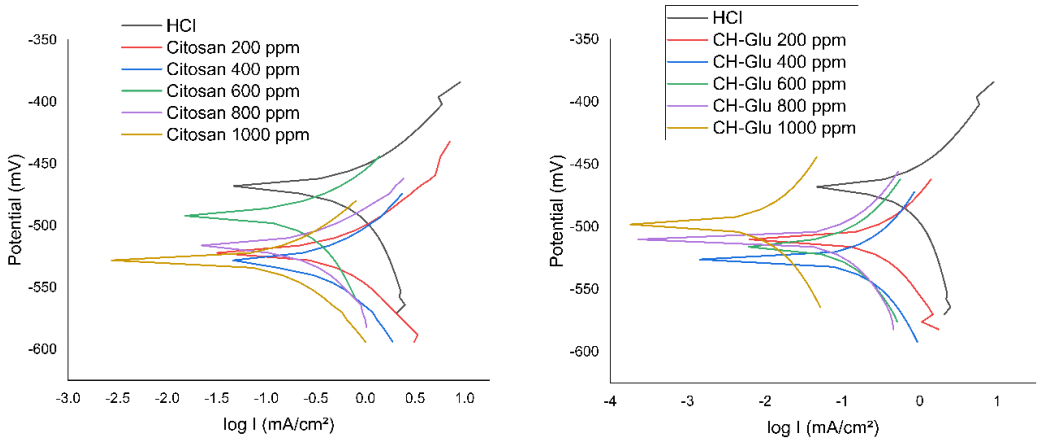


Figure 3. Anodic and cathodic polarization curves of steel electrode in 0.24 M HCl solution containing different concentration of Chitosan & CH-Gluteraldehyde at 25°C.

Table 2. Corrosion parameters of steel electrode in 0.24 M HCl solution containing different concentrations of inhibitors.

Medium	Conc. (ppm)	βa	-βc	-Ecorr	Icorr	IE%
Free HCl		72.3	161	468	0.7663	-
Chitosan	200	60.2	82	522	0.4815	37.2
	400	54.3	65.2	530	0.2912	62
	600	67.4	127	492	0.2492	67.5
	800	47.2	81.97	516	0.2326	69.6
	1000	56.6	61.9	529	0.1255	83.6
Gluteraldehyde	200	59.34	81	510	0.2876	41.3
	400	87	78.5	528	0.2021	50.3
	600	87.6	94.7	517	0.1322	66.9
	800	79.2	102.5	511	0.10419	86.6
	1000	95	104	499	0.0124	98.4

The degree of surface coverage (Θ) of steel surface by the adsorbed of compounds is calculated using the following equation.

$$\theta = 1 - (Iinh/Ifree)$$

Where Ifree and Iinh are the corrosion current densities in absence and presence of the additive's compounds, respectively. The degree of surface coverage in found to increase with increasing concentration of the additives. Plotting of C / Θ against Concentration of inhibitor (C) gives straight lines with unit slopes. This indicates that the adsorption of the inhibitors takes place following Langmuir adsorption isotherm.

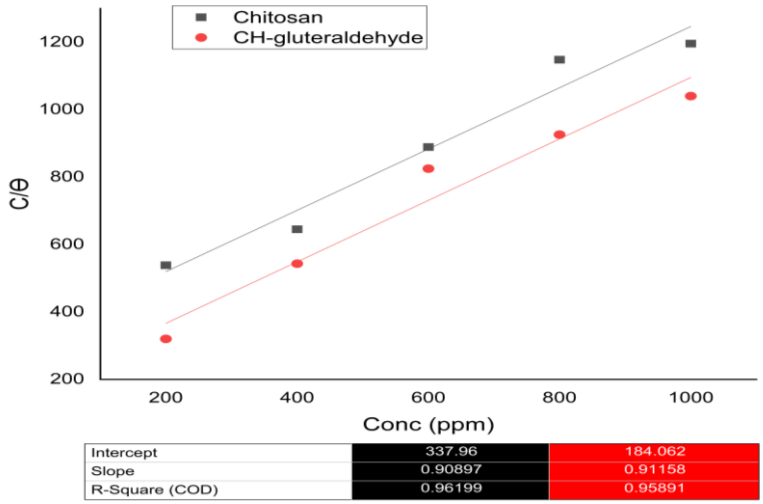


Figure 4.Langmuir adsorption isotherm of the adsorption of chitosan and CH-gluteraldehyde of the mild steel in 0.24M HCl at 25°C.

The effect of temperature of the corrosion parameters such as Icorr, Ecorr and IE% was a studied in 0.24 M HCl solution, containing 1000 ppm of inhibitors over the temperature ranges of 25-65 °C. The results showed that the variation of temperature had almost no effect on the shape of the polarization curves. The data listed in Table 3 showed that, Ecorr shifted to less negative values, whereas the values of Icorr increased with the increase in temperature. This indicates the accelerating effect of rising temperature on the corrosion reaction. On the other hand, the increasing in temperature decreases the inhibition

efficiencies. This is attribute to the acceleration of desorption process by increasing temperature.

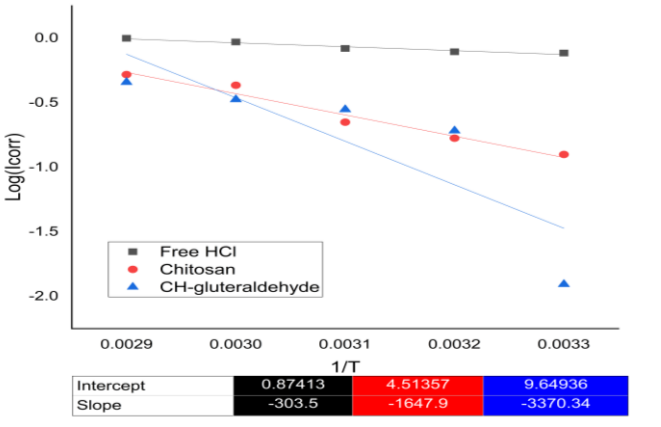
Table 3.effect of temperature on the corrosion parameters of steel electrode in 0.24 M HCl and (0.24M Hcl + 1000ppm) of inhibitor.

Compound	T(K)	-Ecorr	Icorr	IE%
0.24 M HCl	298	519.9	0.7663	0.0
	308	509.9	0.7835	0.0
	318	506.5	0.8309	0.0
	328	498.2	0.9335	0.0
	338	494.8	0.9956	0.0
Chitosan	298	528.6	0.1255	83.6
	308	527.4	0.2662	66
	318	512.5	0.3881	53.3
	328	518	0.4316	53.8
	338	523.6	0.5218	47.6
Gluteraldehyde	298	522.9	0.0124	98.4
	308	511.4	0.1919	75.5
	318	487.6	0.2801	66.3
	328	488.3	0.3346	64.2
	338	466.8	0.4549	54.3

The corrosion reaction is regarded as a rate process which in given by Arrhenius equation.

$$\log(Icorr) = \log(A) - Ea/2.303RT$$

A is Arrhenius factor and Ea is the apparent activation energy of the corrosion reaction. Plotting the log (Icorr) versus (1/T) gave straight lines in Fig (5).



Where Icorr represents the rate of corrosion reaction.

Figure 5. the relation between log (Icorr/T) and 1/T for steel electrode in 0.24 M HCl in absence and presence of 1000 ppm of compounds

The other activation parameters were calculated using the transition state equation:

$$\log\left(\frac{Icorr}{T}\right) = (\log(R/hn)) + \left(\frac{\Delta S*}{2.303R}\right) - \left(\frac{\Delta H*}{2.303RT}\right)$$

Where, R is the universal gas constant (8.314 J / mol.k), n is the Avogadro's number (6.02×10^{23}), h is the plank's constant ($6.62\times10^{-34}m^2kg/s$) where ΔS* and ΔH* are the entropy and the enthalpy change, respectively plotting log (Icorr/T) versus (1/T) gives straight lines Fig (6).

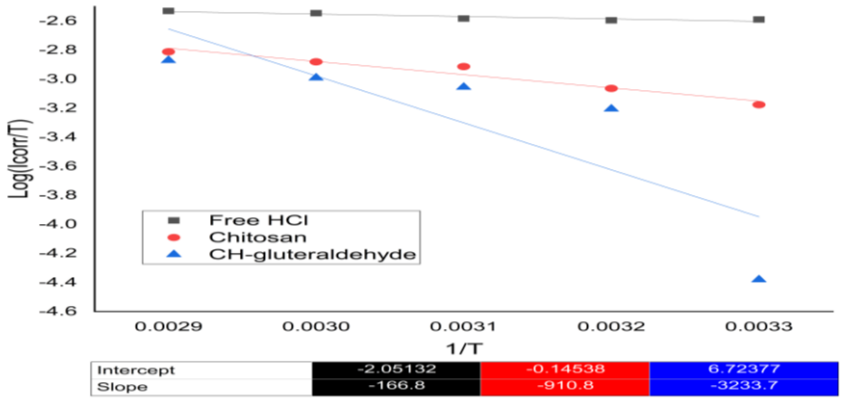


Figure 6. the relation between log (Icorr/T) and 1/T for steel electrode in 0.24 M HCl in absence and presence of 1000 ppm of compounds

The obtained ΔG* values were also listed in Table (4)

Table 4. Activation parameters of the dissolution reaction of steel electrode in 0.24 M HCl solution in absence and presence of 1000 ppm of compounds.

Compound	Ea K.J/mol.k	ΔH* K.J/mol.k	-ΔS* K.J/mol.k	ΔG* K.J/mol.K
Free HCl	5.8	3.2	0.23686	73.78428
Chitosan	31.55	17.4	0.2	77
Gluteraldehyde	26.25	19.4	0.196	77.808

It is obvious that activation energy increases with the presence of the inhibitor and that as a result of the adsorption of the inhibitor on the surface of metal.

The positive sign of ΔH* expresses the endothermic system of the corrosion process and the elevated values of Ea* comparable to the values of ΔH* give the indication of the gaseous nature of the corrosion process that can be easily explained by the evolution of hydrogen gas that accompanied with the volume decrease of the reaction[14].

The negative values of entropy ΔS* refer to the increase of order and that attributed to the formation of metal-Chitosan complex which in turn decreases the freedom of the system.

3.3. Surface Examination

SEM (Fig. 7) shows the formation of corrosive layer in case of mild steel immersed in 0.24M HCl for 3 days and the formation of protective layer by addition of 1000 ppm of our new synthesized chitosan derivatives and immersed in 0.24M HCl for 3 days and it is obvious that the metallic surface appears less affected with corrosion.[15]

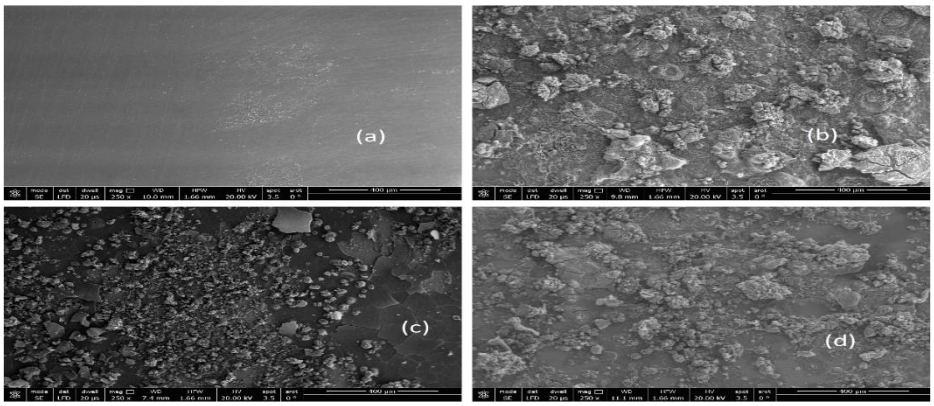


Figure 7. (a) SEM of mild steel surface (b) SEM of mild steel immersed in 0.24M HCl for 3 days. (c) SEM of mild steel immersed in 0.24M HCl for 3 days with 1000 ppm of chitosan. (d) SEM of mild steel immersed in 0.24M HCl for 3 days with 1000 ppm of CH-glutaraldehyde.

EDX curves (Fig.8) shows the decrease in weight% of oxygen and increase of weight% of Fe which reflects the efficiency of the added inhibitors comparable to the curve of mild steel in HCl.

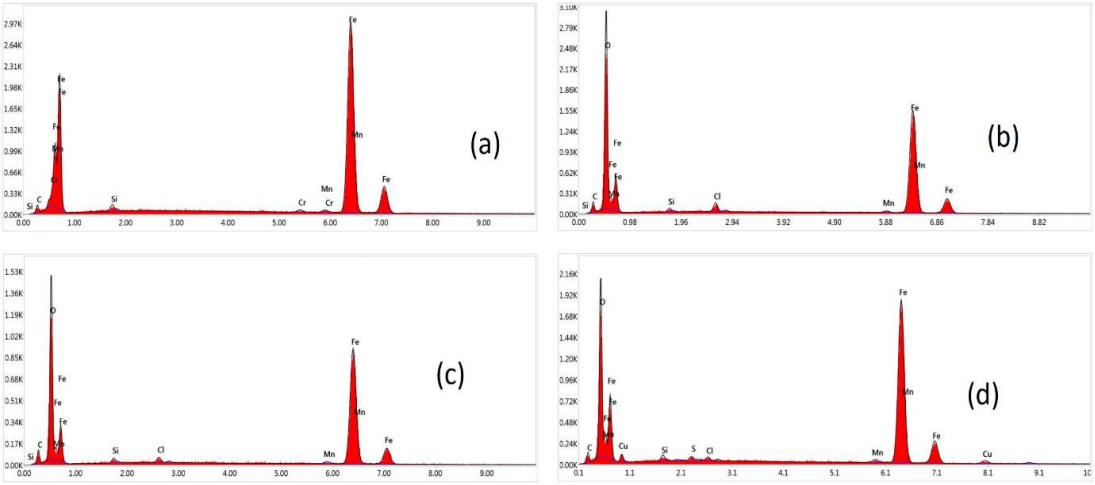


Figure 8. (a) EDX spectra of free mild steel. (b) EDX spectra of mild steel immersed in 0.24M HCl for 3 days. (c) EDX spectra of mild steel immersed in 0.24M HCl with 1000 ppm chitosan for 3 days. (d) EDX spectra of mild steel immersed in 0.24M HCl with 1000 ppm CH-gluteraldehyde for 3 days.

4. Conclusion

In this paper, the effect of cross-linked chitosan with glutaraldehyde on the corrosion behavior of mild steel was studied using electrochemical measurements, and SEM. This work provides a conclusion that the new synthesized CH-glutaraldehyde gives a higher corrosion inhibition effect for mild steel in 0.24M HCl in comparison to Chitosan alone.

Potentiodynamic polarization curves and Energy Dispersive X-Ray Analysis (EDX) results showed a better corrosion behavior of chitosan coated substrates in 0.24M HCl at 298 k with respect to bare mild steel. Good inhibition efficiency (IE) has been found in 0.24M HCl solution reaches to 98.4%.

5. References

[1] M. Rizvi, An Overview of Corrosion, Organic Corrosion Inhibitors, (2021) 1-17.

[2] M. Bouklah, B. Hammouti, M. Benkaddour, T. Benhadda, Thiophene derivatives as effective inhibitors for the corrosion of steel in 0.5 m H2SO4, Journal of Applied Electrochemistry, 35 (2005) 1095-1101.

[3] M. Azhar, B. Mernari, M. Traisnel, F. Bentiss, M. Lagrenée, Corrosion inhibition of mild steel by the new class of inhibitors [2,5-bis(n-pyridyl)-1,3,4-thiadiazoles] in acidic media, Corrosion Science, 43 (2001) 2229-2238.

[4] P.A. Rasheed, A. Alfantazi, K.A. Jabbar, K.A. Mahmoud, Inhibition of Microbially Influenced Corrosion by Chitosan@lignosulfonate Nanospheres Under Dynamic Flow Conditions, Journal of Bio- and Tribo-Corrosion, 7 (2021) 103.

[5] M.A. Quraishi, D.S. Chauhan, V.S. Saji, Heterocyclic biomolecules as green corrosion inhibitors, Journal of Molecular Liquids, 341 (2021) 117265.

[6] E. Berdimurodov, D.K. Verma, A. Kholikov, K. Akbarov, L. Guo, The recent development of carbon dots as powerful green corrosion inhibitors: A prospective review, Journal of Molecular Liquids, 349 (2022) 118124.

[7] V. Saraswat, M. Yadav, Improved corrosion resistant performance of mild steel under acid environment by novel carbon dots as green corrosion inhibitor, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 627 (2021) 127172.

[8] M. Abdallah, H.M. Altass, A.S. Al-Gorair, J.H. Al-Fahemi, B.A.A.L. Jahdaly, K.A. Soliman, Natural nutmeg oil as a green corrosion inhibitor for carbon steel in 1.0 M HCl solution: Chemical, electrochemical, and computational methods, Journal of Molecular Liquids, 323 (2021) 115036.

[9] E. Berdimurodov, A. Kholikov, K. Akbarov, L. Guo, S. Kaya, D.K. Verma, M. Rbaa, O. Dagdag, Novel glycoluril pharmaceutically active compound as a green corrosion inhibitor for the oil and gas industry, Journal of Electroanalytical Chemistry, 907 (2022) 116055.

[10] E. Berdimurodov, A. Kholikov, K. Akbarov, L. Guo, S. Kaya, D.K. Verma, M. Rbaa, O. Dagdag, New and Green Corrosion Inhibitor Based on New Imidazole Derivate for Carbon Steel in 1 M Hcl

Medium: Experimental and Theoretical Analyses, International Journal of Engineering Research in Africa, 58 (2022) 11-44.
[11] E. Berdimurodov, A. Kholikov, K. Akbarov, L. Guo, S. Kaya, K.P. Katin, D.K. Verma, M. Rbaa, O. Dagdag, R. Haldhar, Novel gossypol–indole modification as a green corrosion inhibitor for low–carbon steel in aggressive alkaline–saline solution, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 637 (2022) 128207.
[12] Y. Feng, J. He, Y. Zhan, J. An, B. Tan, Insight into the anti-corrosion mechanism Veratrum root extract as a green corrosion inhibitor, Journal of Molecular Liquids, 334 (2021) 116110.
[13] S.N. Mousavi, A. Bahrami, M. Sadri, A. Alipour, Optimization of an ecofriendly coating containing chitosan and gelatin as corrosion inhibitor of carbon steel grade E by Response Surface Method, Journal of Particle Science & Technology, 5 (2019) 23-31.
[14] B.V. Appa Rao, S.S. Rao, Synergistic Inhibition of Corrosion of Carbon Steel by the Ternary Formulations containing Phosphonate, Zn (II) and Ascorbic Acid, Research Journal of Recent Sciences, 1 (2012) 93-98.
[15] J. Tang, Y. Shao, T. Zhang, G. Meng, F. Wang, Corrosion behaviour of carbon steel in different concentrations of HCl solutions containing H2S at 90°C, Corrosion Science, 53 (2011) 1715-1723.