A Review on Anticorrosion Activity of 5-Chloroistin Derivatives on Mild Steel in Acidic Media.

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In an acidic environment, the corrosion phenomenon deteriorates mild steel, hence the organic corrosion inhibitors could figure out this problem. This paper gives a comprehensive review details an investigation on the protection of mild steel in acidic media by adding 5-Chloroisatin derivatives as organic inhibitors at different concentrations analyzed by weight loss, electrochemical impedance spectroscopy, Tafel polarization and scanning electron microscope (SEM). The main results have shown that the 1-allyl-5-chloro-indoline-2,3-dione (TZ_{ACI}), 5-chloro-1-octylindoline-2,3-dione (TZ_{COI}) and 5-chloro-1-(2-(dimethylamino) ethyl) indoline-2,3-dione (TZ_{CDI}) are excellent corrosion inhibitors of mild steel in acid medium with an efficiency higher than 90%. The inhibitors adsorptions on the mild steel surface follow the Langmuir adsorption isotherm.

Introduction

The corrosion of materials is the degradation of metals in the technological world today, which is often electrochemical in nature[1]. In this field, engineers and scientists are persistent in seeking better and more efficient ways to prevent and control corrosion of metals that affects many sectors as agriculture, medicine, polymer and various industries[2].

In this context, the addition of organic inhibitors to the corrosive media is one of the most practical methods to decrease the rate of corrosion processes and prevent the reaction of the metal with the media[3]. Some of them are very economical, readily available, some of them are practical, biodegradable and convenient, but all of them are subjected to protection against corrosion in acidic media[4].

The Heterocyclic compounds[5] are of mainly interest in organic chemistry[6–10], most of them contain hetero-atoms such as phosphorous, nitrogen, sulfur and oxygen, they have a significant active role as anti-viral[11], anti-bacterial[12–14], anti-and inflammatory [15]. 5-Chloroisatin derivatives are very omnipotent class of these heterocyclic systems[16] due their wide-ranging activities[17] and also their anticorrosion applications[18]. The synthetic products summarized in this review have been tested as corrosion inhibitors for mild steel on various types of acid medium by weight-loss method

and electrochemical such as impedance spectroscopy and potentiodynamic polarization studies. The surface of metals was confirmed by Scanning electron microscope (SEM) analysis.

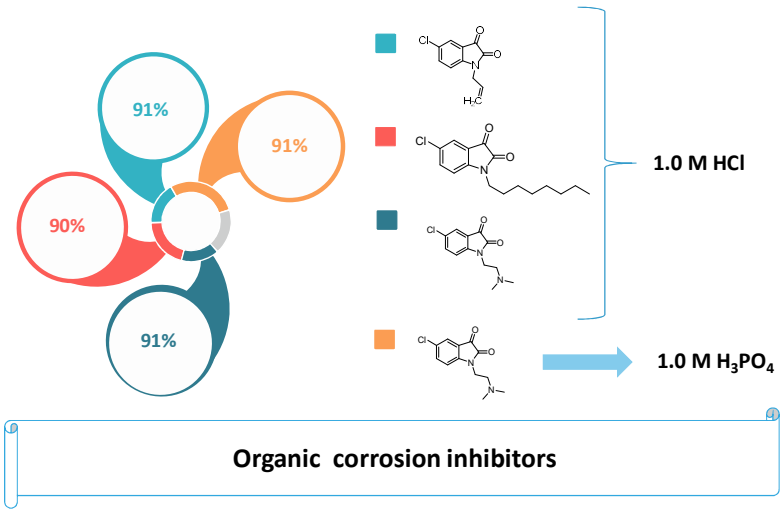


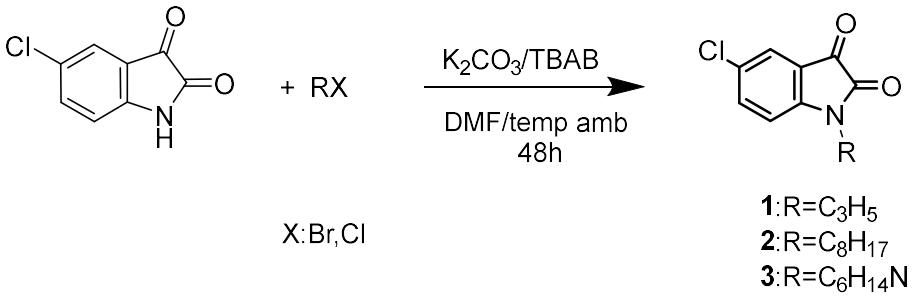
Figure 1. Illustration of 5-Chloroisatin derivatives corrosion inhibitors

5-Chloroisatin derivatives (N-Substituted 5-Chloroisatin Derivatives) as corrosion inhibitors

5-Chloroisatin (5-Chloro-1*H*-indole-2,3-dione) with the chemical structure of $C_8H_4ClNO_2$ is reactive at different positions including the nitrogen atom 1[19], two carbonyl groups at positions 2 and 3 and the C2–N sigma bond[20]. It comprises two cyclic rings, one of which is six-membered and the other is five-membered[21, 22].

N-Substituted 5-Chloroisatin Derivatives are one of the most important heterocyclic derivatives, which have been known as very effective corrosion inhibitors[23].

The scheme involves the synthesis of the three N-alkylated 5-Chloroisatin compounds used in this work, namely 1-allyl-5-chloro-indoline-2,3-dione (TZ_{ACI}), 5-chloro-1-octylindoline-2,3-dione (TZ_{COI}) and 5-chloro-1-(2-(dimethylamino) ethyl) indoline-2,3-dione (TZ_{CDI}), according to N-alkylation published method[24].



Scheme 1. Synthesis of N-Substituted 5-Chloroisatin Derivatives

Materiel and methods

Metals

The tested materiel in this study is mild steel, the size of the specimen was 1.5 x 1.5 cm and it is abraded using 120, 600 and 1200 emery sheets, rinsing with distilled water, degreasing with ethanol, and drying it at hot air.

Solutions

The aggressive solutions of 1.0 M HCl and 1.0 M H_3PO_4 were prepared by dilution of analytical grade respectfully 37% HCl and 85% H_3PO_4 with distilled water.

Weight loss measurements

The weight loss is the simplest method for monitoring the corrosion inhibition efficiency of a metal in acidic solutions.

Table 1 shows the inhibition efficiency of mild steel corrosion in 1.0 M HCl and 1.0 M H_3PO_4 solutions, at different concentrations of the inhibitors TZ_{ACI}, TZ_{COI} and TZ_{CDI}.

Table 1. Weight loss results of mild steel in acidic solutions with different concentrations of TZ_{ACI}, TZ_{COI} and TZ_{CDI}.

	Concentration(M)	C_R**(mg.cm^2.h^1)**	η**(%)**
TZ_{ACI}	1.0 M HCl	0.82	--
	10^{-3}	0.07	91
	10^{-4}	0.15	82
	10^{-5}	0.21	74
	10^{-6}	0.32	61
TZ_{COI}	1.0 M HCl	0.82	--
	10^{-3}	0.08	90
	10^{-4}	0.13	84
	10^{-5}	0.23	72
	10^{-6}	0.34	59
TZ_{CDI}	1.0 M HCl	0.45	--
	10^{-3}	0.04	91
	10^{-4}	0.07	83
	10^{-5}	0.22	51
	10^{-6}	0.24	46
TZ_{CDI}	1.0 M H_3PO_4	0.47	
	10^{-3}	0.03	91
	10^{-4}	0.07	83
	10^{-5}	0.22	51
	10^{-6}	0.23	49

In the weight loss method it was detected that the corrosion rate remarkably decreased while the inhibition efficiency (η%) increased with the increase in the inhibitors concentrations TZ_{ACI}, TZ_{COI} and TZ_{CDI} reaching a maximum value at a concentration of 10^{-3} M.

This may be due to the adsorption of the inhibitor molecule at the metal surface as the first step in the mechanism of inhibition in aggressive medium.

Potentiodynamic polarization study

The anodic and cathodic polarization curves of the mild steel electrode, with and without different concentrations of inhibitors, in the presence of 1.0 M HCl and 1.0 M H_3PO_4 are shown in **Figure 2**.

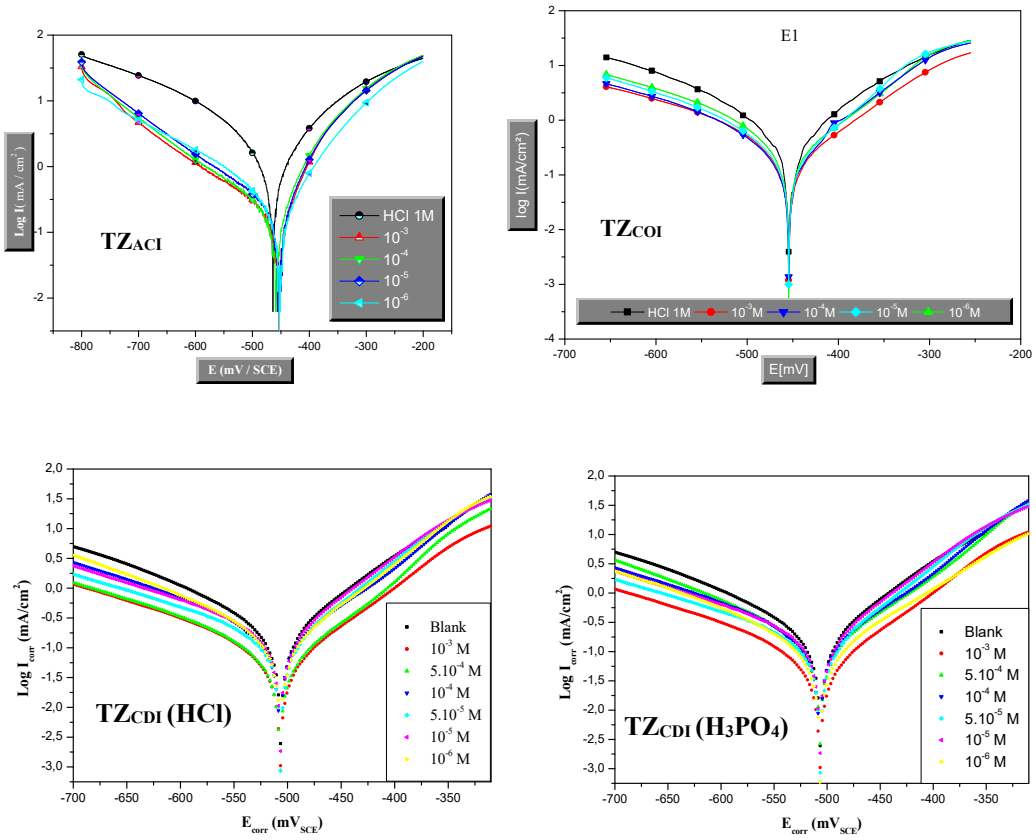


Figure 2. Potentiodynamic polarization curves of mild steel in medium acids with and without various concentrations of TZ_{ACI}, TZ_{COI} and TZ_{CDI}.

The examination of Tafel polarisation plots shows that the both anodic dissolution of mild steel and cathodic reduction reactions were inhibited after adding the organic inhibitors to the corrosive medium. This behavior indicates that the inhibitors taken for this study were considered as mixed inhibitors[25].

Electrochemical impedance spectroscopy characterizations

The Nyquist diagram of a mild steel corrosion in 1.0 M HCl and 1.0 M H_3PO_4 with different concentrations of TZ_{ACI}, TZ_{COI} and TZ_{CDI} are shown in **Figure 3**

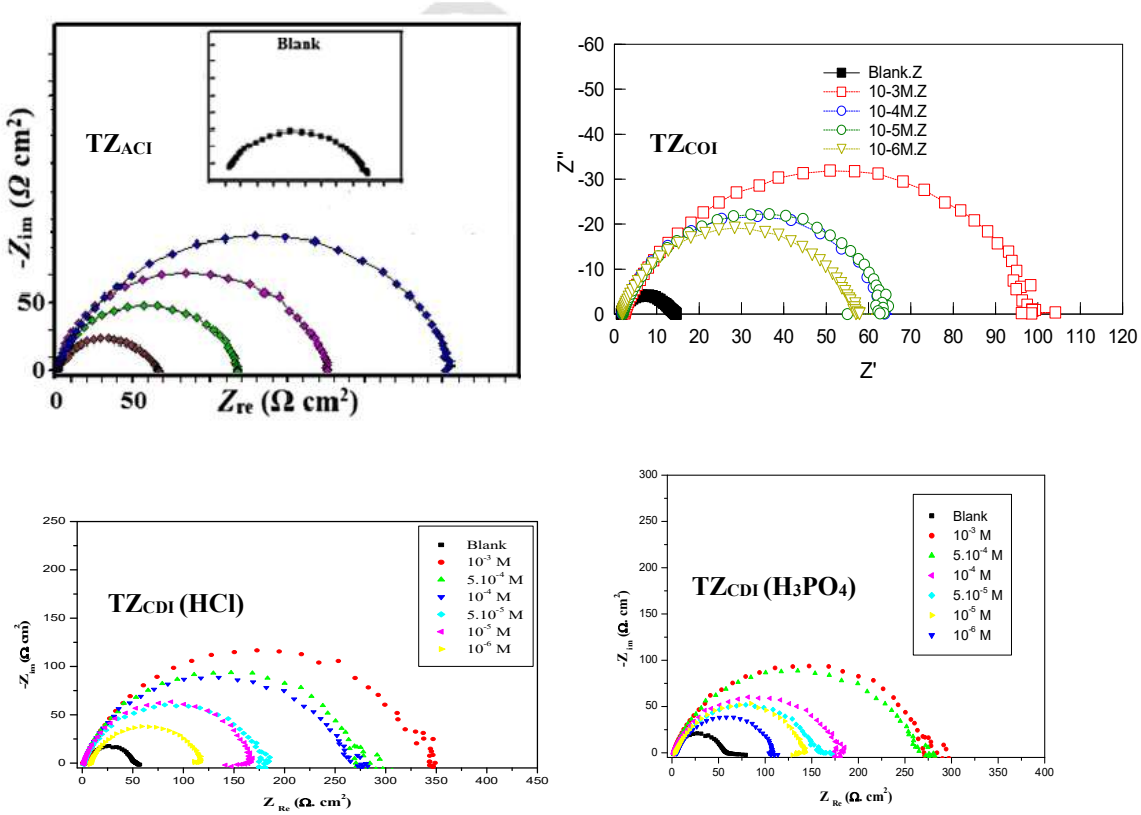


Figure 3. Nyquist diagrams of mild steel in medium acids with and without various concentrations of TZ_{ACI}, TZ_{COI} and TZ_{CDI}

These graphs clearly exhibit a large capacitive loop in the form of a semicircle whose center is located below the axis of the reals. This shape generally indicates that the corrosion reaction is controlled by a process of transfer of charges on a heterogeneous and irregular solid surface electrode[26].

Effect of temperature

In order to get more information about the stability of a corrosion inhibitor in an aggressive medium, we have examined the influence of temperature on its inhibitory efficacy.

It is remarked (**Table 2**) that the efficiency of inhibitors decreases with increase in temperature indicates that the inhibitors film formed on the metal surface is less protective in nature at higher temperature[27].

Table 2. Effect of temperature results of mild steel in 1.0 M HCl and 1.0 M H_3PO_4 with different temperatures

	Temperature	C_{inh}**(mol/L)**	C_R**(mg.cm^{-2}.h^{-1})**	η **(%)**
TZ_{CDI}(HCl)	**303**	Blank 10^{-3}	0.080 0.005	--- 93.7
	313	Blank 10^{-3}	0.101 0.008	--- 92.0
	323	Blank 10^{-3}	0.388 0.041	--- 89.4
	333	Blank 10^{-3}	0.615 0.124	--- 79.8
$TZ_{CDI}(H_3PO_4)$	**303**	Blank 10^{-3}	0.113 0.007	--- 94.1
	313	Blank 10^{-3}	0.138 0.011	--- 92.0
	323	Blank 10^{-3}	0.386 0.039	--- 89.9
	333	Blank 10^{-3}	0.644 0.127	--- 80.3

Langmuir adsorption isotherm

The study of the adsorption isotherm can provide information about the corrosion inhibition behavior of organic inhibitors.

Figure 4 shows that the variation of the ratio C/θ depending on the inhibitor concentration *C* using the gravimetric measurements is linear, confirming that all the inhibitors on the mild steel surface obeyed Langmuir adsorption isotherm[28].

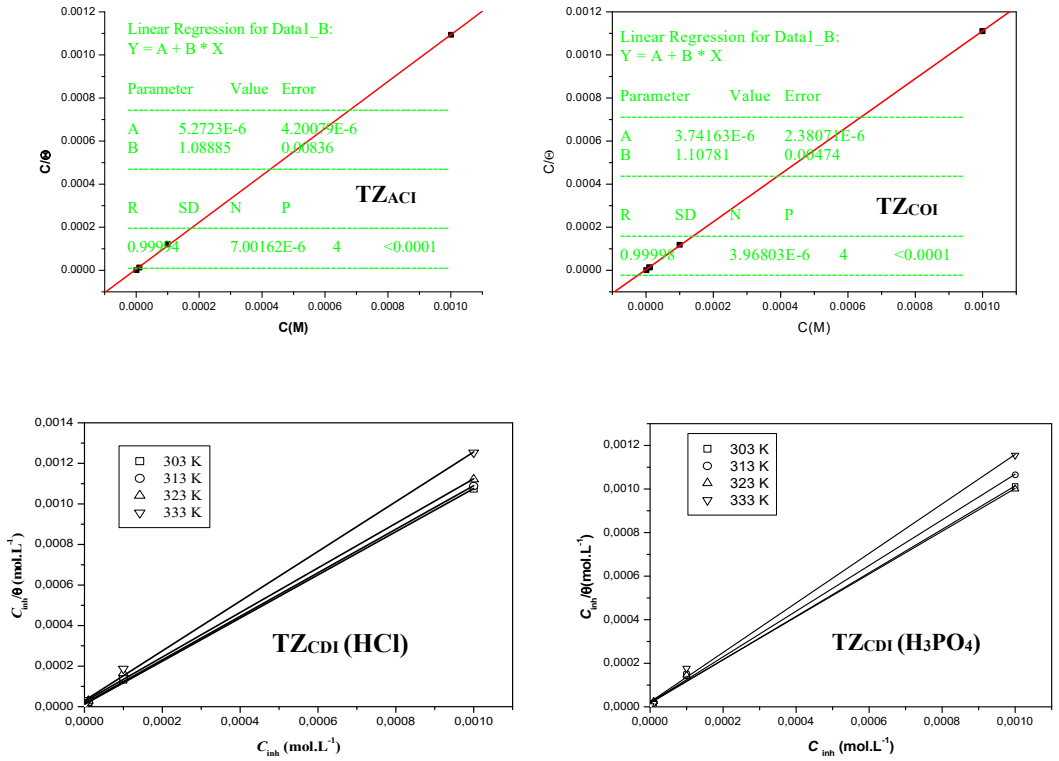


Figure 4. Langmuir adsorption plots for mild steel in acid solutions with TZ_{ACI}, TZ_{COI} and TZ_{CDI}

The adsorptive equilibrium constant (K) and the free energy values of adsorption ($\Delta G°_{ads}$) values were calculated and given in **Table 3**.

Table 3. Equilibrium constant and standard free energy of adsorption of mild steel in acids with TZ_{ACI}, TZ_{COI} and TZ_{CDI}

Inhibitors	Slope	R^2	K_{ads}(M^{-1})	$\Delta G°_{ads}$ (kJ mol^{-1})
TZ_{ACI}	1.08	0.999	1.9 10^5	-17.97
TZ_{COI}	1.10	0.999	2.610^5	-42.26
TZ_{CDI}(HCl)	1.06	0.999	1.610^5	-40.45
TZ_{CDI}(H_3PO_4)	1.05	0.999	1.675	-40.5

The negative value of $\Delta G°_{ads}$ indicates that the inhibitors TZ_{COI} and TZ_{CDI} are chemisorbed and the TZ_{ACI} inhibitor is physisorbed due to, the values of $\Delta G°_{ads}$ up to −20 kJ/mol signify physisorption, while the values around −40 kJ/mol or higher suggest chemisorptions[29].

Surface analysis

Scanning electron microscopy (SEM) images are given in **Figure 5** to see the changes that occurred during corrosion process.

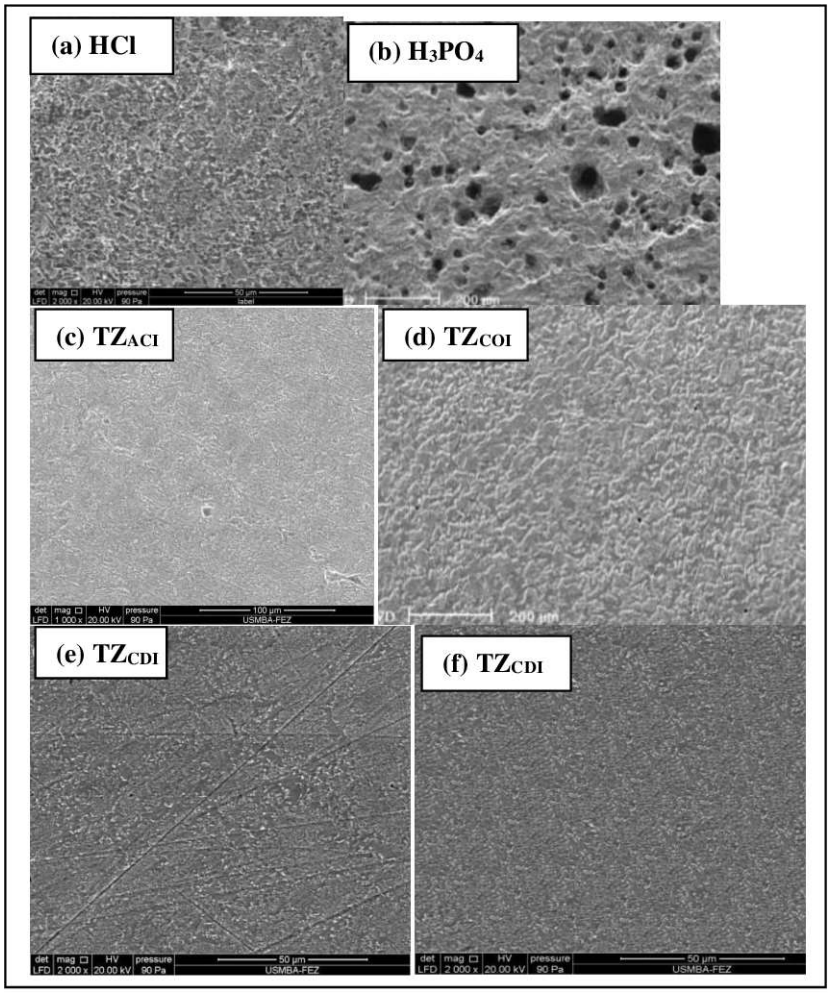


Figure 5. SEM images of mild steel: a, b) mild steel immersed in 1.0 M hydrochloric acid 1.0M and phosphoric acid c, d, e) mild steel immersed in 1.0 M hydrochloric acid in presence of TZ_{ACI}, TZ_{COI} and TZ_{CDI} and f) mild steel immersed in 1.0 M phosphoric acid in presence of TZ_{CDI}

The Images of the mild steel surface reveals that the surface is strongly damaged in the absence of inhibitor. But in the presence of inhibitor-free region due to the metal dissolution in acidic media. In contrast, in the presence of inhibitors, a relatively smoother and less corroded morphology of steel surfaces can be observed.

This is due to the formation of adsorption layer of molecules of these inhibitors which depress the corrosion on the metal surface[30].

Conclusion

According to the results the corrosion inhibition mechanism based on 5-Chloroisatin derivatives 1-allyl-5-chloro-indoline-2,3-dione (TZ_{ACI}), 5-chloro-1-octylindoline-2,3-dione (TZ_{COI}) and 5-chloro-1-(2-(dimethylamino) ethyl) indoline-2,3-dione (TZ_{CDI}) composites used to protect mild steel in an acidic medium was successfully investigated. We could summarize the following conclusions:

1. From weight class method, the efficiencies of these organic compounds TZ_{ACI}, TZ_{COI} and TZ_{CDI} increase with increasing inhibitors concentrations and reached maximum values of 91%.
2. Potentiodynamic polarization studies indicate that these 5-Chloroisatin derivatives act as mixed type of inhibitors by an adsorption process.

3. Electrochemical impedance results suggest that the obtained Nyquist diagrams exhibit one single capacitive loop, pointing out that mild steel corrosion in essentially under charge transfer control.

4. The adsorption of the inhibitors TZ_{ACI}, TZ_{COI} and TZ_{CDI} on the mild steel specimen in acidic media solution follows the Langmuir adsorption isotherm.

5. The adsorption on the steel surface is done by chemisorptions type for TZ_{COI} and TZ_{CDI} and physisorption type for TZ_{ACI}.

6. The formatted thin layers of the inhibitors on the mild steel's surface are confirmed by the smooth surface of SEM images in HCl and H_3PO_4.

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