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WATERMELON PEEL EXTRACT AS GREEN CORROSION INHIBITOR FOR ST-37 CARBON STEEL IN SEAWATER

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Abstract
Corrosion engineering has taken great interest in many industries that required high-cost management to overcome the serious problems. This work has investigated the role of watermelon peel extract as green inhibitor to protect carbon steel in seawater. This investigation has studied the corrosion rate and inhibition efficiency applying weight loss method. The laboratory result shows the optimum inhibition efficiency found to be 71.64% at 5% inhibitor concentration in 100 ml seawater at room temperature. The effects of temperature and immersion time on inhibition efficiency have also been examined. This study has used Arrhenius equation based on activation energy to determine type of adsorption encountered with corrosion process. The result shows a chemical adsorption justified by its high adsorption heat and strengthened by FTIR (Fourier Transformation Infra-Red) and UV-Vis (Ultra Violet-Visible) examinations. The phytochemical examination of watermelon peel extract gives positive response to flavonoid, alkaloid, and saponin. The finding is useful for many industries encountered with carbon steel corrosion in corrosive medium using green inhibitor. The novelty of this study is emphasized on the beneficiation of natural organic waste (watermelon peel extract) used for corrosion inhibition as the major issue of this work.

Keywords: carbon steel, corrosion rate, inhibition efficiency, watermelon peel extract.

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1. Introduction

In recent decades, green corrosion inhibition has taken great interest of many corrosion engineers. Many corrosion researchers have considered to use natural products, natural polymers, plants, and fruit extracts as green corrosion inhibitors[1–6]. It is known that such green compounds are less destructive to human and environment and can be applied as moderately good corrosion inhibitors. They possess some benefits over chemical inhibitors since they are relatively low cost, natural, readily available and less harmful due to more biodegradable[3, 6]. Moreover, the presence of N, O, and S hetero-atomic organic compounds in green corrosion inhibitor acted as electron donor in π-orbital may impede corrosion rate between reactive anodic metal and corrosive medium[7–8].

Vessels and piping, as well as construction material in marine equipment usually apply stainless steel due to its high corrosion resistance towards corrosive saline medium[9–11]. Stainless has better corrosion resistance properties over mild steel due to the presence of chromium, nickel, manganese, molybdenum, and other metal alloys at certain concentrations, therefore, austenitic steel has many used for marine device in seawater[12–13]. The present work has used low carbon steel (<< 0.2% C) on reasoning of moderately yield strength and corrosion resistance. Table 1 shows the specification of fabricated ST-37 steel applied for this study.

Table 1 Composition of elements in ST-37 steel [14].

Element	%	Element	%
Fe	99.310	S	0.015
Mn	0.375	Co	0.007
C	0.118	Nb	0.006
Si	0.055	Cu	≤ 0.004
W	0.046	Mo	≤ 0.02
Ni	0.026	Al	≤ 0.002
Cr	0.021	V	≤ 0.001
P	0.017		

Watermelon is attributed to vine-like flowering plants that is belongs to the family of *Cucurbitaceae*. Table 2 shows the taxonomy of *Citrullus lanatus* in watermelon peel[14]. The *Citrullus lanatus* is under the genus *Citrullus* because it is a desert vine and native to Eurasia and Africa[4,15].

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Table 2 Taxonomy of Citrullus lanatus in watermelon plant [14]

Domain	: Eukarya
Kingdom	: Plantae
Phylum	: Embryophyta
Class	: Dicotyledoneae
Ordo	: Cucurbitales
Family	: Cucurbitaceae
Genus	: Citrullus
Species	: *Citrullus lanatus*

The Greek word "citrus" is referred to fruits. Therefore, it is known as large edible fruits with a hard green rind and a watering reddish, yellowish, or pink pulp[15]. Furthermore, the watermelon peel extract contains some valuable amount of saponin, alkaloids, hydrogen cyanide, tannins, phytate, phenol, oxalate and flavonoids. The watermelon peel as agricultural waste product was reported as a source rich in citrulline, a non-essential amino acid. Fig. 1 shows the chemical structure of citrulline. The citrulline contains heteroatoms (O and N) and aromatic ring, which are regarded as potential corrosion inhibitor.

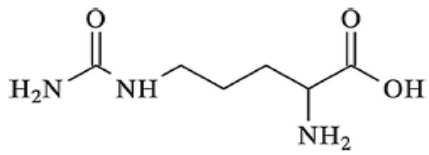

Fig. 1 Chemical structure of citrulline [15]

However, phytochemical compounds such as flavonoid, alkaloid, saponin, steroid, and terpenoid that possess corrosion inhibition character will be justified their existence in watermelon peel through phytochemical analysis conducted in this study.

Up to date, watermelon has been known for fruit cocktails, juices, and nectars. Only little known that the agricultural waste product can be used for corrosion inhibition. Petchiammal applied watermelon rind extract and watermelon leaf to protect zinc in seawater, while Odewunmi applied watermelon peel extract as corrosion inhibitor for mild steel in acidic media (HCl and H_2SO_4)[15,16]. To the best of our knowledge, the utilization of watermelon peel extract to protect low carbon steel in saline medium has never been reported.

Until now, only few articles related to issue on corrosion inhibition on beneficiation of natural organic waste used as inhibitor have ever been published. On account of this, the role of water melon extract for corrosion inhibitor can be viewed as moderately good novelty. This study is ongoing with the current issue on corrosion inhibition that takes great interest in the field of corrosion engineering.

Therefore, the aims of this study is (i) to examine the active compounds in watermelon peel extract and characterized the product by FTIR and UV-Vis examinations, (ii) to investigate the effect of watermelon peel extract inhibitor on corrosion rate and inhibition efficiency of low carbon steel in saline water using weight loss method, (iii) to examine the type of adsorption whether physical or chemical adsorption using thermodynamics study based on activation energy. Fig. 2 shows the layout of the present work.

2. Experimental and Procedures

2.1 Material and Apparatus

This work applied ST-37 carbon steel, watermelon peel extract, a given volume of seawater, acetone, methanol, HCl, HNO_3 1%, ethanol 70%, Mg powder, and $FeCl_3$ 1%. All chemicals used in analytical grade.

This investigation used blender, analytical balance, abrasive paper, water bath, thermometer, desiccator, oven, FTIR and UV–Vis spectrophotometer.

2.2 Extraction of watermelon peel and characterizations by FTIR and UV–Vis

The procedure of watermelon peel extract is as follows: (i) the endocarp of watermelon peel was cut into small pieces, (ii) the small pieces of watermelon peel endocarp was washed and rinsed with clean water, (iii) 750g watermelon peel pieces was added by 1500 ml distilled water and blended, (iv) then the solution was filtered using a vacuum pump (v) the filtrate as the stock solution of watermelon peel extract inhibitor was stored and diluted to obtain given varied inhibitor concentrations.

2.2.1 Phytochemical analysis

The phytochemical analysis identified active compounds in watermelon peel extract known as flavonoid, saponin, alkaloid, steroid and terpenoid. The phytochemical analysis was conducted by following the previous procedure[17].

(i) Identification of flavonoid

About 1g watermelon peel extract in fine cutting and 5 ml ethanol were taken into a reaction tube. Then 0.1g Mg powder and 2 drops of concentrated HCl was added into the reaction tube. A red color appeared in ethanol layer indicated the presence of flavonoid.

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(ii) Identification of saponin

About 1g watermelon peel extract in fine cutting was boiled in distilled water, shaken, and remained for 15 min. The formation of stable foam for moderate time indicated the presence of saponin.

(iii) Identification of alkaloid

About 1g watermelon peel extract in fine cutting was grinded in a mortar and then added by 10 ml ammonia-chloroform. The mixture was filtered and taken into a reaction tube, then added by 5 ml sulfuric acid 2 N and remained for a while. Then the upper layer was taken and dropped onto a drop plate, then dropped by *dragendorf* reagent. The formation of orange color indicated the presence of alkaloid.

(iv) Identification of steroid and terpenoid

About 1g watermelon peel extract added by chloroform and dropped the solution onto drop plate and remained for a while. Then added by droplets of acetate anhydride and concentrated sulfuric acid. The formation of green color or bluish green indicated the presence of steroid, while red or purple color formation indicated the presence of terpenoid.

2.2.2 FTIR and UV–Vis characterizations

The FTIR and UV–Vis characterizations were conducted for watermelon peel extract, respectively, before and after corrosion experiment. The FTIR characterization was scanned for wavenumber range of 4000–500 cm^{-1}[15]. The UV-Vis characterization was scanned for wavelength range of 200–400 nm.

2.3 Effect of watermelon peel extract inhibition on carbon steel corrosion in saline water

The preparation of steel sample is as follows: (i) A given sized steel was fined using abrasive paper and washed by detergent and distilled water; (ii) The steel was immersed in a mixture of HNO_3 1% and acetone to remove any grease pasted to steel surface; (iii) After that, the steel was dried in an oven at 40^{o}C for 5 min.; (iv) Then, the steel was put in a desiccant for 15 min., and (v) Finally, the steel was weighed designated as inhibitor free steel weight (Wo).

The effect of % inhibitor coating was determined as follows: The as-prepared steel was submerged in a 100 ml solution of watermelon peel extract with varied concentrations (5, 10, 15, and 20 % v/v) for 2h, respectively. Then, the steel samples were dried in an oven at 40^{o}C for 5 min. and put in a desiccant for 15 min. After that, steel samples were weighed to obtain their respective increased weights and the % inhibitor coating on steel surface can be determined.

Furthermore, all steel samples were submerged in 100 ml seawater for a-day. The corrosion rate and inhibition efficiency were determined.

In order to examine the effect of immersion time on corrosion rate of carbon steel in sea water and inhibitor solution, the procedure is as follows: the steel sample was immersed in a mixture of 100 ml seawater and watermelon peel extract at varied concentrations (0, 5, 10, 15, and 20%). The immersion time in seawater was varied for 1, 2, 3, 4, 5, 6, and 7 days. After given time, the steel sample was taken and washed with soap using fine brush. Afterwards, the steel sample was submerged in solution mixture of nitric acid and acetone, and then was dried in an oven at 40^{o}C for 5 min. Then the steel sample was put in a desiccant for 15 min. Furthermore, all steel samples were respectively weighed and designated as W_1[18].

2.4 Determination of % inhibitor layer, corrosion rate and inhibition efficiency applying weight loss method

Some fundamental equations in corrosion field are given below:

The determination of % inhibitor coating was defined as follows:

$$\%\ inhibitor\ coating = \frac{final\ weight - initial\ weight}{initial\ weight} \times 100 \quad (1)$$

The determination of corrosion rate was defined based on weight loss method [19]:

$$C_r = \frac{w_1 - w_2}{A\ x\ t} = \frac{\Delta\ w}{A\ x\ t} \quad (2)$$

C_r = Corrosion rate (g/cm^2. day)
w_1 = weight before submersion (g)
w_2 = weight after submersion (g)
Δw = weight loss (g)
A = area of corrosive steel (cm^2)
t = time of submersion (day)

The determination of inhibition efficiency was defined as follows [20]:

$$IE = \frac{C_0 - C_{inh}}{C_0} \times 100\% \quad (3)$$

IE = inhibition efficiency (%)
C_0 = corrosion rate inhibitor free (g/cm^2.day)
C_{inh} = corrosion rate with inhibitor (g/cm^2.day)

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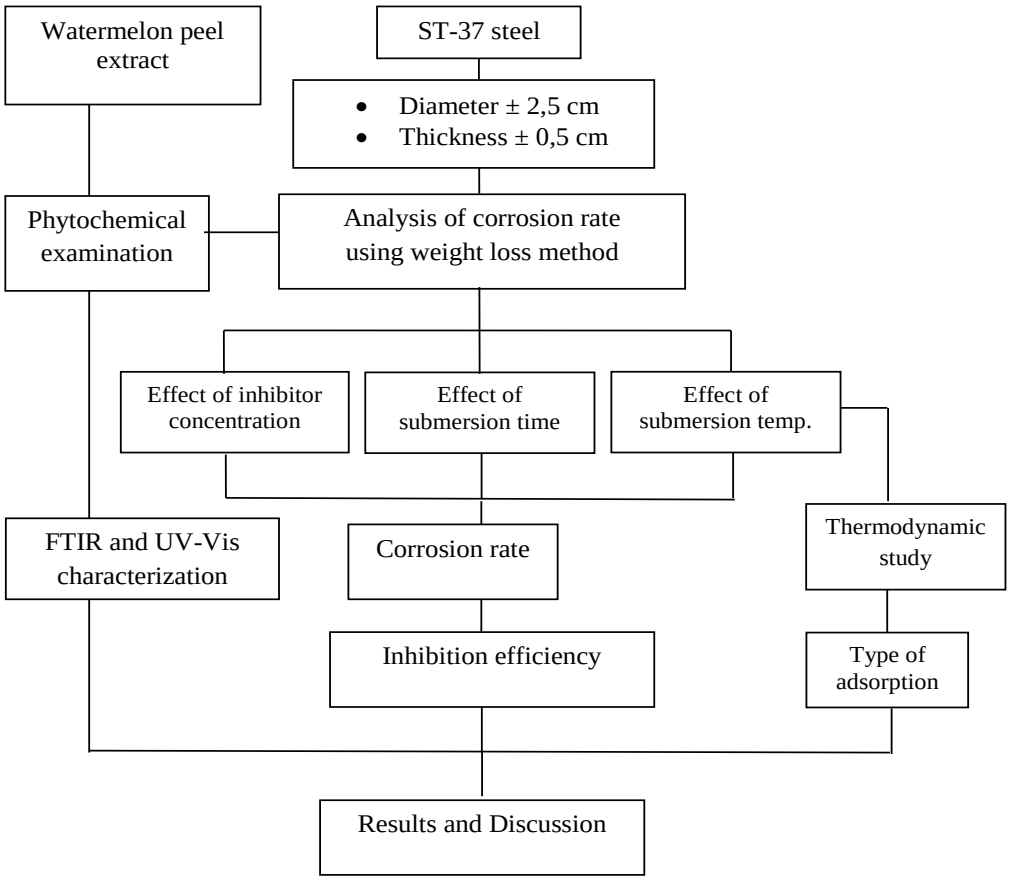

Fig. 2. Layout of the present study related to watermelon peel extract inhibition on low carbon steel corrosion in saline medium.

2.5 Examination of type of adsorption

In the thermodynamic study, the Gibbs free energy for adsorption or well known as heat of adsorption is an indication for type of interaction between inhibitor material and metal surface whether it shows physical adsorption or typical chemisorption[19]. According to Aljourani, if the heat of adsorption is about -20 kJ/mol or less negative, it is an indication of physical adsorption, on the other hand, if the heat of adsorption is around -40 kJ/mol or more negative, it shows a chemical adsorption[21].

In the Arrhenius equation, the heat of adsorption is expressed as energy of activation and given below[22]:

$$\log C_r = \frac{-E_a}{2.303\,RT} + \log A_r \quad (4)$$

C_r = corrosion rate (g/cm^2.day)
E_a = energy of activation (kJ/mol)
T = temperature (K)
R = universal constant (8.314 kJ/mol)
A_r = Arrhenius factor, depends on chemical reaction

3 Results and Discussion

3.1 Phytochemical analysis

As already mentioned above, phytochemical compounds in corrosion inhibitors possess heteroatoms (N, O, and S) and aromatic character that displays important role in corrosion inhibition. The study of Suedile on zinc corrosion in NaCl solution using *Mansoa alliacea* plant investigated phytochemical test on alkaloid, saponin, flavonoid, quinone, triterpene, and coumarine and concluded that the active compounds showed potential corrosion inhibition[6].

The results of phytochemical analysis on watermelon peel extract are given in Table 3 below:

Table 3 Results of phytochemical analysis of watermelon peel extract.

Phytochemical compound	Test result
Flavonoid	+
Alkaloid	+
Saponin	+
Steroid	-
Terpenoid	-

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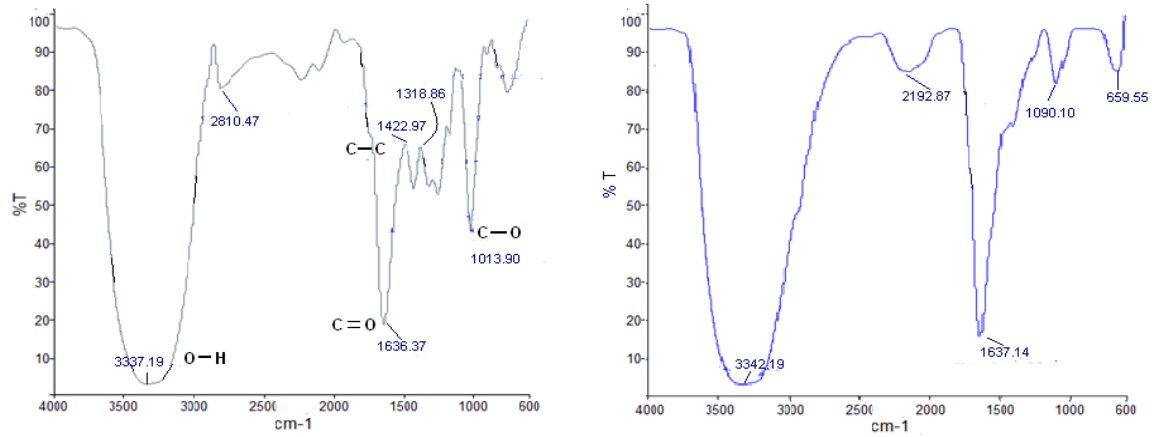
3.2 FTIR and UV-Vis characterization

Fig. 3 shows the FTIR spectra of watermelon peel extract before immersion (a) and after immersion in a-day seawater using 5% inhibitor (b). The 5% inhibitor was selected on account of optimum results obtained from corrosion rate and inhibition efficiency experiments. As shown in Fig. 3 the -OH and C=O functional groups are undergone a little shift to shorter wavelength, the absorption peak of -OH group shifted from 3337.19 cm^{-1} to 3342.19 cm^{-1}, while the absorption peak of C=O group shifted from 1636.37 cm^{-1} to 1637.14 cm^{-1}, both shifts due to immersion of watermelon peel extract in seawater for a-day. After the immersion in seawater for a-day, two absorption peaks in relation to $-CH_2-$ and $-CH_3$ with respective to 1422.97 cm^{-1} and 1318.86 cm^{-1} belong to watermelon peel extract are disappeared after immersion in seawater for a-day. It is assumed the corrosion effect might have broken some chemical bonding in the inhibitor molecule. It is apparently, several absorption peaks in Fig. 3(a) were disappeared in Fig. 3(b) attributed to any change in chemical structure of the inhibitor due corrosion effect by seawater. However, there is an absorption peak appeared at 659.55 cm^{-1} as shown in Fig. 3(b) attributed to the formation of Fe=O bond as a result of interaction between molecule of inhibitor and the carbon steel. In addition, an absorption peak was observed at 1013.90 cm^{-1} (Fig. 3a) undergone a shift to 1090.10 cm^{-1} (Fig. 3b) attributed to C-O bond, and the related absorption peak undergone a significant reduction. It is assumed that the C-O bonds were broken due to immersion in seawater. Suedille [6] reported the FTIR spectra of *Mansoa alliaceae* plant inhibitor due to kind of treatments (reflux and ultrasound assisted extraction) for zinc corrosion in seawater.

Fig. 4 illustrates the UV–Vis spectra of watermelon peel extract before immersion (a) and after immersion in seawater for a-day using 5% inhibitor (b). As shown in Fig. 4, the absorption peak was undergone hypochromic shift from 224 nm (Fig. 4a) to 218 nm (Fig. 4b) as a result of immersion of watermelon peel extract inhibitor in seawater. Moreover, there was a significant change of the peak absorption profile observed in wavelength range of 250–300 nm. With regard to wavelength range of 250–300 nm, Fig. 4(b) shows a significant downward absorption curve instead of more rigid absorption contour shown by Fig. 4(a). The change of absorption curve in the interested wavelength range is assumed in association with typical type of adsorption. It is reasonable since the C=O, -OH, C-O, and N–H in phytochemical compounds of watermelon peel extract inhibitor may have chemical interaction with iron of carbon steel to form Fe ion ligand complex [15].



(a) (b)

Fig. 3. FTIR spectra of watermelon peel extract. (a) before immersion. (b) after a-day immersion in seawater. 5% inhibitor.

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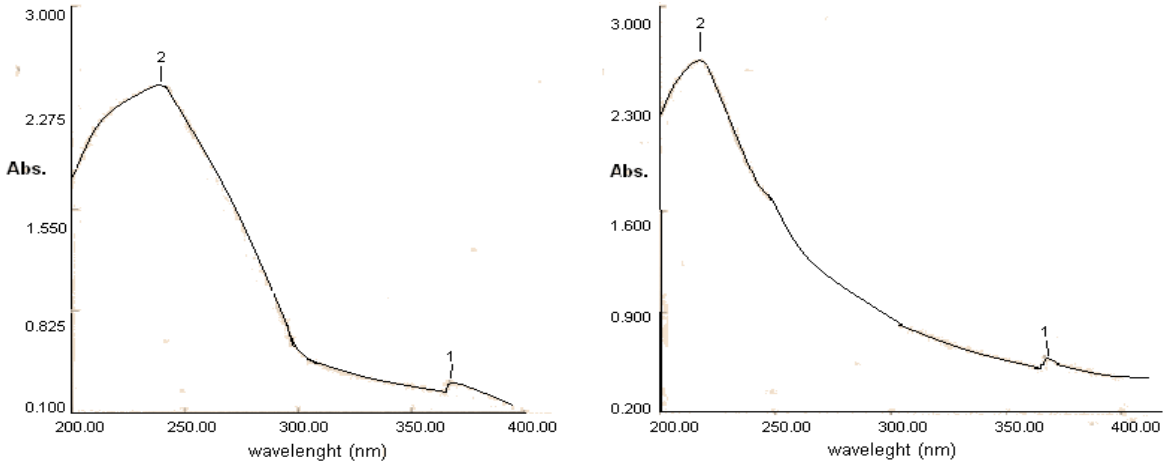

Fig. 4. UV–Vis spectra of watermelon peel extract. (a) before immersion. (b) after a-day immersion in seawater. 5% inhibitor.

Table 4 % inhibitor coating on steel surface. Watermelon peel extract inhibitor. 2h immersion in seawater. Carbon steel with avg. Φ and thickness of 2.54 cm and 0.52 cm, respectively.

Conc. inh. (% w/v)	W_0	W_1	ΔW	% extract coating	% coating (avg.)
5	19.4462	19.4592	0.0130	0.067	0.087
	19.6666	19.6876	0.0210	0.107	
10	19.4905	19.5141	0.0236	0.121	0.103
	19.5543	19.5709	0.0166	0.085	
15	19.5573	19.5802	0.0229	0.117	0.162
	17.7507	17.7874	0.0367	0.207	
20	17.8759	17.9096	0.0337	0.189	0.199
	17.7322	17.7695	0.0373	0.210	

Table 5 Corrosion rate and inhibition efficiency. Carbon steel corrosion. Watermelon peel extract. A-day immersion in seawater. Carbon steel with avg. Φ and thickness of 2.54 cm and 0.52 cm, respectively. Range of exposed area ≈14.1 – 14.4 cm^2. Weight loss method.

Inh. conc. (% w/v)	$W_{0\,(g)}$	$W_{1\,(g)}$	ΔW (g)	$C_r \times 10^{-4}$ (g/cm^2.day)	$\bar{C}_r \times 10^{-4}$ (g/cm^2.day)	IE (%)
0	20.3591	20.3472	0.0119	8.2433	8.7282	0
	20.2310	20.2177	0.0133	9.2131		
5	19.4462	19.4432	0.003	2.1131	2.4749	71.64
	19.6666	19.6626	0.004	2.8366		
10	19.4905	19.4828	0.0077	5.4238	3.4163	60.86
	19.5543	19.5523	0.002	1.4087		
15	19.5573	19.5505	0.0068	4.7898	4.1131	52.88
	17.7507	17.7458	0.0049	3.4362		
20	17.8759	17.8705	0.0054	3.8080	4.3342	50.34
	17.7322	17.7253	0.0069	4.8603		

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Table 6 Effect of immersion time (days) on corrosion rate. Immersion in mixture of seawater and extract solution. Carbon steel corrosion. Watermelon peel extract inhibitor.

Time (day)	$C_0 \times 10^{-4}$ (g/cm^2.day)	$C_1 \times 10^{-4}$ (g/cm^2.day) 5% inh.	$C_1 \times 10^{-4}$ (g/cm^2.day) 10% inh.	$C_1 \times 10^{-4}$ (g/cm^2.day) 15% inh.	$C_1 \times 10^{-4}$ (g/cm^2.day) 20% inh.
1	9.7417	4.3016	7.7051	4.0866	5.3182
2	7.3358	2.5277	3.1213	3.8572	4.1085
3	5.1465	2.0143	0.7944	2.7394	2.4350
4	4.1015	1.5060	1.9664	2.6767	3.3097
5	4.1119	1.3422	2.1343	2.1007	2.9585
6	3.5002	0.7533	1.3794	1.8504	2.2764
7	4.1244	0.9474	1.5872	1.5537	2.8169

Table 7 Effect of temperature on corrosion rate. Immersion (2h) in mixture of seawater and extract solution. Carbon steel corrosion. Watermelon peel extract inhibitor. 10 % inhibitor. Φ = 2.54 cm. Thickness 0.52 cm (avg.). Range of exposed area ≈14.1 – 14.3 cm^2.

Temp. (˚C)	W0 (g)	W1 (g)	ΔW (g)	$C_r \times 10^{-3}$ (g/cm^2.h)	$\bar{C}_r \times 10^{-3}$ (g/cm^2.h)
35	19.3358	19.3203	0.01550	0.5459	0.4854
	19.6126	19.6004	0.01220	0.4249	
45	20.5481	20.5372	0.01090	0.3817	0.3757
	19.4314	19.4209	0.01050	0.3698	
55	17.8834	17.8495	0.03390	1.1872	1.2658
	20.2012	20.1626	0.03860	1.3443	
65	19.5118	19.4278	0.08400	2.9584	2.6041
	19.3719	19.3073	0.06460	2.2499	

3.3 Effect of inhibitor concentration on extract layer

Fig. 5 shows the effect of concentration of watermelon peel extract on extract inhibitor coating on carbon steel surface when the carbon steel submerged in extract solution at given varied concentrations (5%, 10%, 15%, and 20%) for 2h, respectively.

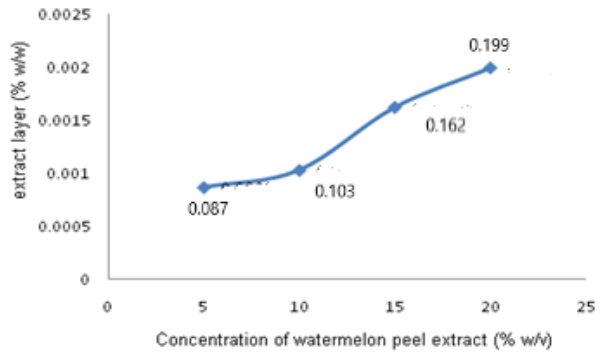

Fig. 5. Carbon steel submerged in varied concentrations of extract solution (5, 10, 15, and 20%) yielded extract layer adhered on steel surface after 2h immersion.

It is not surprising, the extract layer increased with increased concentration of inhibitor solution. This experiment investigated the effect of varied extract concentrations on % extract coating of carbon steel surface.

3.4 Effect of varied extract concentrations on corrosion rate and inhibition efficiency of carbon steel submersion in seawater.

Fig. 6 shows the effect of varied concentrations of watermelon peel extract (5, 10, 15, and 20%) coated on carbon steel surface on corrosion rate and inhibition efficiency of steel submersion in a-day seawater.

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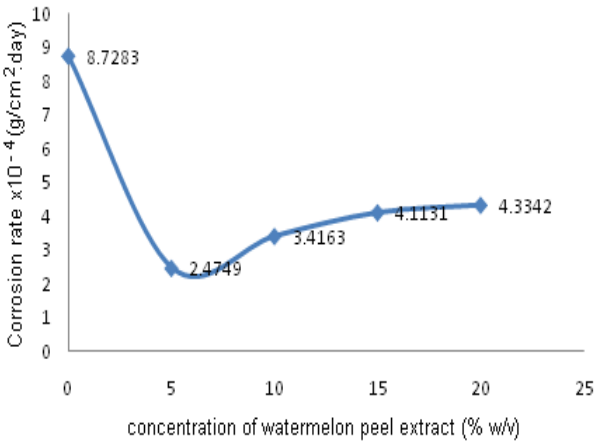

Fig.6. Corrosion rate of carbon steel submersion in a-day seawater at varied extract concentrations (5, 10, 15, and 20%).

As seen in Fig. 6, the corrosion rate of carbon steel in seawater significantly reduced in the presence of inhibitor. This phenomenon is in agreement with previous reports [3,5–6,15]. Fig. 6 shows the corrosion rate slightly increased at certain concentration of extract inhibitor range (> 5–20%). This finding can be elucidated as follows: The oxidized Fe ion of steel attacked by nucleophilic hetero atoms of extract inhibitor during corrosion process. Increased extract inhibitor concentrations (> 5%) yielded more nucleophilic attacked on iron steel yielding more iron converted to more soluble oxidized ion Fe form causing increased weight loss of coated carbon steel, thus, the corrosion rate slightly increased at a given inhibitor concentration range (> 5–20%). Therefore, there is an optimum extract inhibitor concentration found by this study. Odewunmi [15] studied the corrosion of mild steel in strong acid media applying watermelon rind inhibitor. The study of Odewunmi inspired this investigation, however, this study related to carbon steel in seawater and applying different characterizations with respect to phytochemical analysis and characterizations by FTIR and UV–Vis spectrophotometry[15]. Suedile applied *Mansoa alliacea* plant as inhibitor to protect zinc rod in sodium chloride media; the investigation used phytochemical examination and FTIR characterization as did by this study[6]. Fares used Iota-carrageenan inhibitor to protect aluminum in HCl medium in the presence of zwitter-ion[3].

The inhibition efficiency is affected by its corrosion rate as formulated in Eq. (3) mentioned above. Fig. 7 shows the effect of varied concentrations of extract (5, 10, 15, and 20%) on inhibition efficiency of carbon steel corrosion in seawater. More extract inhibitor added caused the inhibition efficiency slightly reduced (Fig. 7). It is not surprising, the trend of inhibition efficiency is inversely proportional to the trend of corrosion rate. Fares reported increased inhibition efficiency found with increased inhibitor concentrations for a certain range, however, as the medium HCl concentrations increased leading to increased weight loss yielding decreased inhibition efficiency[3].

3.5 Effect of submersion time of carbon steel corrosion in mixture of seawater and varied extract inhibitor concentrations (5, 10, 15, and 20%).

Submersion time of carbon steel in mixture of seawater and extract inhibitor solution gives effect on corrosion rate. Fig. 8 shows the effect of submersion time (days) of varied extract inhibitor concentrations on corrosion rate of carbon steel. As seen in Fig. 8, the three-day submersion shows the lowest corrosion rate at 10% extract inhibitor. Although the 10% extract inhibitor yielded the lowest corrosion rate, however, with regard to the given days of immersion (1–7 days) the 5% extract inhibitor can be regarded as the optimum inhibitor concentration in this finding since averagely, the 5% extract inhibitor yielded averagely low corrosion rates compared to the other inhibitor concentrations.

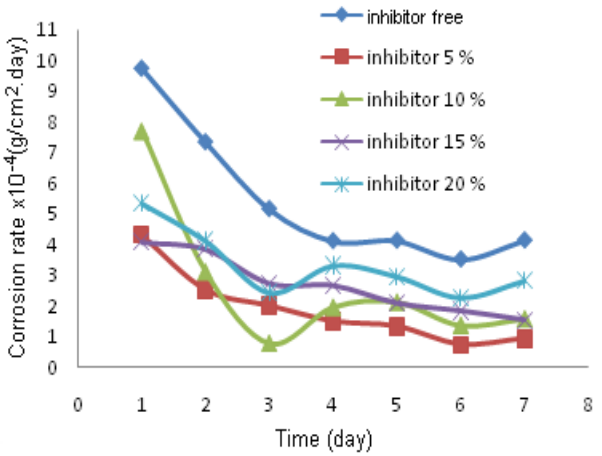

Fig. 8. Effect of submersion time (days) of carbon steel in mixture of seawater and varied extract inhibitor concentrations (5, 10, 15, and 20%).

The fluctuated curve of corrosion rate as shown in Fig. 8 at varied inhibitor concentrations (5, 10, 15, and 20%) during 7-day observation indicated unstable response affected by environment condition regarded ambient temperature and relative humidity from day to day. The 5% inhibitor looks more consistent for corrosion rate response as the day of observation getting longer. The higher inhibitor concentrations (> 5%) show remarkable fluctuated

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response probably due to unstable nucleophilic attacked on Fe of carbon steel as the inhibitor concentration getting higher. The existence of interaction between Fe of carbon steel and nucleophilic phytochemical compounds is strengthened by FTIR justification by formation of Fe=O bond at 659.55 cm^{-1}.

This study justified that temperature yielded significant effect on corrosion rate. Fig. 9 shows that increased temperature of observation (35, 45, 55, and 65°C) yielded increased corrosion rate. The temperature effect is apparent more significant for the corrosion rate without the existence of inhibitor. The presence of extract inhibitor retarded the reaction between Fe of carbon steel and nucleophilic phytochemical compounds in watermelon peel extract. It is reasonable the higher temperature may induce the reaction between Fe of carbon steel and active compounds of watermelon peel extract.

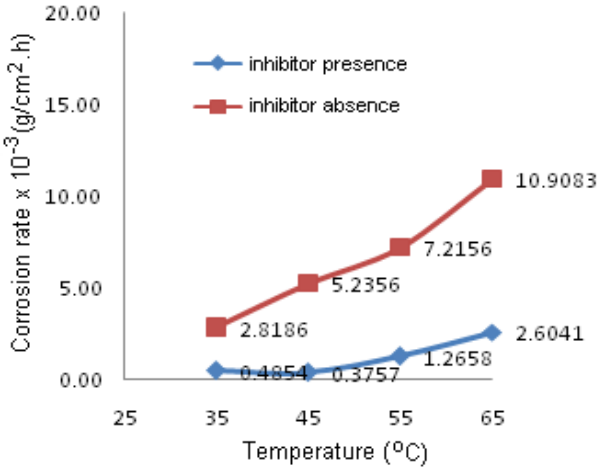

Fig. 9. Temperature effect on corrosion rate in the absence and presence of extract inhibitor. 10% inhibitor. 2h submersion in mixture of seawater and inhibitor solution.

Fares studied effect of temperature (10–40°C) on corrosion rate and inhibition efficiency at varied inhibitor concentrations (400–1600 ppm) on aluminum in HCl medium applying Iota-carrageenan seaweeds extract inhibitor. The finding obtained by this study is in agreement with the report of Fares that increased temperatures induced higher corrosion rates and reduced inhibition efficiency. Fig. 10 shows the effect of temperatures on inhibition efficiency at varied temperatures (35, 45, 55, and 65°C). As already mentioned, this finding is in agreement with Fares report[3].

Fares used thermodynamic equation related to free Gibbs energy vs. temperature to determine type of adsorption[3]. As already mentioned above, if the heat of adsorption less negative than -20 kJ/mol it is attributed to physisorption, on the other hand, if it more negative than -40 kJ/mol it is attributed to chemisorption

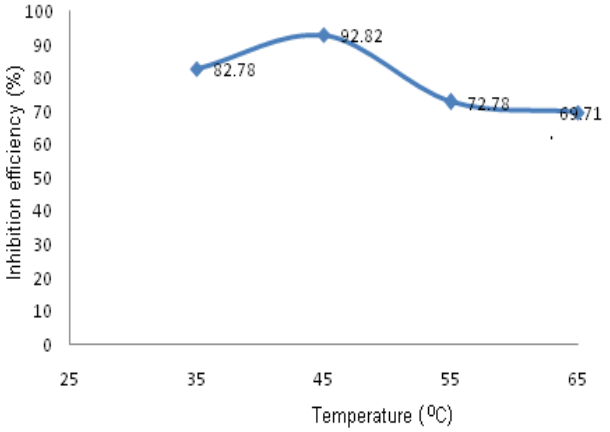

Fig. 10 Temperature effect on inhibition efficiency. 10% inhibitor. 2h submersion in mixture of seawater and extract inhibitor solution.

$$\Delta G^{o}_{ads} = \Delta H^{o}_{ads} - T \Delta S^{o}_{ads} \quad (5)$$

Where ΔH^{o}_{ads} and ΔS^{o}_{ads} are the standard enthalpy and entropy of adsorption, respectively. Derived eq. (5) and rearrangement to obtained ln K vs. 1/T, finally we obtain the heat of adsorption.

However, this study applied Eq. (4) as already described above, then conducted the graph of ln C_r vs. 1/T, we obtained the slope indicated the activation energy referred to heat of adsorption, thus, the type of adsorption could be determined. Fig. 11 shows the regression of ln C_r vs. 1/T for carbon steel corrosion using watermelon peel extract and we obtained the slope.

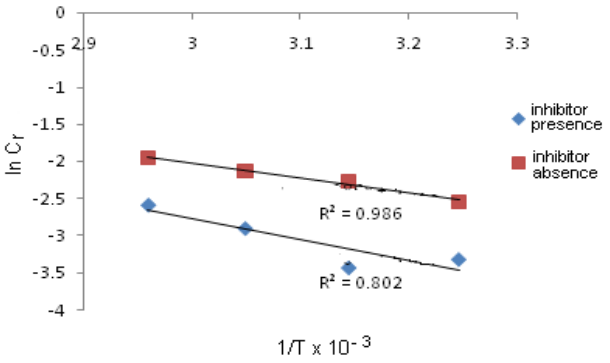

Fig. 11. Plotting corrosion rate vs. reciprocal temperature. Watermelon peel extract inhibitor. 10% inhibitor.

The data of activation energy obtained by this study is shown in Table 8.

Table 8 Data of activation energy derived from Arrhenius equation. Watermelon peel extract inhibitor. Carbon steel corrosion in seawater.

Carbon steel corrosion	Activation energy (kJ/mol)
Absence of inhibitor	– 38,0262
Presence of inhibitor	– 53,6311

As seen in Table 8, the activation energy in the presence of inhibitor is more negative than -40 kJ/mol, therefore, according to the thermodynamics rule, it is attributed to chemical adsorption or chemisorption. This finding is strengthened by the FTIR and UV–Vis examination.

3 Conclusions

The varied temperatures and varied submersion time, as well as varied green inhibitor concentrations give significant effects on corrosion rate and inhibition efficiency. The phytochemical analysis justified the presence of flavonoid, alkaloid, and saponin as the active compounds display important role on corrosion inhibition. The FTIR and UV–Vis characterization justified the occurrence of chemical interactions attributed to bonding ruptures of organic compounds and Fe=O formation. The thermodynamic study justified the corrosion inhibition process attributed to chemical adsorption. The findings give useful information for readers working in construction industries.

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References

[1] Abu-Dalo, M. Al-Rawashdeh, N.A.F. & Ababneh, A. Evaluating the performance of sulfonated Kraft lignin agent as corrosion inhibitor for iron-based materials in water distribution systems. *Desalination. 2013; 313*: 105 – 114.

[2] Akbarzadeh, E. Ibrahim, M. & Rahim, A.A. Corrosion inhibition of mild steel in near neutral solution by Kraft and Soda lignins extracted from oil palm empty fruit bunch. *Int. J. Electrochem. Sci. 2011;6*:5396 – 5416 .

[3] Fares, M.M. Maayta, A.K. & Al-Mustafa, J.A. Corrosion inhibition of iota-carrageenan natural polymer on aluminum in presence of zwitterion mediator in HCl media. *Corrosion Sci. 2012;65*:223 – 230.

[4] Odewunmi, N.A. Umoren, S.A. & Gasem, Z.M. Utilization of watermelon rind extract as a green corrosion inhibitor for mild steel in acidic media. *J. Industrial Eng. Chem. 2015;21*:239 – 247.

[5] Sakhri, A. Perrin, F.X. Benaboura, A. Aragon, E. & Lamouri, S. Corrosion protection of steel by sulfo-doped polyaniline-pigmented coating. *Progress in Organic Coatings. 2011;72*: 473 – 9.

[6] Suedile, F. Robert, F. Roos, C. & Lebrini, M. Corrosion inhibition of zinc by *Mansoa alliacea* plant extract in sodium chloride media: extraction, characterization and electrochemical studies. *Electrochim. Acta. 2014: 133*: 631 – 8.

[7] Alva, S. Hua, T.I Nizar, U.K. Wahyudi, H. & Sundari, R. Sol gel method for synthesis of semiconducting ferrite and the study of FTIR, DTA, SEM and CV. *IOP Conf. Series: Materials Science & Engineering. 2018; 343*: 012002.

[8] Alva, S. Sundari, R. Wijaya, H.F. Majlan, E.H. Sudaryanto, Arwati, I.G.A. & Sebayang, D. Preliminary study on aluminum-air battery applying disposable soft drink cans and Arabic gum polymer. *IOP Conf. Series: Materials Science & Engineering. 2017; 237:* 012039.

[9] Araujo Macedo, R.G.M. Marques, N.N. Tonholo, J. & Balaban, R.C. Water-soluble carboxy methyl chitosan used as corrosion inhibitor for carbon steel in saline medium. *Carbohydrate Polymers. 2019; 205:* 371 – 6.

[10] Deyab, M.A. Efficiency of cationic surfactant as microbial corrosion inhibitor for carbon steel in oilfield saline water. *J. Molecular Liquids. 2018; 255:* 550 – 5.

[11] Obot, I.B. Onyeachu, I.B. & Kumar, A.M. Sodium alginate: A promising biopolymer for corrosion protection of APIX60 high strength carbon steel in saline medium. *Carbohydrate Polymers. 2017; 178:* 200 – 8.

[12] Chen, S. Deng, H. Zhao, Yudi. Lu, S. Zhao, Yao. 'et al'. The effects of Methanococcus maripaludis on the corrosion behavior of EH40 steel in seawater. *Bioelectrochem. 2021;140:* 107824.

[13] Zu, H. Li, X. Lu, X. Wang, J. Hu, Z. & Ma, X. Efficiency of Gemini surfactant containing semi-rigid spacer as microbial corrosion inhibitor for carbon steel in simulated seawater. *Bioelectrochem. 2021;140:* 107809.

[14] Prihati, S.T. Effisiensi penggunaan ekstrak kulit

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semangka (*Citrullus lanatus*) sebagai inhibitor organic terhadap laju korosi baja ST-37 dalam medium air laut (Efficiency of watermelon peel extract (*Citrullus lanatus*) application as organic inhibitor on corrosion rate of ST-37 steel in seawater medium). Thesis, Faculty of Mathematics and Science, Universitas Negeri Padang. 2017.

[15] Odewunmi, N.A. Umoren, S.A. & Gasem, Z.M. Watermelon waste products as green corrosion inhibitors for mild steel in HCl solution. *J. Environ. Chem. Eng. 2014; 3:* 286 – 296.

[16] Petchiammal, A. Deepa Rani, P. Selvaraj, S. & Kalirajan, K. Corrosion protection of zinc in natural sea water using *Citrullus vulgaris* peel as an inhibitor. *Res. J. Chem. Sci. 2012; 2:* 24 – 34.

[17] Bagga, M.K. Gadi, R. Yadav, O.S. Kumar, R. Chopra, R. & Singh, G. Investigation of phytochemical components and corrosion inhibition property of *Ficus racemosa* stem extract on mild steel in H_2SO_4 medium. *J. Environ. Chem. Eng. 2016; 4:* 4699 – 4707.

[18] Altwaig, A.M. Khouri, S.J. Al-luaibi, S. Lehmann, R. Drucker, H. & Vogt, C. The role of alkali extracted lignin as corrosion inhibitor. *J. Mater. Environ. Sci. 2011; 2:* 259 – 270.

[19] Sharfawati, C.S. Aziz, M. Sundari, R. Polarization behavior of carbon steel corrosion in strong acid media in the presence of methyl thiophene inhibitor. *Ind. J. Sci. Res. Tech. 2014; 2:* 25 – 30.

[20] Doner, A. Solmaz, R. Ozcan, M. kardas , G. Experimental and theoretical studies of thiazoles as corrosion inhibitors for mild steel in sulfuric acid solution. *Corrosion Sci. 2011; 53:* 2902 – 2913.

[21] Aljourani, J. Golozar, M.A. & Raessi, K. The inhibition of carbon steel corrosion in hydrochloric and sulfuric acid media using some benzimidazole derivatives. *Mater. Chem. Phys. 2010; 121:* 320 – 5.

[22] Alaneme, K.K. & Sunday, J.O. Corrosion inhibition performance of lignin extract of sun flower (*Tithonia diversifolia*) medium carbon low alloy steel immersed in H_2SO_4 solution. *Leonardo J. Sci. 2012; 20:* 59 – 70.