Chemistry Extended Essay

"Investigation the effect of Papaver Rhoeas, Malva Grandfolia, and Carduus Marianus Leaves Extracts on Mild Steel in HCl solution, by using weight loss method and linear polarisation resistance technique"

Vedat Burak Kandemirli

00129053

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Supervisor: Serenay Tarhan Güler

TED Ankara Collage Foundation High School

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ABSTRACT

We can say mild steel studied corrodes in hydrochloric acid solutions, and also mild steel corrodes when exposed to a solution of HCl and the rate of corrosion increases as the immersion time increases. Therefore, inhibition effect of Papaver rhoeas, Malva Grandfolia, and Carduus Marianus leaves extract as corrosion safe inhibitors on the mild steel corrosion in hydrochloric acid solution was studied using traditional weight loss method as well as linear polarisation resistance technique. Corrosion inhibition efficiency of Papaver rhoeas, Malva Grandfolia, and Carduus Marianus leaves extracts was evaluated using weight loss measurements for effect of various solution concentrations in 1.0M HCl solution. In addition, linear polarisation method estimating of corrosion rate instantaneously was performed to evaluate both various solution concentration and different HCl concentrations, and different immersion time. It was found that three selected extract of Papaver rhoeas, Malva Grandfolia, and Carduus Marianus leaves reduced the corrosion of mild steel with an efficiency of 96.4 %–97.4 % in 1 M HCl for 24 hours immersion time. The inhibition efficiency of Papaver rhoeas leaves is slightly more than those of Malva Grandfolia, and Carduus. The results of both methods showed that the corrosion rate of mild steel exposed to a solution of hydrochloric acid is decreasing and inhibition yield is growing with the concentration of Papaver rhoeas leaves extract, and the best i effect was obtained as Papaver rhoeas leaves volume reached 80 mL for 24 hours immersion time.

I used two methods and one of them is weıght loss and the other is linear polarization and lınear polarization is better than weigtht loss because There are many advantages to linear polarization method. One of them is easy to determine corrosion rate, the other one is corrosion efficiency calculated quickly. To determine corrosion rate at least 24 hours are

required for weight loss method. In weight loss method, coupons are used in corrosion measurement only one times.

Inhibition efficiency studies of Papaver rhoeas, Malva Grandfolia, and Carduus Marianus leaves extract done with the linear polarization method showed that the inhibition efficiency values generally decreased as the concentration of HCl solution increased.

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INTRODUCTION

When I lived in campus of Petrochemical Factory in my childhood, I saw that the color of wire netting, basketball hoop and my bicycle changed. Then in High school, when we studied corrosion, I learned the reason of these changes due to corrosion.

All materials are susceptible to degradation due to interactions with their environments, and corrosion of most metals (and many materials for that matter) is inevitable. [[1]].More serious consequence of corrosion affects our lives during travel from home to work or school. For example, the sudden collapse because of corrosion fatigue of the Silver Bridge over the Ohio River at Point Pleasant, OH in 1967 resulted in the loss of 46 lives and cost millions of dollars. Perhaps most dangerous of all is corrosion that occurs in major industrial plants, such as electrical power plants or chemical processing plants. Plant shutdowns can and do occur as a result of corrosion [[2]].When I read these news, I thought myself is it possible to halt or prevent corrosion in acidic solution. Then I found some chemical substances called inhibitor might prevent the corrosion of mild steel in acidic solution. Then I learned most chemicals are expensive and hazardous. When I investigated I learned some plants were used as inhibitor. So, I selected Papaver rhoeas, Malva Grandfolia, and Carduus Marianus leaves which grow everywhere themselves to see whether they have inhibition effect on corrosion of mild steel in acidic solution. The inhibition effect of all organic compounds increases with increasing the additive concentration and reach a limit in value. Thus limiting value is believed to be related to the formation of a monolayer film of the adsorbent on the active sites of the metal [[3]]. The objective of our study is to find out the inhibitive properties of various concentrations of

[1] www.asminternational.org
[2] Sudhish Kumar Shukla and M.A. Quraishi, Journal of Applied Electrochemistry, 2009, Volume 39, Number 9, Pages 1517-1523
[3] Mahmoud A. Al-Qudah, E-Journal of Chemistry 1011, 8(1), 326-332

Papaver rhoeas, Malva Grandfolia, and Carduus Marianus leaves for the corrosion of mild steel under study in 1.0 M, 2.0 M, 3.0 M HCl solutions with weight loss measurements and linear polarization resistance method. I used different volume of extract to see the limiting value of extract I used. In my knowledge, this is the original study.

1.1 Research Question:

Is it possible to inhibit mild steel corrosion in 1.0 M, 2.0 M, 3.0 M HCl solution at room temperature and under atmospheric pressure by using extracts of Papaver rhoeas, Malva Grandfolia, and Carduus Marianus leaves and compare the methods of weight loss method and linear polarization resistance method for the determination of inhibition efficiency?

Corrosion is the metals deterioration. Most metals corrode when they contact with water acids, bases, salts, etc. Metals will also corrode on exposed to acid vapors, formaldehyde gas, ammonia gas, and sulfur containing gases. Corrosion is an electrochemical process in nature. The oxygen in the air dissolving in the water causes rust to form. We can summarize the chemistry of corrosion as follow,

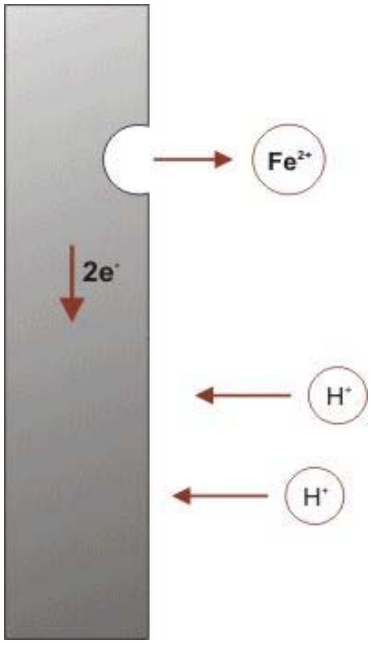
Metal is dissolved and goes into solution (water)

$Fe \rightarrow Fe^{+2} + 2\bar{e}$, this is called anodic reaction and

$O_2 + 2H_2O + 4\bar{e} \rightarrow 4OH^-$, Oxygen dissolved into water called cathodic reaction

$Fe^{+2} + 2OH^- \rightarrow Fe(OH)_2$ This is the final reaction.

All metals and alloys undergo a natural process of corrosion depending on the metal (some more easily oxidized than the others) and the surrounding environment.



The following conditions need occurring corrosion (1) cathode (side for reduction take place) (2) anode (side for oxidation take place), (3) Electrical path to allow electrons to transfer to the corrosion site (4) ionic path allowing the metallic ions to be transported.

These two operations may be close to each other or away from each other according to conditions.

Anodic reaction of the corrosion process metal is dissolved and while ions are formed some electrons are generated as shown in the following equation.

These electrons are consumed in a secondary process called cathodic reaction ($O_2 + 2H_2O + 4\bar{e} \rightarrow 4OH^-$). Charges have to balance each other, that is, there cannot be an oxidation reaction without a reduction reaction happening simultaneously.

1.2 Milk Thistle- Carduus Marianus

Carduus Marianus belonging to the member of Asteracea family is a medicinal plant. It possesses therapeutic properties. Having the activity properties of Carduus Marianus are due to silymarin which is an antioxidant. Silymarin contains flavonoid which is the most well known compound**. [**[4]**]**

[4] Anestis Karkanis, Dimitrios Bilalis, Aspasia Afthimiadou, Industrial Crops and Products 34(2011), 825-830

1.3 Papaver rhoeas

Papaver rhoeas L. (Papaveraceae) is an annual plant in the world. It is reported that plant papaver, rhoeas have emollient, narcotic and sedative properties. The extract of P. rhoeas contains flavonoids which are polyphenolic compounds [5,6]

1.4 Malva Grandfolia

Malva Leaf is an annual or perennial plant that is native to southern Europe and Asia and later introduced to North America. It has the properties such as soothing activity which is demulcent, anti inflammation activity, It is due to flavonoids and anthocyanidins, and, polysaccharides**. [7].**

1.5 Inhibitors

Corrosion inhibitor decreases the corrosion rate by several orders of magnitude when it is added to a corrosive media. Corrosion inhibition of mild steel is a matter of theoretical as well as practical importance [8]. Acids are used in various places industries such as descaling, cleaning, reactions, etc. Inhibitors are used to reduce the rate of dissolution of metals due to their degradation. They have been reported inhibitors are chemical substances containing nitrogen, sulphur and oxygen [9,10,11].Corrosion inhibitor is a chemical compound which is designed to protect adsorbed organic molecules prevents corrosion due to binding the active

[5] Danijela A. Kostic, Snezana S. Mitic, Milan N. Mitic, Aleksandra R. Zarubica, Jasmina M. Velickovic, Aleksandra S. Dordevic and Sasa S. Randelovic, Journal of Medicinal Plants Research Vol. 4(17), pp. 1727-1732
[6] http://www.herbalextractsplus.com/malva-leaf.cfm
[7] http://www.herbalextractsplus.com/malva-leaf.cfm
[8] S.A. Ali. M.T. Saeed. S.V. Rahman. Corros. Sci. 45 (2003) 253-266.
[9] M. Lagrenee. B. Mernari. M. Bouanis. M. Traisnel. F. Bentiss. Corros. Sci. 44 (2002) 573-588.
[10] M. A. Quraishi. R. Sardar. Corrosion 58 (2002) 748-755.
[11] M.A. Quraishi. M. Athar and H. Ali. Br. Corros. J. 37 (2002) 155-158.

sites on the metal surfaces forming a coordinate-type bond [12]. There are two types of adsorption, physical adsorption (physisorption) and chemical adsorption (chemisorption).

Physical adsorption is due to electrostatic interaction between the charged centers of inhibitor molecules and charged metal surface. The chemisorptions of organic molecules are due to offering electrons from occupied molecular orbitals of inhibitor molecules to virtual molecular orbitals of metals. The inhibition efficiency (E %) of inhibitor molecules containing N, O S atoms inhibitor depends strongly on the chemical properties of the molecule. Inhibition efficiency is a process influenced by the type and surface charge of the metallic surface, test conditions and chemical properties of used inhibitors [13]. Corrosion inhibitors can reduce the rate at which corrosion occurs, and block early corrosion damage although they will not completely prevent corrosion or a wide variety of chemicals can be used for this purpose. Unfortunately, due to most of the organic inhibitors used being very expensive and health hazards. It must be used with care to protect the environment. The application is limited because of their toxic properties. For example using of chromates has been banned because of toxicity and the environmental hazards they create. Therefore, it is important to find low-cost inhibitors of the non-hazardous type for the inhibition of corrosion of metals. The investigation of natural products origin as corrosion inhibitors is becoming popular due principally to the low cost and eco-friendliness of these products. Plant extracts constitute several organic compounds which have corrosion inhibiting abilities [14]. The plant extracts are environmentally friendly, non- toxic and readily available. These extracts contain many ingredients. Extracts of plant materials contain a wide variety of organic compounds. Most of them contain heteroatoms such as P, N, S, O. These atoms coordinate with the corroding

[12] C. Cao. Corros. Sci. 1996. 38. 2073–2082.
[13] R. Agrawal. T.K.G. Nambodhiri. J. Appl. Electrochem. 22 (1992) 383.
[14] Peter C. Okafor. Eno E. Ebenso and Udofot J. Ekpe. Int. J. Electrochem. Sci.. 5 (2010) 978 - 993

metal atom (their ions), through their electrons. Hence protective films are formed on the metal surface and hence corrosion is prevented [15].

The objective of our study is to investigate the inhibitive properties of various concentrations of Papaver rhoeas, Malva Grandfolia, and Carduus Marianus leaves for the corrosion of mild steel in 1M, 2M, 3M HCl solutions by using weight loss method and linear polarization resistance method.

METHOD

[See Appendix 1 for the full apparatus and chemical lists].

2.1 Linear polarization resistance method

Linear polarization resistance measures corrosion as an electrochemical method. Electrodes are corroded and metal ions passes easily into solution, so, a small potential applied between the electrodes will produce a high current.

The electrical resistance of any conductor is given by the following formula:

$$R = \frac{V}{I}$$

Where R: Effective instantaneous resistance,

V: Applied voltage,

I: Instantaneous current between current electrodes

So a low polarization resistance. This corresponds to a high corrosion rate.

All measurements were carried out in HCl solutions (1M, 2M and 3M) with and with various concentrations of Papaver rhoeas, Malva Grandfolia, and Carduus Marianus leaves at room temperature[16,17].

[15] M. Sangeetha, S. Rajendrani. T. S.Muthumegala. A.Krishnaveni, Zastita Materijala broj 152 (2011) 3-19
[16] Linear Polarization Resistance (LPR) General Information Caproco Internal coorrosion Monitoring Specialist
[17] ANÔNIMO. 1999. ASTM G31-72: Standard Practice for Laboratory Immersion Corrosion Testing of Metals. American Society for Testing and Materials. Philadelphia. USA.

Table 1: Mild steel composition under study.

Element	Round iron %	Coupons %			Round iron %	Coupons %
C	0.0964	0.1580		Mo	0.0044	0.0071
Mn	0.6760	0.5620		Ni	0.0435	0.1250
Si	0.1860	0.1610		Al	0.0020	0.0023
P	0.0172	0.0122		V	0.0021	0.0010
S	0.0211	0.0187		N	0.0010	0.0099
Cu	0.0628	0.1950		Fe	98.9000	98.6000
Cr	0.0203	0.1130		Ceq	0.2220	0.2980

The composition of mild steel used is given and the percentage of mild steel is given in Table1.

Table 2: Preparation of 1M HCl acid solution in different volume of Papaver rhoeas, Malva Grandfolia and Carduus Marianus leaves extract.

Beaker No	Papaver rhoeas extract (mL) (±0.1)	12M HCL acid solution (mL) (±0.01)	Deionised water (mL) (±0.01)		Carduus arianus extract (mL) (±0.1)	12M HCL acid solution (mL) (±0.01)	Deionised water (mL) (±0.01)		Malva Grandfolia extract(mL) (±0.1)	12M HCL acid solution (mL)	Deionised water (mL) (±0.01)
1	0.0	8.20	91.80		0.0	8.20	91.80		0.0	8.20	91.80
2	5.0	8.20	86.80		5.0	8.20	86.80		5.0	8.20	86.80
3	20.0	8.20	71.80		20.0	8.20	71.80		20.0	8.20	71.80
4	40.0	8.20	51.80		40.0	8.20	51.80		40.0	8.20	51.80
5	60.0	8.20	31.80		60.0	8.20	31.80		60.0	8.20	31.80
6	80.0	8.20	11.80		80.0	8.20	11.80		80.0	8.20	11.80

Table 2 lists the materials which the solutions are prepared.

Table 3: Mild steel coupons weight before and after immersion into 100ml of 1M HCl solutions (a) 24 hours immersion time, (b) 48 hours immersion time.

(a)	**Papaver rhoeas Leaves**		**Carduus Marianus Leaves**		**Malva Grandfolia Leaves**	
	The weight of mild steel coupons (g) ±0.0001					
Extract volume (mL) ±0.1	Before immersion	After 24 hours of immersion	Before immersion	After 24 hours of immersion	Before immersion	After 24 hours of immersion
80.0	16.3415	16.3283	17.5352	17.5107	16.0780	16.0600
60.0	16.2693	16.2530	16.4219	16.4011	16.3203	16.2997
40.0	16.0765	16.0572	16.3207	16.2987	16.1727	16.1528
20.0	16.5492	16.5198	17.6031	17.5655	16.2880	16.2606
5.0	16.2897	16.2478	16.3204	16.2664	16.4559	16.4002
Blank	15.9434	15.3356	15.9434	15.3356	15.9434	15.3356
(b)	**Papaver rhoeas Leaves**		**Carduus Marianus Leaves**		**Malva Grandfolia Leaves**	
Extract volume (mL) ±0.1	Before immersion	for 48 hours immersion	Before immersion	for 48 hours immersion	Before immersion	for 48 hours immersion
80.0	17.5334	174932	16.4075	15.9597	15.8411	15.7863
60.0	16.1889	16.1458	17.4971	17.4399	16.3203	16.1460
40.0	16.2017	16.1621	16.4119	16.3625	17.7868	17.7194
20.0	16.1633	16.1037	16.4359	16.3627	17.4625	17.3792
5.0	16.0655	15.9392	16.2928	16.1364	16.2231	16.0932
Blank	17.1034	15.5796	17.1034	15.5796	17.1034	15.5796

Table 3 lists data on mild steel coupons before and after exposing to the 1.0 M hydrochloric acid solution.

Weight loss of mild steel coupon after immersion into the acidic solution is given by the following formula

$$\Delta W = W_B - W_A$$

Where: ΔW = Loss in mass of mild in the corrosive solution (hydrochloric acid solution)

W_B = Weight of metal before immersion into the acidic solution.

W_A = Weight of metal after immersion into the acidic solution.

Weight loss for 1st trial, time 24 hours is calculated as following:

$$\Delta W = 15.9434g \mp 0.0001 - 15.3356g \mp 0.0001 = 0.6078g \mp 0.0002$$

Table 4: The weight data of mild steel coupons immersed into 1.0 M HCl in different concentrations of the Papaver rhoeas, Malva Grandfolia and Carduus Marianus leaves extract.

Extract volume (mL) ±0.1	**Papaver rhoeas Leaves**	**Carduus Marianus Leaves**	**Malva Grandfolia Leaves**	**Papaver rhoeas Leaves**	**Carduus Marianus Leaves**	**Malva Grandfolia Leaves**
	Weight loss (g) ±0.0002 after 24 hours			Weight loss (g) ±0.0002after 48 hours		
80.0	0.0132	0.0245	0.0180	0.0402	0.4478	0.0548
60.0	0.0163	0.0208	0.0206	0.0431	0.0572	0.1743
40.0	0.0193	0.0220	0.0199	0.0396	0.0494	0.0674
20.0	0.0294	0.0376	0.0274	0.0596	0.0732	0.0833
5.0	0.0419	0.0540	0.0557	0.1263	0.1564	0.1299
Blank	0.6078	0.6078	0.6078	1.5238	1.5238	1.5238

Table 4 lists the weight loss of the mild steel coupons corrosion in 1.0 M HCl solution for different concentrations of the Papaver rhoeas, Malva Grandfolia, and Carduus Marianus leaves extract for different time.

Table 5: Resistance of mild steel coupons immersed into 1.0 M HCl in different concentrations of the Papaver rhoeas, Malva Grandfolia, and Carduus Marianus leaves extract.

Extract volume (mL) ±0.1	**Papaver rhoeas Leaves** (±0.1)			**Carduus Marianus Leaves** (±0.1)			**Malva Grandfolia Leaves** (±0.1)		
	hours								
	1	24	48	1	24	48	1	24	48
80.0	1028.0	478.6	802.4	993.1	6 36.8	1207.0	1097.0	369.4	124.6
60.0	1196.0	836.1	469.4	1006.0	334.7	477.6	762.5	1042.0	82.0
40.0	1169.0	645.0	287.1	215.1	189.7	270.8	284.6	496.7	249.9
20.0	1033.0	1071.0	634.7	692.4	187.9	700.9	822.8	162.1	468.7
5.0	661.3	379.3	453.5	492.5	355.2	396.7	644.8	345.3	281.8
Blank	43.8	13.9	8.5	43.8	13.9	8.5	43.8	13.9	8.5

Linear Polarization Resistance measurements made after the immersion period of 1 hour 24 hours and 48 hours immersion in 1M HCL solution are given in Table 5.

Table 6: Mild steel coupon resistance in 2.0 M HCl and 3.0M HCL in different concentrations of the Papaver rhoeas, Malva Grandfolia and Carduus Marianus leaves extract.

E Extract volume (mL) ±0.1xtract volume (ml)	**Papaver rhoeas Leaves** (±0.1)	**Carduus Marianus Leaves** (±0.1)	**Malva Grandfolia Leaves** (±0.1)	**Papaver rhoeas Leaves** (±0.1)	**Carduus Marianus Leaves** (±0.1)	**Malva Grandfolia Leaves** (±0.1)
	2.0M			**3.0M**		
Blank	56.6	56.6	56.6	33.5	33.5	33.5
80.0	434.0	438.4	387.4	256.7	184.9	171.5
60.0	414.5	131.0	186.4	428.3	118.6	396.9
40.0	344.6	529.4	136.3	223.6	186.8	265.6
20.0	380.4	212.2	281.4	265.2	180.7	213.2
5.0	264.8	423.0	148.2	95.4	135.4	92.4

Linear Polarization Resistance measurements made after the immersion period of 1 hour immersion in 2M, 3M 1.0 M HCL solution in varying concentration (80ml, 60ml, 40ml, 20ml and 5 ml) of extract for Papaver rhoeas, Malva Grandfolia, and Carduus Marianus leaves are given in Table 5 and Tale 6.

2.5 Qualitative data:

Hydrogen gas freely bubbling during the corrosion of a steel alloy coupon, Color change of surface of mild steel alloy coupon. The color of 1.0 M solution after immersion of mild steel changes to gray. The color of solution is reddish brown. (Figure 1).

<table>
<tr>
<td> 
Before immersion HCl solution</td>
<td> 
After immersion HCl solution</td>
<td colspan="2"> 
Hydrogen gas bubbling when coupons were immerse into the beaker</td>
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<tr>
<td colspan="2"> 
The color of 1M HCl solutions with and without inhibitor at the time of the beginning of immersion</td>
<td colspan="2"> 
The color of 1M HCl solution with and without inhibitor at the time of the end of immersion</td>
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Figure 1 Qualitative observation of corrosion in 1M HCl of mild steel

RESULT AND DISCUSSION

The weight loss of mild steel coupons exposed 1.0 M HCl solution, in the absence and presence for different concentrations from the extract of Papaver rhoeas, Malva Grandfolia, and Carduus Marianus leaves, was determined after 24 hours and 48 hours immersion. The inhibition efficiency is calculated by using the following formula for weight loss method.

$$\%I.E = \left[\frac{(\Delta W_{corr} - \Delta W_{inh})}{\Delta W_{corr}}\right] x100$$

Where, W_{corr} and W_{inh} are the data of the weight loss per unit area of mild steel coupons exposed acid solution without and with of varying concentration (80ml, 60ml, 40ml, 20ml and 5 ml) of extract for Papaver rhoeas, Malva Grandfolia, and Carduus Marianus leaves.

The calculation for 80 mL extract of Papaver rhoeas leaves is given as an example:

Where: ΔWcor = 0.6078 (Weight loss for blank without inhibitor)

ΔW_{inh} = 0.0132 (Weight loss with inhibitor).

$$\%I.E = \left[\frac{(0.6078 \mp 0.0002 - 0.0132 \mp 0.0002)}{0.6078 \mp 0.0002}\right] x100 = 97.8\,\%$$

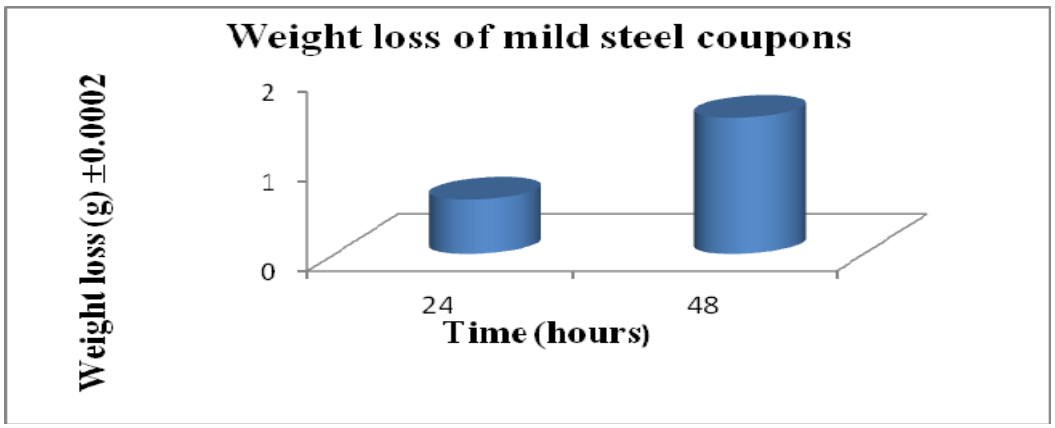


Figure 2. Variation of weight loss (grams) of mild steel coupons as a function of immersion time (hours) in1M HCl solution at room temperature.

We can conclude from the figure 2 that mild steel coupons corrodes in 1.0M HCl solutions. Weight loss of mild steel after 24 hours and 48 hours immersion in 1M 50.0ml HCl solution is 0.6078 g and 1.5238 g, respectively.

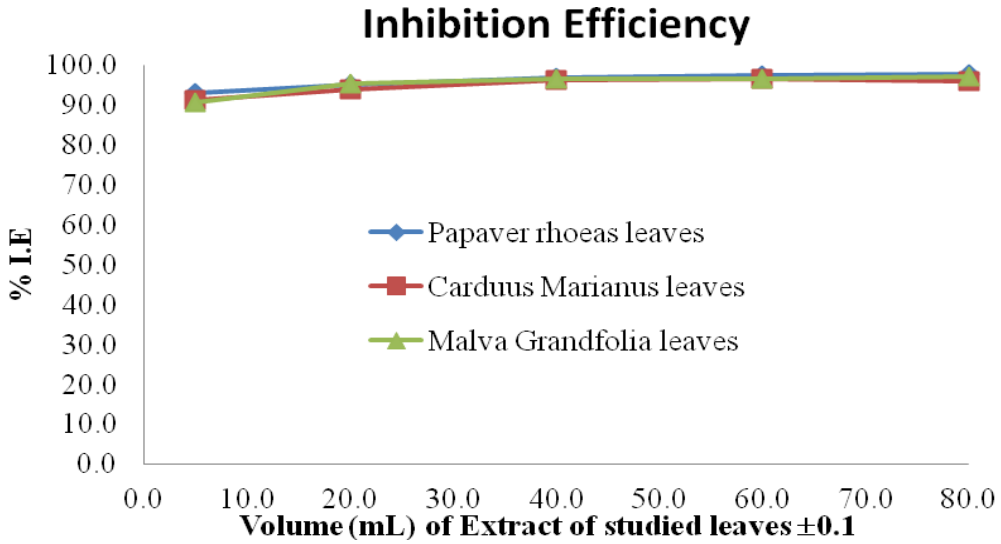


Figure 3. Inhibition efficiency (%I.E.) of mild steel exposed in 1.0 M HCl for varying volume from extract of Papaver rhoeas, Malva Grandfolia, and Carduus Marianus leaves for 24 hours.

As shown in Figure 3 and Figure 4, Papaver rhoeas showed the best protection with all concentration. As the concentration of Papaver rhoeas leaves extract increased inhibition efficiency increased and the best inhibition efficiency was obtained when Papaver rhoeas leaves volume reached 80 mL for 24 hours immersion time. The inhibition efficiency increased up to a maximum value (96.6%) at 40ml, as the concentration of Carduus Marianus leaves increased for 24 hours immersion time. The inhibition efficiency for Malva Grandfolia leaves increased as the inhibitor concentration increased and reaches 97 % at 80 ml extract of Malva Grandfolia leaves for 24 hours immersion time.

The inhibition efficiency of mild steel exposed 1.0 M hydrochloric acid solution in 5 mL, 20 mL, 40 mL, 60 mL, 80mL extract from Carduus Marianus leaves was found as 89.7%, 95.2 % 96.8%, 96.2%, 90.4 % for 48 hours immersion time. The reason of decrease in the efficiency of inhibition in high concentration is due to desorption.

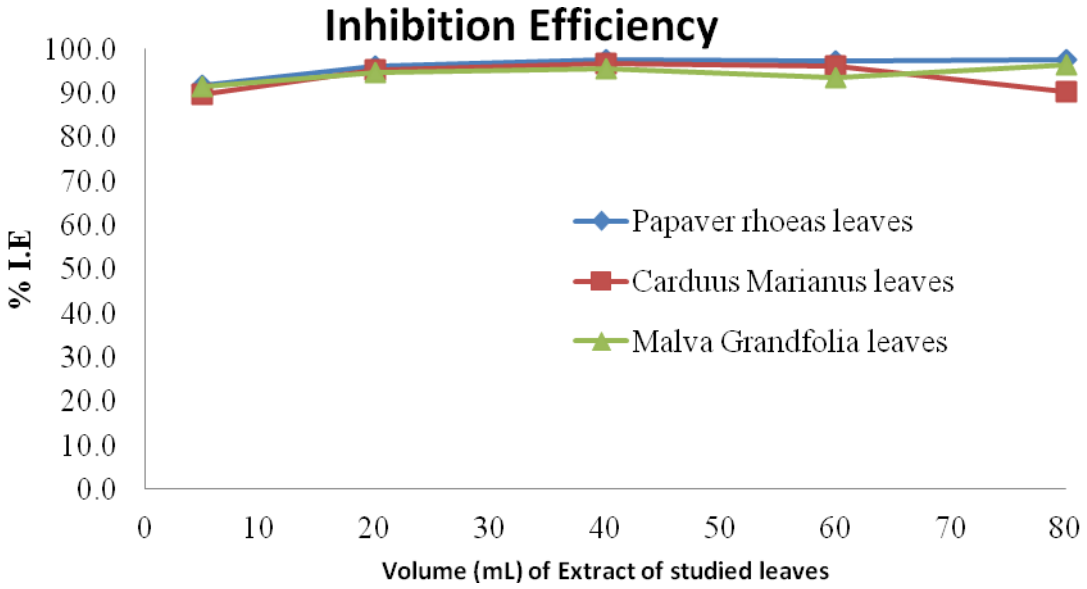


Figure 4. Inhibition efficiency (%I.E.) of mild steel in 1.0 M HCl containing different concentrations from extract for Papaver rhoeas, Malva Grandfolia, and Carduus Marianus leaves for 48 hours immersion time.

The maximum inhibition efficiency (I.E %) for 48 hours immersion time was observed at 40 ml for extract of Papaver rhoeas, Carduus Marianus, Malva Grandfolia leaves. Papaver

rhoeas leaves showed the best protection. Concentration changes of above 40mL lead to smaller changes in inhibition efficiency.

The mild steel electrical resistance in varying HCl solution concentration, presence and absence different concentrations extract of Papaver rhoeas, Malva Grandfolia, and Carduus Marianus leaves was determined for different immersion time. The electrical resistance technique is one of the most widely used methods for measuring material loss during the corrosion of the metal.

The inhibition efficiency (IE %) for each concentration of inhibitors calculated in 1 M HCl in the without and with extract of Papaver rhoeas leaves at different concentrations is shown in Figure 5. The electrical resistance measurement method has shown that inhibition efficiency of extract for Papaver rhoeas leaves increases when extract concentration is over the range 40 and 60ml. The maximum inhibition efficiency for 1 hour immersion time was found up to 96.3% at 40mL volume for Papaver rhoeas leaves extract.

The inhibition efficiency (I.E %t) for Malva Grandfolia leaves extract in 1 M HCl solution is given in Figure 6. We can observe from the graph that, as the immersion time is increased from 1 hour to 24 hours and to 48 hours the inhibition efficiency increases. Thus it is appropriate to say that increase in time favors the inhibition efficiency of extract of Carduus Marianus leaves in 1M hydrochloric acid solution.

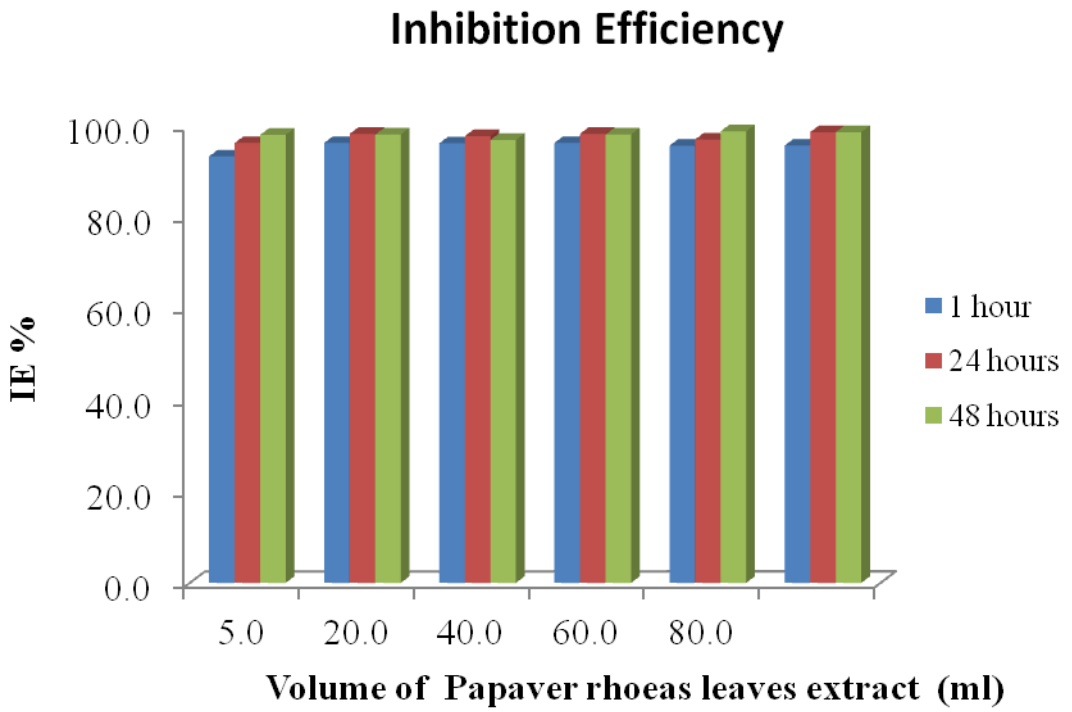


Figure 5. Inhibition efficiency (%I.E.) of Papaver rhoeas leaves extract on mild steel in 1.0 M HCl for 1hour, 24 hours and 48 hours immersion time.

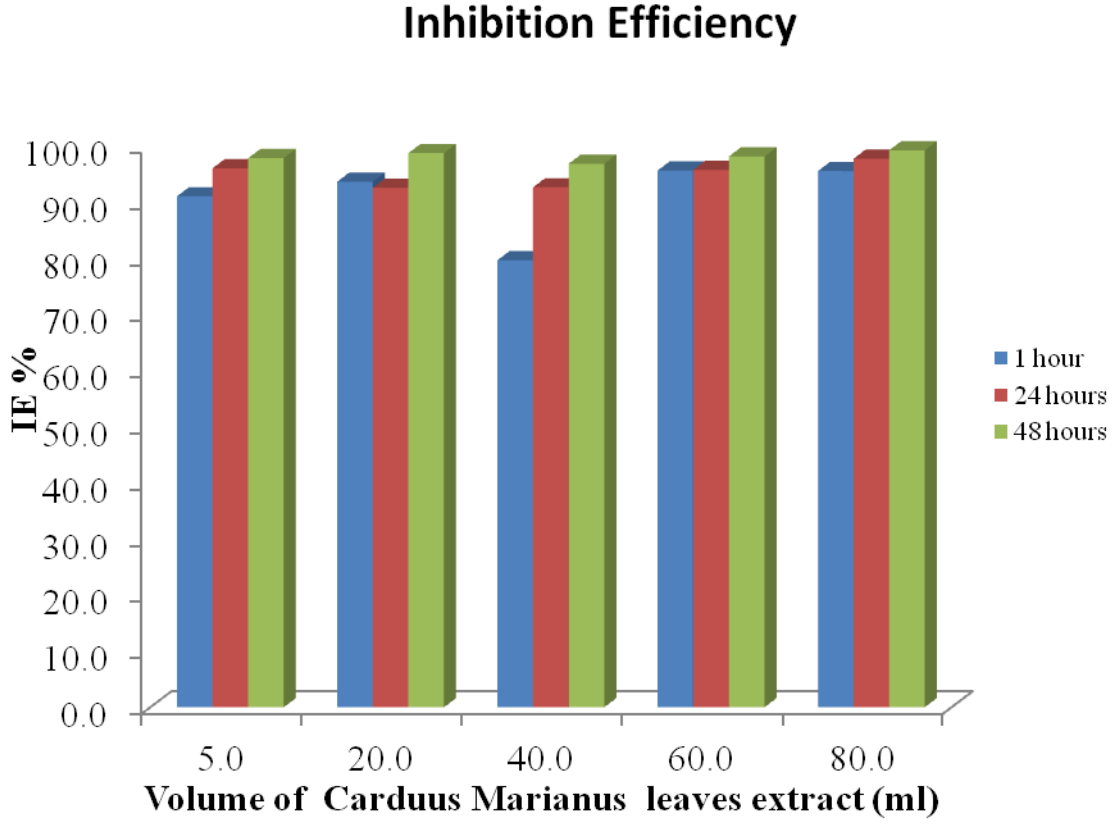


Figure 6. Inhibition efficiency (%I.E.) of Carduus Marianus leaves extract on mild steel in 1.0 M HCl for 1hour, 24 hours and 48 hours immersion time.

Figure 7 represents the inhibition efficiency (%I.E.) of Carduus Marianus leaves extract on mild steel in 1.0 M HCl for 1hour, 24 hours and 48 hours immersion time. The maximum inhibition efficiency obtained for extract of Carduus Marianus leaves at an inhibitor concentration of 60mL in 1M hydrochloric solution was 98.7% for 24 hours immersion time.

The obtained values of inhibition efficiency (E%) at varied extract of Papaver rhoeas, Malva Grandfolia, and Carduus Marianus leaves in 1.0 M, 2.0M, 3.0 M hydrochloric acid solution for 1 hour immersion time are presented in Table 6.

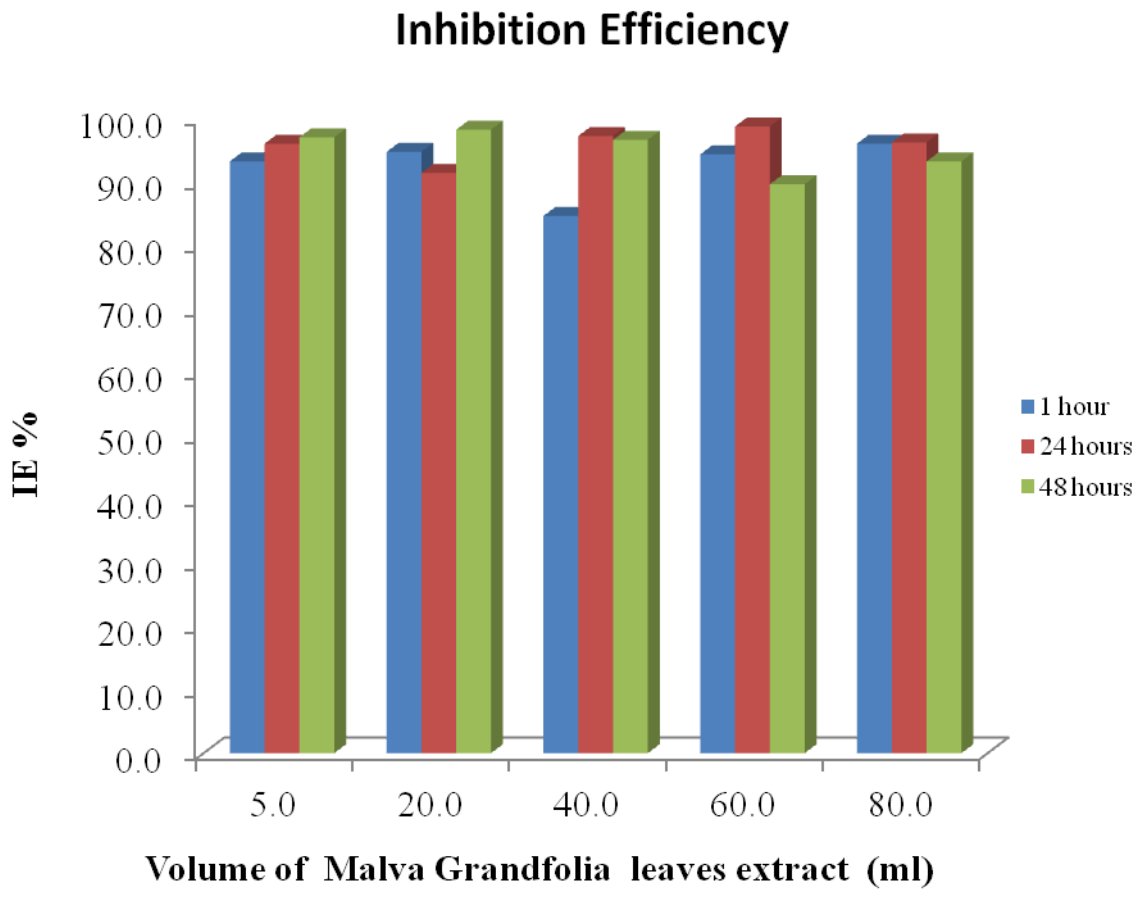


Figure 7. Inhibition efficiency (%I.E.) of Malva Grandfolia leaves extracts on mild steel corrosion in 1.0 M HCl for 1hour, 24 hours and 48 hours immersion times.

The results show that the inhibition efficiency values generally decreased as hydrochloric acid concentration increased.

t test was made to compare weight loss method and linear polarization method and the data of t test for extract of Papaver rhoeas, Malva Grandfolia, and Carduus Marianus leaves in 1.0 M, hydrochloric acid solution is given in Appendix 1 as Table 7.

Table 7: Inhibition efficiency (E %)

Extract volume (mL) ±0.1	Papaver rhoeas leaves (±0.1)			Malva Grandfolia leaves (±0.1)			Carduus Marianus leaves (±0.1)		
	HCl concentration								
	1.0 M	2.0 M	3.0M	1.0 M	2.0 M	3.0M	1.0 M	2.0 M	3.0M
5.0	93.4	78.6	64.9	91.1	86.6	75.2	93.2	61.8	63.7
20.0	95.8	85.1	87.4	93.7	73.3	81.5	94.7	79.9	84.3
40.0	96.3	83.6	85.0	79.7	89.3	82.1	84.6	58.5	87.4
60.0	96.3	86.4	92.2	95.7	56.8	71.7	94.3	69.7	91.6
80.0	95.7	87.0	86.9	95.6	87.1	81.9	96.0	85.4	80.5

Inhibition efficiency (E%) for varied extract of Papaver rhoeas, Malva Grandfolia, and Carduus Marianus leaves in 1.0 M, 2.0M, 3.0 M hydrochloric acid solution for 1 hour immersion time in Table 6

Assumptions: Two populations are independent and assumed to be normal and their variances are not known. However, we can compute their corresponding sample variances. The two experiments are compared at the level of 0.05 significance level.

H_0 is accepted. Therefore, two experiments are not different at the level of 0.05.

H_0 is rejected. Therefore two experiments are different at the level of 0.05.

CONCLUSION

To our knowledge no experimental effect of Papaver rhoeas, Malva Grandfolia, and Carduus Marianus leaves extract as corrosion safe inhibitors on corrosion of mild steel in hydrochloric acid solution have been listed in the literature. Therefore, my research question

was whether it is possible to inhibit mild steel corrosion in HCl solution by using extracts of Papaver rhoeas, Malva Grandfolia, and Carduus Marianus leaves.

Extracts of natural plants are environmentally friendly. non toxic and relatively less expensive, so in this study we used Papaver rhoeas, Malva Grandfolia. and Carduus Marianus leaves which are naturally occurring substances extract as inhibitor to investigate corrosion inhibitors for mild steel in HCl solution. We used weight loss method and linear polarization method. A study of three leaves extracts of Papaver rhoeas, Malva Grandfolia, and Carduus Marianus extract has proved to be an excellent inhibitor on mild steel under study in different hydrochloric acid solution. Weight loss method has shown that inhibition efficiency of Papaver rhoeas leave extract increases with increasing inhibitor concentration for 24 hours immersion time. The inhibition efficiency values calculated according to carried out weight loss method and linear polarization resistance method were compared with t test and found that the two means are not different at the level of 0.05 for Papaver rhoeas, malva grandfolia and Carduus Marianus extract at 24hours and for Papaver rhoeas, malva grandfolia extract at 48hours immersion time. Only for Carduus Marianus was found that the two means are different at the level of 0.05 for at 48hours immersion time. In my knowledge, this is the original study.

EVALUATION

In this study I only carried out loss weight method and linear polarization method to determine corrosion rate and also compared each other measuring the corrosion rate with two methods. The correlation inhibition efficiency calculated with weight loss method and linear polarization method is sometimes good agreement but sometimes bad. In t test, the results of two methods were found different at the level of 0.05 for only Carduus Marianus at 48hours immersion time. I could not find any correlation in one of the 6 t test. There are many advantages to linear polarization method. One of them is easy to determine corrosion rate, the

other one is corrosion efficiency calculated quickly. To determine corrosion rate at least 24 hours are required for weight loss method. In weight loss method, coupons are used in corrosion measurement only one times, but cylindrical mild steel can be used in many times after cleaning. Plant leaf extracts were freshly without waiting in anywhere used in corrosion experiment.

Trials and average values of carried out study are given in Appendix II with the standard error deviation. These errors may be due to dirt of surface of mild steel, temperature fluctuations. Therefore surface of coupons should be very clean and shiny. Temperature fluctuations should be avoided for the accuracy of experiment.

I determined corrosion rate in room temperature. The temperature effect on inhibition can also be studied detailed interpretation. In general, corrosion rate of metals increases with increase of temperature. Some mild steel has got critical pitting temperature, they do not pit in room temperature. Further experiments may be done in high temperature whether Papaver rhoeas, Malva Grandfolia and Carduus Marianus leave extracts prevent or not.

In further investigation different electrochemical methods such as potentiodynamic polarization, electrochemical impedance spectroscopic techniques can be used to determine corrosion mechanism.

Measurements may be carried out in more often the concentration range to determine the limiting value of extract volume precisely to prevent corrosion inhibition of mild steel in HCl acid.

Measurement may be carried out in different media to determine the effect of extracts in different acids, such as nitric acid, sulfuric acid, or in different bases.

Extracts obtained with the different extraction conditions from the plant leaves under study can be used as inhibitor to see the effect of extraction conditions. Extraction of plant leaves

can be done in water at 100^{o}C in different times. For example extraction time can be changed extractions can be done in different solvent. Papaver rhoeas, Malva Grandfolia and Carduus Marianus root extracts can be used. Extraction conditions can be determined according to inhibition efficiency.

APPENDIX 1

1. VARIABLES

Dependent variables: Inhibition efficiency, amount of corrosion

Independent variables: Volume of extracts of Papaver rhoeas added,

Volume of extracts of **Malva Grandfolia** added,

Volume of extracts of **Carduus Marianus** added,

Molarity of HCl solution.

Controlled Variables:

The mild steel coupons (size and type of coupon are the same (4.00cm x1.90cm x0.03 cm)

The mild steel rods (size and type of coupon are the same)

The temperature of the experiment room is constant with 30 ℃.

The time period metals will be in HCl solution.

The time period metals will be in HCl solution with inhibitor.

Molarity of HCL solution

The volume of leave extract used

Pressure of the room is same as the experiments are done in the same room

Size of corrosion cell: 100ml

Material List:

mild steel coupons (4.00cm x1.90cm x0.03 cm)

mild steel rod

emery paper

electrochemical analyzer (computer integrated CHI660B model)

electronic scale

drying oven

15 x100 mL beaker (±1mL)

25 mL Graduated Cylinder (±1mL)

3 x 500.00 mL volumetric flask (±0.01 mL)

10.00 mL Pipette (±0.01 mL)

5.00 mL Pipette (±0.01 mL)

1.00 mL Pipette (±0.001 mL)

Thermometer (±0.01 ^{o}C)

Chemicals

acetone

polyester

Cu-wire

1000 ml % 37 HCl solution

15 g Papaver rhoeas leaves (0.0001g)

15 g Malva Grandfolia leaves (0.0001g)

15 g Carduus Marianus leaves **(**0.0001g)

2.2 Experimental Procedure

The inhibitors used were water extract of Papaver rhoeas, Malva Grandfolia, and Carduus Marianus leaves. They were collected from Afyon region. They were dried at room temperature. Then leaves are separated from the other parts of plant by hand. They were grinded and waited in hot water (70^{0}C) for 2 hours, then filtered and used as corrosion inhibitor. To find inhibition efficiency of Malva Grandfolia, and Carduus Marianus leaves extract, for weight loss method and linear polarization method were used.

2.3 For weight loss experiment

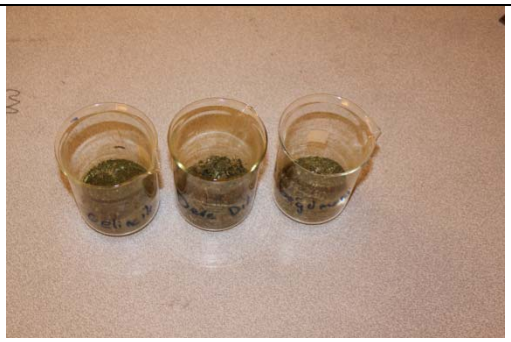
1. 1. The elemental composition of cylindrical mild steel and coupons mild steel were given in Table 1.
2. The mild steel sheet was prepared as rectangular coupons measuring 4.00cm x1.90cm x0.03 cm by mechanically.
3. Each mild alloy coupon was washed to remove any traces of grease or dust, and then rubbed with emery paper. Each mild alloy coupon was cleaned by deionised water.
4. They were cleaned in acetone.
5. They were put into drying oven for drying.
6. They were put in moisture-free desiccators to avoid contamination before using for weight loss experiments.
7. They were weighted after drying.
8. 15 gr dried Papaver rhoeas leaves were waited in 500 ml hot water (70^0C) for 2 hours and then filtered and six different concentrations (0.0 ml, 5.0 mL, 20.0mL, 40.0mL, 60.0 mL and 80.0 mL of the extract) were added to the each volumetric flask and 8.2 ml hydrochloric acid solution was added and each solution completed to 100ml with distilled water.
9. 50 mL of solution prepared in step 6 was added to each beaker (0.0 ml, 5.0 mL, 20.0mL, 40.0mL, 60.0 mL and 80.0 mL of the extract) and Each coupon was immersed in each beaker.
10. They were kept immersed in the solution for 24 hours (Close the beaker with cling film to keep volume constant). To prevent the temperature change of HCl solution during the corrosion put the beakers into water bath, dried in acetone and then reweighed.
11. After 24 hours of immersion the specimens were washed with water and scrubbed with brittle brush several times inside water to remove corrosion product.

12. Each mild alloy coupon exposed HCl solution were cleaned in deionised water and then in acetone.
13. They were kept in desiccators to avoid contamination before using for weight loss experiments.
14. They were weighed again after drying in oven.
15. Step 2-12 was repeated for 48 hours immersion time.
16. The same procedure was done for Malva Grandfolia, and Carduus Marianus leaves.

2.4 For Linear Polarization Resistance

1. Cylindrical mild steels were mounted in araldite resin of the size 1 cm^2.

1. 2. Emery paper was used to polish them. After polishing, deionised water and acetone were used to clean.
2. 15 gr dried Papaver rhoeas leaves were waited in 500 ml hot water (70^0C) for 2 hours and then filtered
3. 5.0 mL of Papaver rhoeas leave extract was added to the volumetric flask and 8.2 ml hydrochloric acid solution was added and solution completed to 100ml with distilled water (The molarity of HCl is 1.0 M).
4. They were kept immersed in the solution for 1 hour
5. The resistance of immersed coupons into the solution was measured.
6. The steps for 0.0 mL, 20.0 mL, 40.0mL, 60.0 mL and 80.0 mL of the Papaver rhoeas leaves extract were repeated.
7. The same steps were repeated for 2.0 M and 3.0 M hydrochloric acid solutions.
8. The similar procedures were carried out for Malva Grandfolia, and Carduus Marianus leaves.



Some photographs of my experiment

Table 7: t-Test: Two sample assuming equal variances for extract of Papaver rhoeas, Malva Grandfolia and Carduus Marianus leaves in 1.0 M hydrochloric acid solution.

	Variable 1	*Variable 2*	*Variable 1*	*Variable 2*
Papaver rhoeas	24 hours		48 hours	
Mean	96.04	97.56	95.96	98.08
Variance	3.653	0.738	5.963	0.467
observation	5	5	5	5
Cumulative Variance	2.1955		3.215	
Hypothesized Mean Difference	0		0	
df	8		8	
t Stat	-1.62199		-1.86946	
P(T<=t) one tail	0.071732		0.049245	
t Critical one tail	1.859548		1.859548	
P(T<=t) two tail	0.143464		0.098489	
t Critical two tail	2.306004		2.306004	
Malva Grandfolia				
Mean	95.32	95.9	94.32	94.92
Variance	6.707	7.47	3.617	12.292
observation	5	5	5	5
Cumulative Variance	7.0885		7.9545	
Hypothesized Mean Difference	0		0	
df	8		8	
t Stat	-0.34445		-0.33637	
P(T<=t) one tail	0.369695		0.372623	
t Critical one tail	1.859548		1.859548	
P(T<=t) two tail	0.739391		0.745246	
t Critical two tail	2.306004		2.306004	
Carduus Marianus				
Mean	94.78	95	93.66	98.22
Variance	5.482	5.185	11.248	0.837
observation	5	5	5	5
Cumulative Variance	5.3335		6.0425	
Hypothesized Mean Difference	0		0	
df	8		8	
t Stat	-0.15062		-2.9331	
P(T<=t) one tail	0.442001		0.009454	
t Critical one tail	1.859548		1.859548	
P(T<=t) two tail	0.884003		0.018908	
	2.306004		2.306004	

APPENDIX 2

Table 1: Variation of weight loss (grams) of mild steel with time (hours) in1M HCl solution at room temperature.

	1st exp (±0.00001)	2nd exp (±0.0001)	Average (±0.0001)
24hours	0.61034	0.6052	0.6078
48hour	1.53450	1.5131	1.5238

Table 2: Inhibition efficiency (%I.E.) of mild steel in 1.0 M HCl containing different concentrations from extract of Papaver rhoeas, Malva Grandfolia, and Carduus Marianus leaves for 24 hours.

Vol (±0.1)	% IE Papaver rhoeas leaves (±0.1)				% IE Carduus Marianus leaves (±0.1)				% IE Malva Grandfolia leaves (±0.1)			
	1st exp	2nd exp	Average	S^2	1st exp	2nd exp	Average	S^2	1st exp	2nd exp	Average	S^2
5.0	92.2	90.0	93.1	2.4	92.01	90.2	91.1	0.5	89.0	92.6	90.8	0.1
20.0	93.9	93.5	95.2	0.1	92.8	94.8	93.8	1.2	96.0	95.0	95.5	2.0
40.0	81.2	78.2	96.8	4.5	95.0	97.8	96.4	0.3	98.0	95.4	96.7	0.3
60.0	95.4	96.0	97.3	0.1	94.5	98.7	96.6	4.5	95.0	98.2	96.6	0.0
80.0	94.0	97.2	97.8	5.1	97.0	95.0	96.0	3.3	98.0	96.0	97.0	0.2

Table 3: Inhibition efficiency (%I.E.) of mild steel in 1.0 M HCl containing different concentrations from extract for Papaver rhoeas, Malva Grandfolia, and Carduus Marianus leaves for 48 hours.

Vol(±0.1)	% IE Papaver rhoeas leaves (±0.1)											
	1 hour				24 hour							
	1st exp	2nd exp	Average	S^2	1st exp	2nd exp	Average	S^2	1st exp	2nd exp	Average	S^2
5.0	92.0	91.4	91.7	0.1	88	91.4	89.7	5.7	93.0	90.0	91.5	4.5
20.0	95.01	97.2	96.1	2.4	93	97.4	95.2	9.6	92.1	96.9	94.5	11.5
40.0	98.3	96.5	97.4	1.6	97.1	96.5	96.8	0.1	94.3	96.9	95.6	3.3
60.0	96.1	98.3	97.2	2.4	94	98.4	96.2	9.6	94.8	92.4	93.6	2.8
80.0	95.0	99.8	97.4	11.5	88	92.8	90.4	11.5	95.0	97.8	96.4	3.9

Table 4: Inhibition efficiency (%I.E.) of mild steel in 1.0 M HCl containing different concentrations from extract for Papaver rhoeas leaves for 1hour, 24 hours and 48 hours immersion.

	% IE Papaver rhoeas leaves (±0.1)											
	1 hour				24 hour							
Vol(±0.1)	1st exp	2nd exp	Average	S^2	1st exp	2nd exp	Average	S^2	1st exp	2nd exp	Average	S^2
5.0	92.3	94.5	93.4	2.4	97.5	95.2	96.3	2.6	98.8	97.4	98.1	0.9
20.0	95.4	97.3	96.3	1.8	98.8	97.9	98.3	0.4	97.5	98.9	98.2	0.9
40.0	97.1	95.4	96.3	1.4	97.1	98.6	97.8	1.1	96.8	97.2	97.0	0.1
60.0	95.6	97.1	96.3	1.1	98.9	97.8	98.3	0.6	98.9	97.5	98.2	0.9
80.0	94.5	97.0	95.7	3.1	96.8	97.4	97.1	0.2	99.2	98.6	98.9	0.2

Table 5: Inhibition efficiency (%I.E.) of mild steel in 1.0 M HCl containing different concentrations from extract of Carduus Marianus leaves for 1hour, 24 hours and 48 hours immersion.

	% IE Carduus Marianus(±0.1)											
	1 hour				24 hour							
Vol(±0.1)	1st exp	2nd exp	Average	S^2	1st exp	2nd exp	Average	S^2	1st exp	2nd exp	Average	S^2
5.0	92.2	90.0	91.1	2.4	95.6	96.6	96.1	0.5	97.6	98.2	97.9	0.2
20.0	93.9	93.5	93.7	0.1	93.4	91.8	92.6	1.2	97.4	99.0	98.8	2.0
40.0	80.4	70.0	79.7	0.9	92.3	93.1	92.7	0.3	96.5	97.3	96.9	0.3
60.0	95.4	96.0	95.7	0.2	94.3	97.3	95.8	4.5	98.2	98.2	98.2	0.0
80.0	94.0	97.2	95.6	5.1	96.5	99.1	97.8	3.3	99.6	99.0	99.3	0.1

Table 6: Inhibition efficiency (%I.E.) of mild steel in 1.0 M HCl containing different concentrations from extract for Malva Grandfolia leaves for 1hour, 24 hours and 48 hours immersion.

	% IE Malva Grandfolia leaves(±0.1)											
	1 hour				24 hour							
Vol(±0.1)	1st exp	2nd exp	Average	S^2	1st exp	2nd exp	Average	S^2	1st exp	2nd exp	Average	S^2
5.0	94.2	92.2	93.2	2.0	97.8	94.2	96.0	6.4	95.6	98.4	97.0	3.9
20.0	95.4	94.0	94.7	0.9	90.2	92.6	91.4	2.8	97.8	98.6	98.2	0.3
40.0	83.3	85.9	84.6	3.3	97.9	96.5	97.2	0.9	95.8	97.4	96.6	1.2
60.0	95.6	93.0	94.3	3.3	98.0	99.4	98.7	0.9	90.4	88.8	89.6	1.2
80.0	97.8	94.2	96.0	6.4	94.0	98.4	96.2	9.6	94.5	91.9	93.2	3.3

Table 7: Inhibition efficiency (E%) with inhibitor concentration (extract of Papaver rhoeas, leaves in 1.0 M, 2.0M, 3.0 M hydrochloric acid solution for 1 hour immersion time.

	% IE Papaver rhoeas leaves (±0.1)											
	1.0M				2.0M				3.0M			
Vol(±0.1)	1st exp	2nd exp	Average	S^2	1st exp	2nd exp	Average	S^2	1st exp	2nd exp	Average	S^2
5.0	92.3	94.5	93.4	2.4	79.2	78.0	78.6	0.7	67.2	62.6	64.9	10.5
20.0	95.4	97.3	96.3	1.8	84.4	85.8	85.1	0.9	86.5	88.3	87.4	1.6
40.0	97.1	95.4	96.3	1.4	83.2	84.0	83.6	0.3	85.6	84.4	85.0	0.7
60.0	95.6	97.1	96.3	1.1	87.7	85.1	86.4	3.3	91.2	93.2	92.2	2.0
80.0	94.5	97.0	95.7	3.1	85.4	88.6	87.0	5.1	86.5	87.3	86.9	0.3

Table 8: Inhibition efficiency (E%) with inhibitor concentration (extract of Malva Grandfolia leaves, leaves in 1.0 M, 2.0M, 3.0 M hydrochloric acid solution for 1 hour immersion time.

	%IE of Malva Grandfolia leaves (±0.1)											
	1.0M				2.0M				3.0M			
Vol(±0.1)	1st exp	2nd exp	Average	S^2	1st exp	2nd exp	Average	S^2	1st exp	2nd exp	Average	S^2
5.0	94.2	92.2	93.2	2.0	85.3	87.9	86.6	3.3	74.5	75.9	75.2	0.9
20.0	95.4	94.0	94.7	0.9	75.3	71.3	73.3	8.0	82.3	80.7	81.5	1.2
40.0	83.3	85.9	84.6	3.3	88.6	90.0	89.3	0.9	83.4	80.8	82.1	3.3
60.0	95.6	93.0	94.3	3.3	55.6	58.0	56.8	2.8	73.4	70.0	71.7	5.7
80.0	97.8	94.2	96.0	6.4	86.7	87.5	87.1	0.3	82.8	81.0	81.9	1.6

Table 9: Inhibition efficiency (E%) with inhibitor concentration (extract of Carduus Marianus leaves, leaves in 1.0 M, 2.0M, 3.0 M hydrochloric acid solution for 1 hour immersion time.

	%IE of Carduus Marianus leaves(±0.1)											
	1.0M				2.0M				3.0M			
Vol(±0.1)	1st exp	2nd exp	Average	S^2	1st exp	2nd exp	Average	S^2	1st exp	2nd exp	Average	S^2
5.0	92.2	90.0	91.1	2.4	60.2	63.4	61.8	5.1	64.9	62.6	63.7	2.6
20.0	93.9	93.5	93.7	0.2	77.9	81.9	79.9	8.0	84.5	84.1	84.3	0.1
40.0	81.4	78.0	79.7	5.7	56.4	60.6	58.5	8.8	88.7	86.1	87.4	3.3
60.0	95.4	96.0	95.7	0.1	68.1	71.3	69.7	5.1	92.1	91.1	91.6	0.5
80.0	94.0	97.2	95.6	5.1	84.1	86.7	85.4	3.3	79.1	81.9	80.5	3.9