Nigerian Research Journal of Chemical Sciences **(ISSN: 2682-6054)**
Vol. 7, 2019

Investigation of Inhibitive and Adsorption Properties of *Potulaca Oleracea* Leaves on Mild Steel in 1M HCl

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ABSTRACT

Environmental safety and issues of corrosion among industries have always been a global concern. The recent trend is to save humans in an environment by using eco-friendly inhibitors. In this study the inhibition efficacy of *Potulaca oleracea* extract on the corrosion of mild steel in 1M HCl has been studied by weight loss measurements at various temperatures. The inhibition efficiency was higher in HCl environment with addition of *P. oleracea* extract at 30^{o}C compared with increase of inhibitor at 60^{o}C. The inhibition efficiency increased with increase of inhibitor concentration but decreased with rise in temperature. Based on the values of activation energy, free energy of adsorption and variation of inhibition efficiency with temperature, a physical adsorption mechanism was proposed for the adsorption of *Potulaca oleracea* on the surface of mild steel. It was found to follow Langmuir adsorption isotherm.

KEY WORDS*:* Corrosion, hydrochloric acid, inhibition, mild steel, p*otulaca oleracea*.

INTRODUCTION

Corrosion is an irreversible interfacial physicochemical interaction of a material (metal, alloy, ceramic, glass, wood, polymer, steel and concrete) with its environment which results in consumption of the material or dissolution of the materials and changes in the properties of the material leading to the impairment of its function. Many metals used in production occur naturally in an ore and therefore must be separated out, leading to reduced stability. Corrosion is an undesirable phenomenon that ought to be prevented. There are several ways of preventing corrosion and the rates at which it can propagate with a view of improving the lifetime of metallic and alloy materials. The use of inhibitors for the control of corrosion of metals and alloys which are in contact with aggressive environment is one among the acceptable practices used to reduce and /or prevent corrosion [1]. An inhibitor is a substance (or a combination of substances) added in a very low concentration to treat the surface of a metal that is exposed to a corrosive environment that terminates or diminishes the corrosion of a metal. They are known as site blocking elements, blocking species or adsorption site blockers due to their adsorptive properties [2]. Plants are sources of naturally occurring compounds some with complex molecular structures and having different chemical, biological and physical properties. The naturally occurring compounds are mostly used because they are environmentally acceptable, cost effective, and have abundant availability. These advantages are the reasons for the use of extracts of plants and their products as corrosion inhibitors for metals and alloys under different environment [3]. *Portulaca Oleracea* is an annual succulent plant in the family Portulacaceae, which may reach 40 cm in height. It has smooth reddish prostrate stems and alternate leaves clustered at stem joints and ends. The yellow flowers have five regular parts and are up to 6 mm wide. Depending upon rainfall, the flowers appear at any time during the year. The flowers open singly at the centre of the leaf cluster for only a few hours on sunny mornings [4].

MATERIALS AND METHOD

Sample Collection and Preparation

Potulaca oleracea leaves were collected in the premises of College of Science and Technology (Waziri Umaru, Federal Polytechnic) in Birnin Kebbi metropolis, Kebbi State, Nigeria.

P. oleracea leaves were washed in a clean container with distilled water, air dried under room temperature. It was then ground into fine powder using a mortar and pestle. The fine powder was then stored in a clean polythene bag.

EXTRACTION PROCEDURE

The extraction was carried out according to Sawyer *et al* [5] using methanol and ethanol as the solvents. 100 g of the sample was weighed each using electronic weighing Balance into a container containing 700 ml of methanol and ethanol respectively. The mixture was shaken well and allowed to soak for 72 h, after which the mixture was filtered using filter paper into a stainless bowl. Each filtrate was then subjected to evaporation (i.e exposed to air) for about 65 to 72 hours, in order to leave the samples free of methanol and ethanol respectively. After the extraction, the dried extract was subjected to phytochemical test and it was used as a corrosion inhibitor using gravimetric method [5].

PHYTOCHEMICAL TEST PROCEDURES

The followings phytochemical test was carried out on extract according to Harbone [6].

MATERIALS PREPARATION

Mild steel compositions are Fe=99.11, Mn=0.359, C=0.149, Cr =0.055, S= 0.059 and Ni= 0.048 were used for the study. The steel were cut to form different coupons of dimension of 1.5x1.0 cm. Each coupon was polished mechanically using a silicon carbide paper washed thoroughly with distilled water and degreased with ethanol and acetone air dried in a desiccator. Weights of the samples were taken using an electronic weighing Balance. All the reagents used for the study were analytically graded and distilled water was used during the experiment.

GRAVIMETRIC METHOD

After initial weighing of each coupon as (w_1), the coupon were immersed in 200 ml of 1M HCl solution (as blank) in a beaker and in different concentrations (0.1- 0.8) of plant extracts with thread for 2 hours in water bath at a temperature of 30 ºC and 60 ºC. After which the coupons were removed, washed, dried and final weights were recorded as (w_2). The weight loss (Δw), corrosion rate (C.R), inhibition efficiency (% I.E) and the surface coverage were calculated at different concentrations of the inhibitor, using the following equation [7].

$$\% \text{ I.E} = I = \frac{\Delta w_1}{w_2} \times 100$$

Where Δw_1 and Δw_2 are weight loss in the absence and presence of inhibitor

$$C.R = \frac{\Delta w}{At}$$

Where Δw = Change in weight,

A = Area in cm^2

t = Time in hour,

$$\Theta = \frac{\Delta w_1}{w_2}$$

RESULTS AND DISCUSSION

The values of corrosion rate derived from weight loss measurements of mild steel in the presence and absence of *P. oleracea* extract in 1M HCl at different temperatures (303K and 333K) in methanol and ethanol extract is shown in figures 1 and 3. The figures1 and 3 show that the corrosion rate reduces from (65.2×10^{-3} to 7.16×10^{-3}) at 303k and ($13.2 \times 10^{-3}$to 4.06×10^{-3}) at

333k in methanol and increase from (67.5 x 10^{-3}to4.77 x 10^{-3}) and from (8.12 x 10^{-3} to 3.26 x 10^{-3}) at 303k and 333k) respectively, with increase in *P. oleracea* extract concentration from 0.1 to 0.8 g/L. The rate of corrosion that was observed to be high in the blank. The corrosion rate begins to reduce considerably when the inhibitor was introduced. This indicates that the plant extracts inhibit the corrosion of mild steel in 1M HCl solution [8]. The percentage of inhibition efficiency against various concentration of *P. oleracea* extract for mild steel in 1M HC at different temperature (303k and 333k) is shown in figures 2 and 4. The result shows that the inhibition efficiency increased with increase in *P. oleracea* extract concentration and decreased with rise in temperature The maximum inhibition efficiency (89.0% and 69%) were obtained for methanolic extract at 303k and 333k in figures 2 and (91.8% and 59.8%) %) were obtained for ethanolic extract at 303k and 333k figures 4. Percentage of inhibition efficiency is achieved at a concentration of 0.8 g/L for methanolic extract and at 0.5 g/L for ethanolic extract before equilibrium of bio-inhibitor concentration at 303k and 333k respectively. The corrosion inhibition performance of the plant extract could be due to the presence of surface active constituents which normally enhance the film formation over the metal surface, thus reducing corrosion [9].

Activation Energy

Arrhenius equation was used to investigate the effect of temperature on the corrosion of mild steel in the presence and absence of *P. oleracea* bio-inhibitor using equation 2.

$$CR = Ae^{(-Ea/RT)} \quad (1)$$

$$\log (CR_2/CR_1) = E_a/2.303R(1/T_1-1/T_2) \quad (2)$$

Where CR_1 and CR_2 are the corrosion rate at the temperature T_1 (303k) and T_2 (333k) respectively. The values of corrosion rate obtained from the weight loss measurements are substituted in Equation 2 and the calculated values of activation energy are presented in Table 1 and 2. Activation energy increased from -19.73 to 56.97 and from 5.13 to 53.76 kjmol^{-1}, in methanol and ethanol extract respectively, with increase in bio-inhibitor concentration. The value of E_a obtained from the blank is lower than that of the values obtained for a system containing various concentrations of the *P. oleracea* extract. This result indicated that the *P. oleracea* inhibitor is adsorbed on the surface of mild steel by physical adsorption.

Adsorption consideration

The heat of adsorption on mild steel in the presence of bio-inhibitor is calculated using equation 3 [7].

Qads = 2.303R $\left[\log(\emptyset_2/1-\emptyset_2)-\log(\emptyset_2/1-\emptyset_{1)}\right]x\ (T_2T_1\ /T_2{-}T_1)$ …(3)

Where R is gas constant, $\emptyset_1\ and \emptyset_2$ are surface coverage at temperature T_1 and T_2 respectively. The calculated values of Qads are reported in Table 1 and 2. The negative values indicated that the adsorption of bio-inhibitor on mild steel surfaces is exothermic [10].

The adsorption isotherms are used to investigate the mode of adsorption and the characteristics of adsorption of inhibitors on the metal surface. In this study the Langmuir isotherm is investigated using equation 4.

$\left({C}/{\emptyset}\right)$ = C + $\frac{1}{K}$ ………… (4)

From equation 4 a plot of (C/Ө) versus log c, which is linear plots are generated (fig. 5 and 6) the plot reveals that the data obeys Langmuir adsorption isotherm.

The equilibrium constant of adsorption of *P. oleracea* extract on the surface of mild steel related to the free energy of adsorption ΔG^o was evaluated using equation 5.

ΔG^o = -2.303 RT log (55.5k) …………….. (5)

Where R is the gas constant, T is the temperature and K is the equilibrium constant of adsorption. The values of K obtained from Langmuir and adsorption were substituted in Equation 5. The calculated values of ΔG^o are recorded in table 3 and 4 for methanol and ethanol extracts. The negative value of ΔG^o suggested that the adsorption of *P. oleracea* extract onto steel surface is a spontaneous process. That is physisorption process (ΔG^o< 40 KJ/mol) [11].

Table 1: Showing the calculated activation energy and heat of adsorption of methanol extract of *P. oleracea* in 1M HCl media at 303K and 333K.

Conc(g/L)	Ea ($KJmol^{-1}$)	Q_{ads}($KJmol^{-1}$)
Blank	19.73	-
0.1	26.91	-6.33
0.2	28.40	-17.03
0.3	27.15	-13.26
0.4	31.11	-17.90
0.5	58.17	-50.98

0.6	56.97	-48.93
0.7	50.65	-38.73
0.8	48.53	-35.64

Table 2: Showing the calculated activation energy and heat of absorption of ethanol extract of *P. oleracea* in 1M HCl media at 303K and 333K.

Conc(g/L)	Ea ($KJmol^{-1}$)	Q_{ads}($KJmol^{-1}$)
Blank	5.13	-
0.1	17.43	-39.15
0.2	43.84	-44.11
0.3	50.11	-56.14
0.4	44.44	-58.50
0.5	45.01	-52.81
0.6	46.34	-53.42
0.7	49.42	-28.95
0.8	53.76	-28.95

Table 3: Showing the Langmuir Adsorption parameters for the adsorption of methanolic extract of *P. oleraceae* extract on the surface of mild steel.

Adsorption isotherm	Temp	Slope	K	R^2	ΔG^o
	303	0.9	16.67	0.9987	-17.2
Langmuir	333	1.1	4.16	0.994	-15.06

Table 4: Showing the Langmuir Adsorption parameters for the adsorption of ethanolic extract of *P. oleraceae* extract on the surface of mild steel.

Adsorption isotherm	Temp	Slope	K	R^2	ΔG^o
	303	1.06	12.5	0.9888	-16.48
Langmuir	333	1.18	4.17	0.9913	-15.06

Phytochemical consideration

Result of phytochemical analysis shows that the maximum inhibition efficiency may be predominantly by the adsorption of the plant phytochemical constituents on the surface of the metal by the interaction of π- electrons or lone pair of hetero atoms with metal. These bioactive constituents (Tannin, Steroids, Flavonoids, Alkaloids, Saponins and Glycosides) molecules are capable of blocking the active sites and protect the metal from dissolution process.

Table 5: Showing the phytochemical constituent of the extract

Constituent	Methanol	Ethanol
Alkaloids	+	+
Tannins	+	+
Flavonoids	+	+
Steroids	+	+
Volatile oil	+	+
Glycosides	+	+

Key (+) = Presence

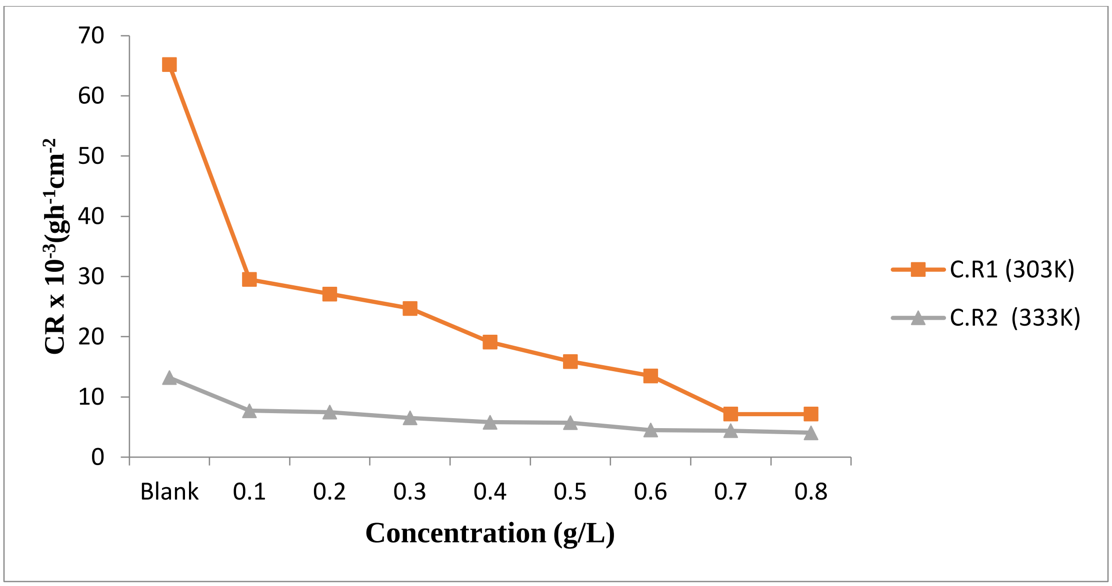


Figure 1: Showing the corrosion rate of mild steel in methanolic extract of *P. oleraceae* extract in 1M HCl at 303K and 333K.

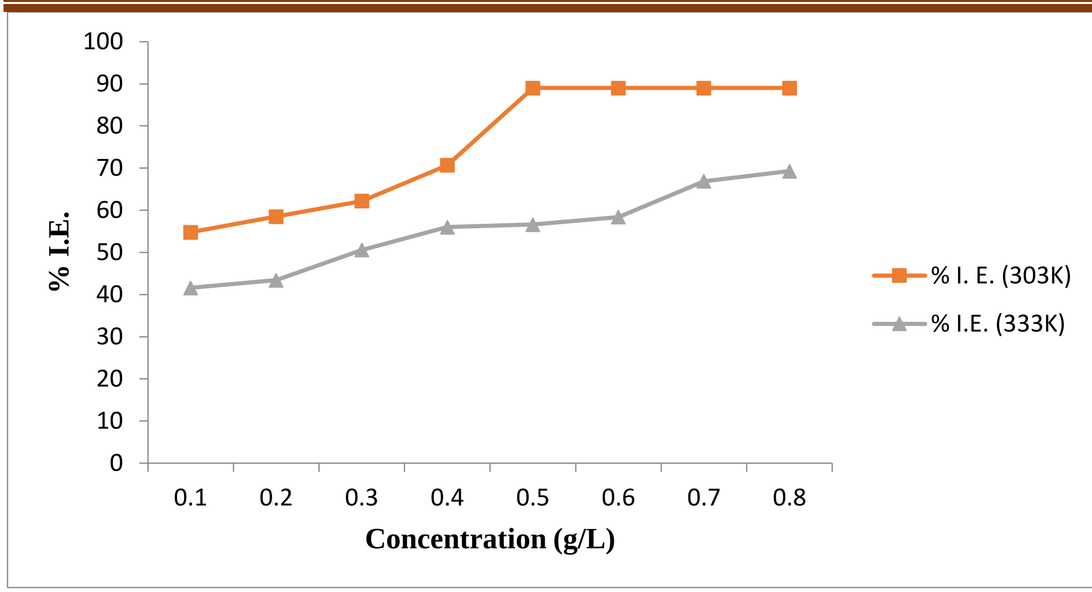
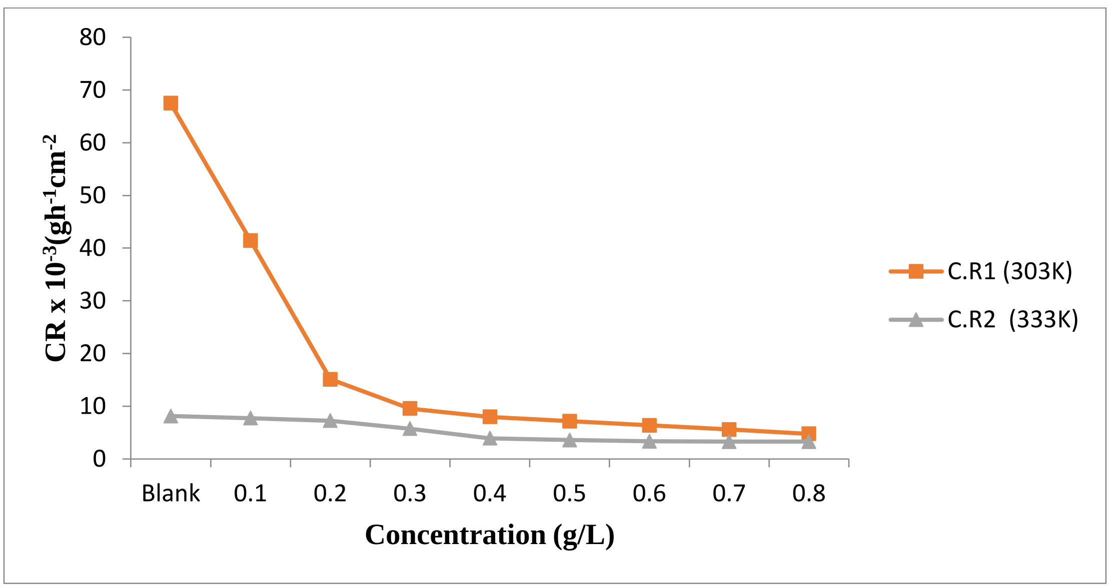


Figure 2: Showing inhibition efficiency of methanolic extract of *P. oleraceae* extract in 1M HCl at 303K and 333K.



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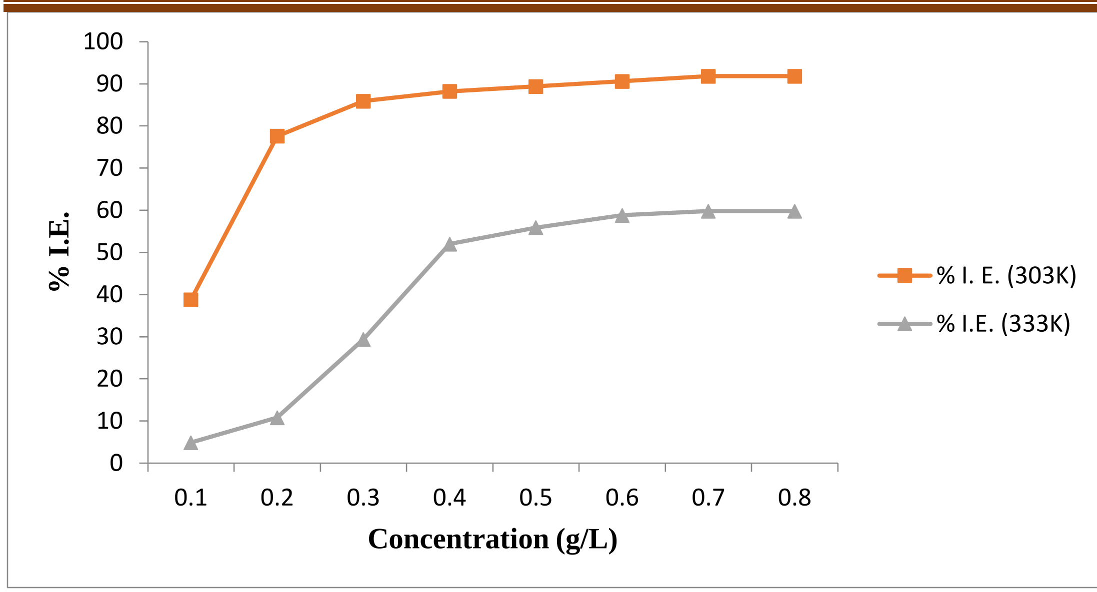

Figure 4: Showing inhibition efficiency of ethanolic extract of *P. oleraceae* extract in 1M HCl at 303K and 333K.

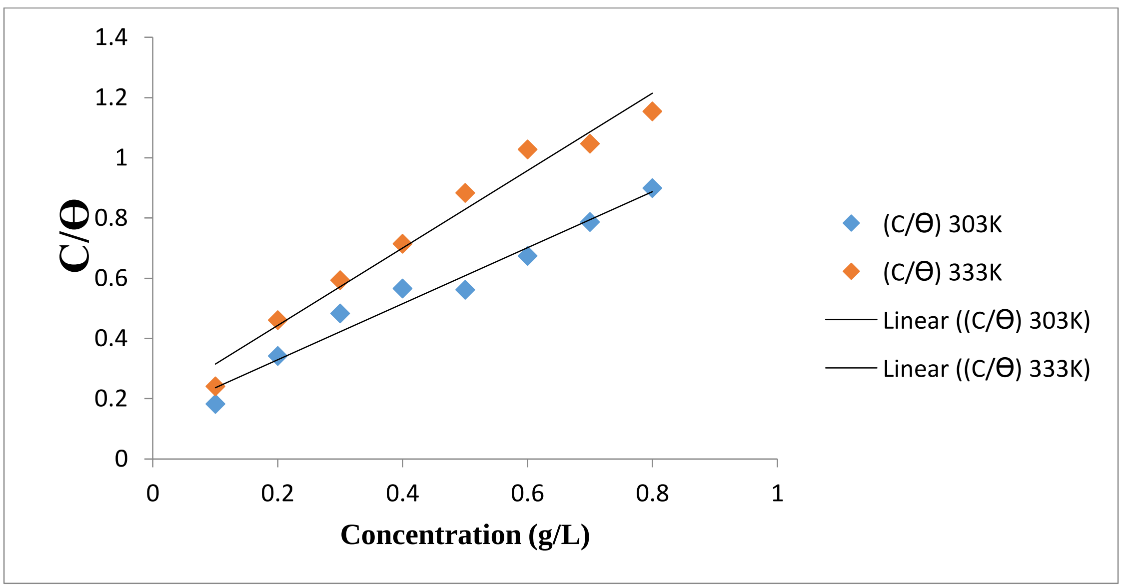

Figure 5: Showing the graph of (C/Θ) against concentration for methanolic extract of *P. oleracea* at 303k and 333k

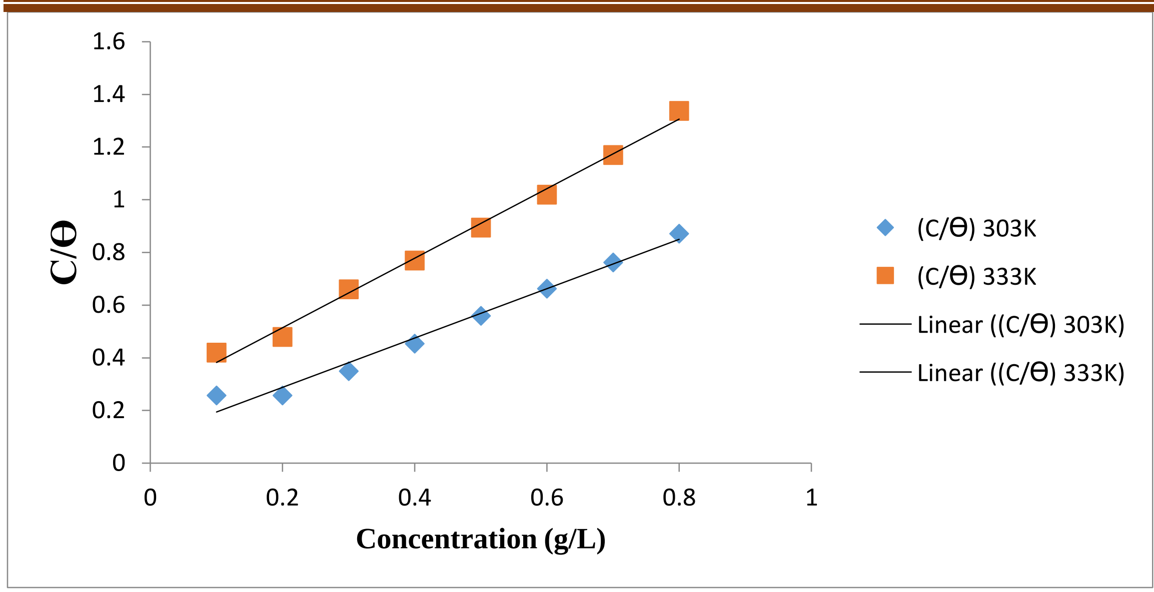

Figure 5: Showing the graph of (C/Θ) against concentration for ethanolic extract of *P. oleracea* at 303k and 333k

CONCLUSION

Potulaca oleracea inhibitor acts as an effective and efficient inhibitor for mild steel in 1M HCl. The inhibition efficiency increased with increase of inhibitor concentration to reach maximum before it reaches equilibrium but it gradually decreased with increase in temperature. The adsorption of the inhibitor on the mild steel surface is an exothermic, spontaneous process and it is consistent with the mechanism of physical adsorption. The adsorption process follows Langmuir isotherms.

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