IJCPE
Iraqi Journal of Chemical and Petroleum Engineering

Iraqi Journal of Chemical and Petroleum Engineering
Vol.15 No.3 (September 2014) 9-18
ISSN: 1997-4884

University of Baghdad
College of Engineering

Corrosion Inhibition of Mild Steel by *Curcuma* Extract in Petroleum Refinery Wastewater

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Abstract

The inhibitor property of *curcuma longa L.* extract in different concentrations of simulated refinery wastewater (0.05% - 2% wt) and at various temperatures (30, 35 and 40 ˚C) was investigated using weight loss method. The results showed that the presence of about 1.2 % (v/v) of curcuma extract gave about 84% inhibition indicating its effectiveness on mild steel corrosion in simulated refinery wastewater, besides the adsorption process on the mild steal surface obeyed the Langmuir adsorption isotherm.

Keywords: Corrosion, oil industry, Steel, Curcuma extract

Introduction

Mild steel is one of the most widely used engineering materials, despite its relatively limited corrosion resistance. Corrosion is one of the main concerns in the durability of metallic materials and their structures. Many efforts have been made to develop a corrosion inhibition process to prolong the life of existing structures and minimize corrosion damages [1].

Water pollution not only is harmful to mankind but also is harmful to metallic equipment such as pipelines, storage tanks, pumps, heat exchangers, etc., that are used in handling wastewater [2]. In addition to causing the eventual failure of the metallic equipment, corrosion by industrial wastewater leads to water pollution by the dissolved metal ions such as Cu^{++}, Cd^{++} and Pb^{++}, which themselves also may be toxic [3]. The type and rate of corrosion depends on the nature and concentration of pollutants present in the wastewater. Steel suffers severe corrosion attack in wastewater containing electrolytes. The rate of corrosion depends, amongst other factors, upon the concentration of oxygen and the motion of water. Steel with residual stresses undergoes stress corrosion cracking in wastewater containing nitrates, for example in the case of agricultural runoff waters containing nitrate fertilizer. Mild steel sustains severe damage in wastewater solutions containing chlorides, where pitting corrosion and stress corrosion cracking take place [4, 5].

Crude oil usually contains some water-dissolved salts such as $CaCl_2$ and $MgCl_2$. Before processing crude oil in the distillation tower, the water should be removed first by a process known as dehydration and desalting. Early water removal from crude oil minimizes corrosion of process equipment such as pumps, heat exchangers, distillation towers and condensers. On the other hand, the equipment used for handling water that has been separated from the oil can suffer from severe corrosion, depending upon the salt content of water [6].

A wide range of materials known as inhibitors are used to control the corrosion. The recent trend is towards developing environment friendly inhibitors. Most of the natural products are non-toxic, bio-degradable and readily available in plenty. Various parts of plants-seeds, fruits, leaves, flowers, etc. have been used as corrosion inhibitors [7]. The present work is another trial to find the effect of aqueous extract of the plant material known as Curcuma powder as a green inhibitor for mild steel in petroleum refinery wastewater produced from desalting process of crude oil.

Experimental Work

Synthetic magnesium chloride solution, simulated refinery wastewater, produced from desalting process of crude oil [8] were used, under static conditions in the presence and absence of *curcuma* extract as a corrosion inhibitor of concentrations of 1, 5 and 9 ml/250ml of $MgCl_2$ solution which was used as corrosive media at 30 ˚C. The corrosion rate of mild steel was found by weight loss method.

Materials

A mild steel sheet (supplied by engineering Lab. and Inspection department, Ministry of Science and Technology) was used as working electrode with the following chemical composition:

Table 1: The chemical composition of mild steel coupon (wt %)

Component	wt%
Carbon	0.069
manganese	0.441
Nickel	0.026
sulfur	0.005
silicon	0.009
Fe	Remainder

Test specimens of rectangular shape with 1.5 cm (width), 3.5 cm (length) and 0.1 cm thickness were used in weight loss method.

Solutions

- Simulated petroleum refinery wastewater: The wastewater was prepared by dissolving appropriate amount of $MgCl_2$ in one liter of distilled water.
- Aqueous extract of *Curcumin* dye:

10 g of rhizome (*Curcuma longa* L.) powder was weighed and boiled with double distilled water. The yellow dye curcumin was filtered to remove suspending impurities and made up to100 ml. The curcumin dye (CD) was used as corrosion inhibitor in the present study [9].

Weight loss Method

A. Specimen Preparation:

Coupon specimens were annealed in a vacuum at 600 ˚C for 1.0 h and the furnace was cooled to room temperature. This was carried out in order to remove mechanical stresses. An annealed specimens were abraded in sequence under running tap water using emery paper of grade 120, 220, 320,400 and 600, respectively ,washed with running tap water followed by distilled water ,dried on clean tissue, immersed in benzene for 5 seconds and dried with clean tissue ,immersed in acetone for 5 seconds and dried with clean tissue and then kept in desiccators over silica gel until use.

B. Procedure:

1. The dimensions of each specimen were measured with Vernier to the 2nd decimal of millimeter and weighed accurately to the 4th decimal of gram before using.
2. Specimens were completely immersed in 250 ml of corroding solution contained in (500 ml) beakers. They were exposed for period of 24 h, at required temperature, desired concentration of inhibitor and required concentration of solutions.

After each test, the specimen was washed with running tap water, scrubbed with a brush to remove corrosion products, washed with tap water followed by distilled water and dried on a clean tissue, immersed in benzene, dried, immersed in acetone, dried and left in a desiccators over silica gel for one hour before weighting.

Results and Discussion

A total of 18 runs for weight loss measurements were made expressing the corrosion rate of mild steel in simulated petroleum refinery wastewater with an increasing concentration from 0.05 to 2% wt. The parameters studied were concentration of $MgCl_2$ and concentration of corrosion inhibitor (aqueous extract of *Curcuma*).

Corrosion rate calculations from weight loss data were performed according to Eq. 1:

$$CR = \frac{Weightloss\ (g)}{\text{Area (m2)*Time (days)}} \qquad \ldots(1)$$

The results showed in Tables 2 and 3 express the corrosion rate and inhibition efficiency of mild steel in simulated petroleum refinery wastewater with different concentrations of aqueous extract of *Curcuma* as green inhibitor.

Table 2: Corrosion Rate (gmd) of mild steel in simulated petroleum refinery wastewater with different concentration of extracted *Curcuma* at 30 ˚C

Curcuma (ml/250 ml soln.)	$MgCl_2$ wt%		
	0.05	1.025	2
0	4.9263	4.4162	4.0235
1	2.8959	2.7220	3.4620
3	0.7761	2.0883	3.1772
5	0.9939	1.5426	2.6560
7	1.2715	1.4540	2.0344
9	1.7013	1.6263	2.2035

Table 3: Inhibition Efficiency (IE %) of different concentrations of extracted Curcuma in simulated petroleum refinery wastewater at 30 ˚C

Curcuma (ml/250ml soln.)	$MgCl_2$ wt%		
	0.05	1.025	2
1	41.21	38.36	13.96
3	84.25	52.71	21.03
5	79.83	65.07	33.99
7	74.19	67.08	49.44
9	65.47	63.17	45.24

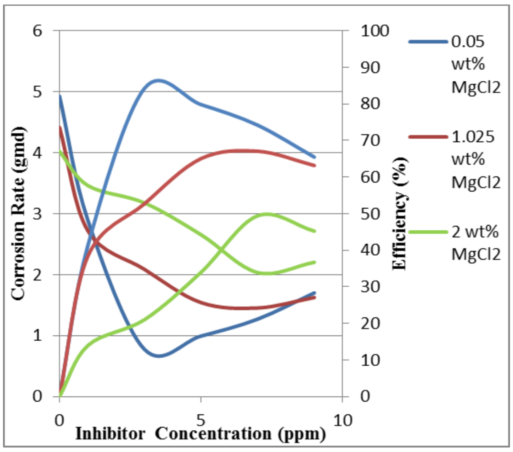

Fig. 1: Corrosion rate and inhibition efficiency of mild steel as function of inhibitor concentrations (extracted Curcuma concentration) in simulated petroleum refinery wastewater at 30 ˚C

The results showed in Tables 2 and 3 and Figure 1 indicate that the addition of aqueous extract of *Curcuma* as corrosion inhibitor to different concentrations of simulated petroleum refinery wastewater decreased the corrosion rate of mild steel. (ie., the maximum corrosion inhibition achieved was 84.25% and the minimum one was 13.96%).

Regression analysis was utilized by using *STATISTICA* program version 10.1 to generate a model to describe the response of the mild steel with correlation coefficient of R^2=0.91 through implementing the 2nd order polynomial model.

$$CR\ (gmd) = 4.005950 - 0.164999X_1 - 0.914977X_2 + 0.190011X_1^2 + 0.067442X_2^2 + 0.053740X_1X_2 \quad \ldots(2)$$

Where X_1 and X_2 are $MgCl_2$ concentration, and inhibitor concentration, respectively.

Equation 2 is applied to estimate the corrosion rate of the mild steel in simulated petroleum refinery wastewater.

The quantitative description of the physical condition effect on corrosion rate of mild steel in simulated petroleum refinery wastewater performed. An empirical modeling technique called response surface methodology is used to evaluate the relationship between the controllable experimental variables and observed results [10]. Figures 2 and 3 show the effect of studied variables on the corrosion rate and inhibition of mild steel in refinery wastewater, respectively.

Figure 2 corroborates that the minimization of corrosion rate of mild steel is possible in refinery wastewater containing low concentration of $MgCl_2$% and high concentration of extracted Curcuma. The darker the red color means higher corrosion rate, while the darker the green color means the lowest one.

Figure 3 shows the response surface for the inhibition of mild steel due to the effect of $MgCl_2$% concentration and *Curcuma* extract concentration. The darker the red color means the higher the inhibition efficiency, while the darkest the green one means the lower the inhibition efficiency.

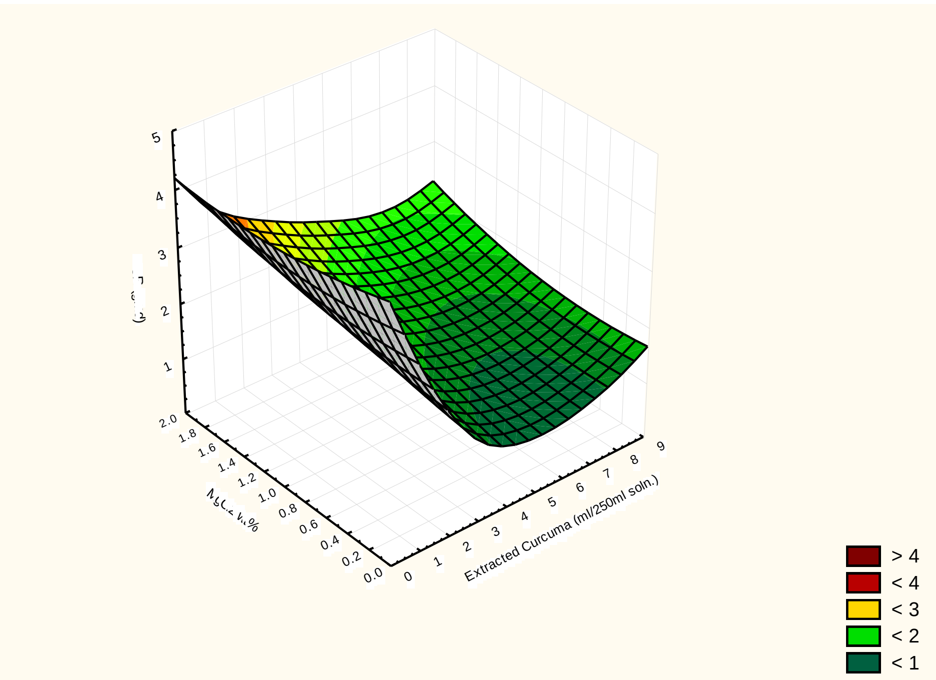

Fig. 2: Corrosion rate response surface for $MgCl_2$ concentration and extracted Curcuma

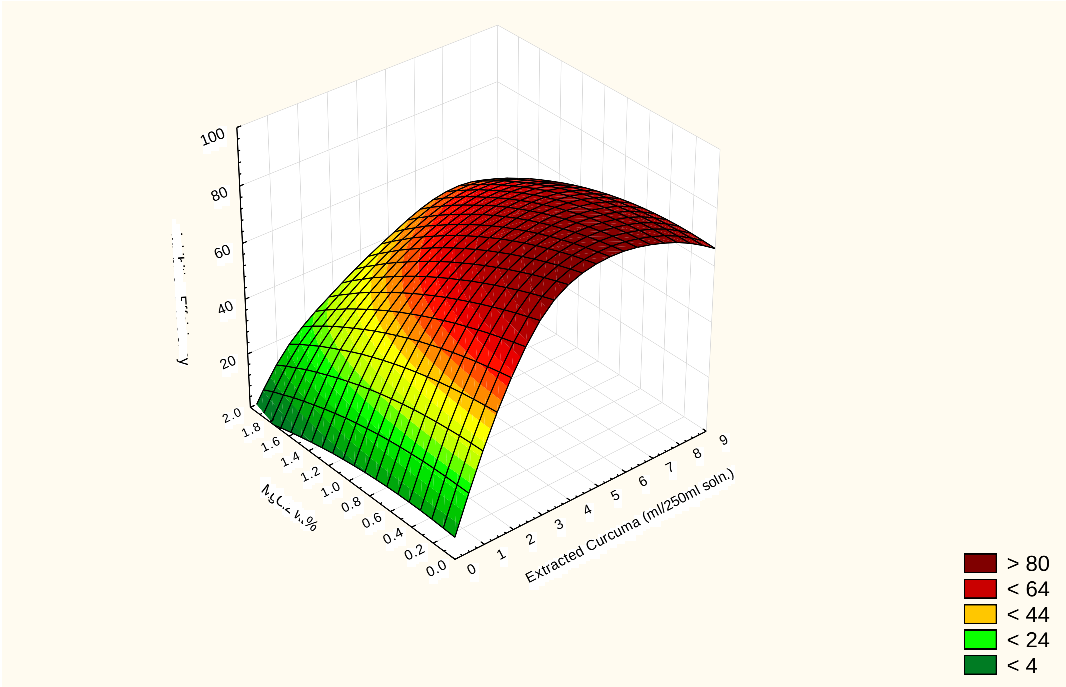

Fig. 3: Inhibition efficiency response surface for $MgCl_2$ concentration and extracted *Curcuma*

Adsorption Studies and Inhibition Mechanism

The primary step in the action of inhibitors in $MgCl_2$ solution is generally agreed to be adsorption on the metal surface. This involves the assumption that the corrosion reactions are prevented from occurring over the area (or active sites) of the metal surface covered by adsorbed inhibitor species, whereas these corrosion reactions occurred normally on the inhibitor-free area [11]. Accordingly, the fraction of surface covered with inhibitor species ($\theta = \frac{IE\%}{100}$) can be taken as a function of inhibitor concentration and solution temperature. The surface coverage (θ) data are very useful while discussing the adsorption characteristics. When the fraction of surface covered is determined as a function of concentration at constant temperature, adsorption isotherm could be evaluated at equilibrium condition. The dependence of the fraction of the surface covered θ on the concentration C of the inhibitor was tested graphically by fitting it to Langmuir's isotherm, which assumes that the solid surface contains a fixed number of adsorption sites and each site holds one adsorbed species. Fig. 4 shows the linear plots for C/ θ versus C with R^2 = 0.97 as correlation coefficient, suggesting that the adsorption obeys the Langmuir's isotherm:

$$C/\theta = 1/K + C \qquad \ldots(3)$$

Where C is the equilibrium inhibitor concentration, K adsorption equilibrium constant, representing the degree of adsorption (i.e. the higher the value of K indicates that the inhibitor is strongly adsorbed on the metal surface), the average value of K was 2.25 l/g which was obtained as the reciprocal of intercept of Langmuir line, and the slop of this line is nearly 0.5 meaning that each inhibitor molecule occupies half active site on the metal surface.

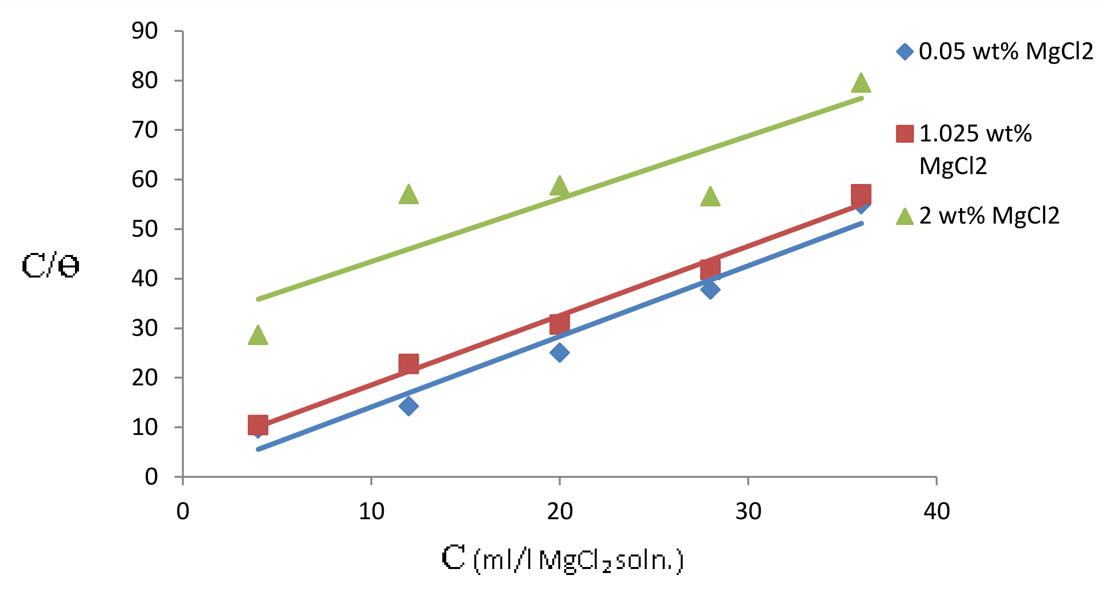

Fig. 4: Longmuir adsorption isotherm for extracted Curcuma on mild steel

Table 4: A Longmuir adsorption isotherm for *curcuma* extract on mild steel

Inhibitor Conc. (C) ml/l $MgCl_2$ soln.	C/ θ for 0.05% $MgCl_2$	C/ θ for 1.025% $MgCl_2$	C/ θ for 2% $MgCl_2$
1	9.71	10.43	28.65
3	14.24	22.77	57.06
5	25.05	30.74	58.84
7	37.74	41.74	56.63
9	54.99	56.99	79.58

The Effect of Temperature

An attempt was made to find the effect of temperature on the corrosion rate of mild steel in refinery waste water. Table 5 shows the corrosion rate of mild steel in different concentrations of wastewater at different temperatures.

Table 5: Corrosion rate of mild steel in different concentrations of wastewater at different temperatures

$MgCl_2$ (wt%)	Temperature				
	25 °C	30 °C	35 °C	40 °C	E(cal/g mol)
0.05	3.06	4.93	5.16	5.56	6855
1.025	2.92	4.42	4.58	5.46	7133
2	2.78	4.02	4.35	5.43	7765

The activation energy was calculated by plotting log C.R versus 1/T from the Arrhenius equation

$$C.R = A \exp(-E/RT) \qquad \ldots(4)$$

Where A = constant, R= gas constant, E=activation energy and T=temperature in K.

As shown in Figure 5, the rate of mild steel corrosion increased with increasing solution temperature, and the activation energy obtained was 7.76 kcal/mol. The small value of the activation energy (7.76 kcal/mol) shows that the corrosion of mild steel in $MgCl_2$ solutions is a diffusion-controlled process [12]; i.e. the rate of mild steel corrosion is controlled by the diffusion of O_2 from the solution bulk to the metal surface (Figure 6). This was consistent with previous studies [13, 14, 15], which reported that the corrosion of steel in the pH range 4-10 is controlled by the rate of diffusion of dissolved O_2 from the solution bulk to the metal surface. Increasing the solution temperature increases the rate of corrosion (Figure 7), primarily as a result of increased reaction kinetics, perhaps assisted by a reduction in the viscosity of the solution, with a consequent increase in the O_2 diffusivity, according to the Stokes-Einstein equation [16]:

$D\mu/T$ = constant …(5)

Where D=diffusion coefficient and μ= solution viscosity.

In view of this, all effects that tend to increase the rate of transfer of dissolved oxygen from the solution to the metal surface, such as stirring, vibration, solution flow, etc. tend to increase the rate of corrosion.

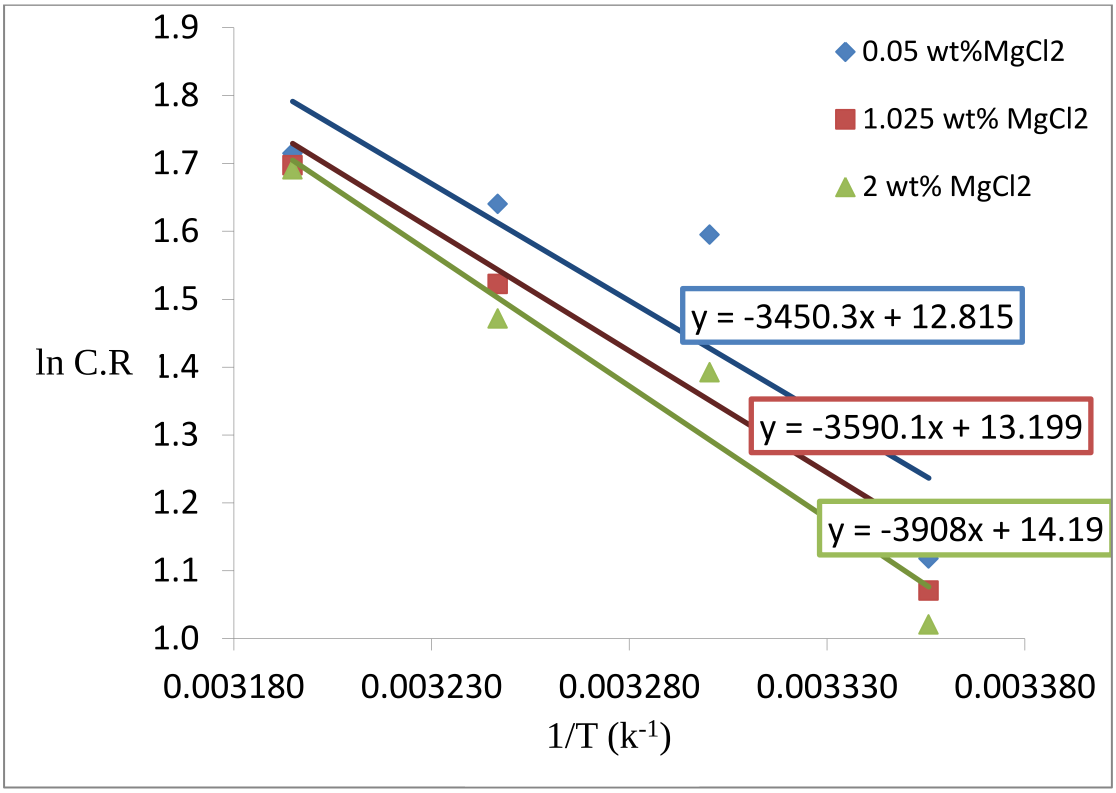

Fig. 5: Arrhenius plot of the experimental results at different MgCl2 concentration

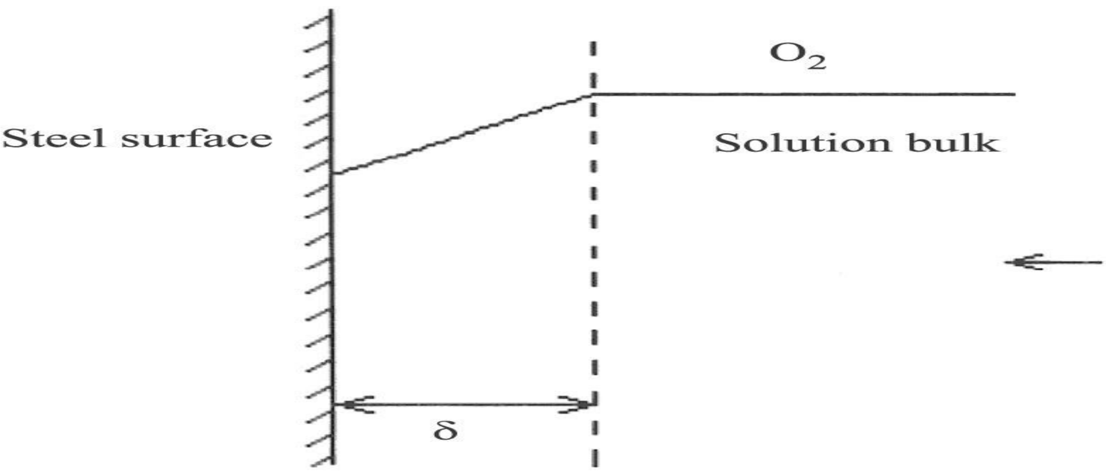

Fig. 6: Diffusion layer through which O_2 diffuse from the solution bulk to the steel surface [12]

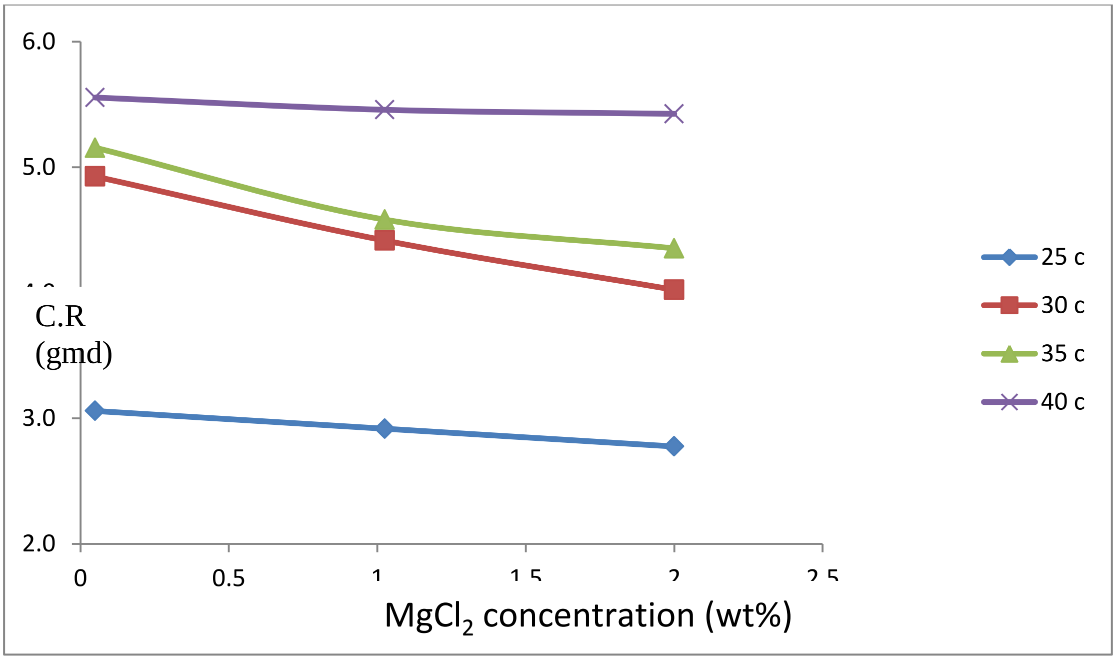

Fig. 7: Effect of concentration of MgCl2 on the rate of corrosion at different temperatures

The Effect of Temperature in Presence of the Inhibitor

An attempt was made to find the effect of temperature on the corrosion rate of mild steel in refinery wastewater in presence of the inhibitor. Table 6 shows the corrosion rate of mild steel in different concentrations of wastewater at different temperatures with the maximum concentration of the extracted *curcuma* 9 ml/250ml $MgCl_2$ solution.

The activation energy was calculated by plotting log C.R versus 1/T from the Arrhenius equation. As shown in Figure 8, the rate of mild steel corrosion increased with increasing solution temperature, and activation energy obtained was 5 kcal/mol.

The inhibition efficiency of the maximum concentration of the extracted Curcuma (9 ml/250ml $MgCl_2$ solution) with different concentrations of $MgCl_2$ solution at different temperatures is presented in Table 7.

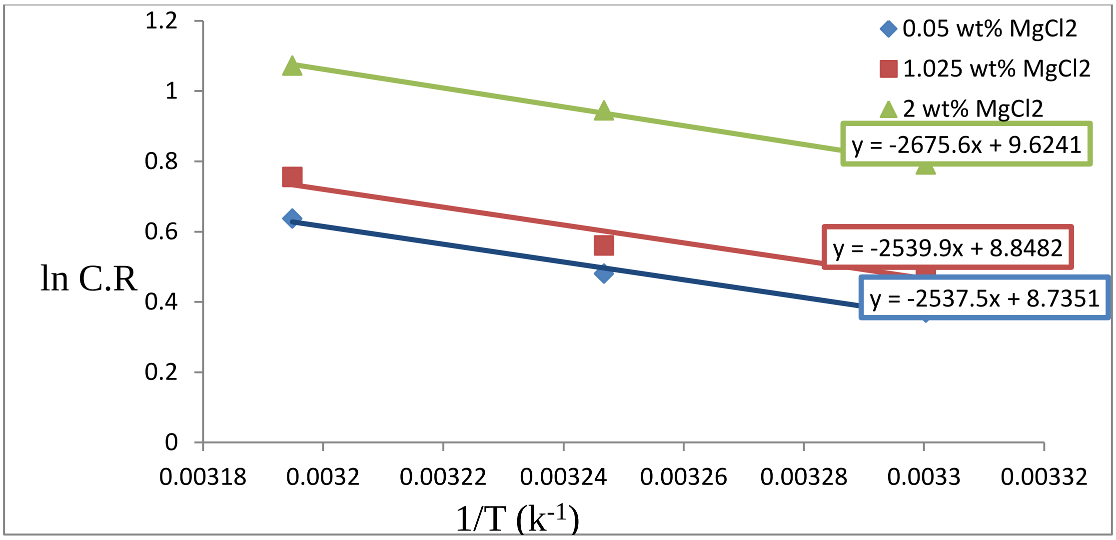

Fig. 8: Arrhenius plot of the experimental results at different $MgCl_2$ concentrations with existing of extracted curcuma 9 ml/250ml $MgCl_2$ soln

Table 6: Corrosion rate of mild steel in different concentrations of wastewater at different temperatures with extracted *curcuma* 9 ml/250ml $MgCl_2$ solution

$MgCl_2$ (wt%)	Temperature			
	30 °C	35 °C	40 °C	E(cal/ gmol)
0.05	4.9263	5.1556	5.5556	5042
1.025	4.4162	4.5828	5.4577	5046
2	4.0235	4.3538	5.4255	5316

Table 7: Inhibition efficiency of the optimum concentration of extract curcuma (9 cc/250ml $MgCl_2$soln.) at different temperatures

$MgCl_2$ wt%	Temperature		
	30 °C	35 °C	40 °C
0.05	70.65	68.66	65.98
1.025	63.17	61.8	61.02
2	45.24	40.95	45.16

Conclusions

1. The green corrosion inhibitor made up by the *Curcuma* extract successfully reduced the corrosion rates of mild steel in simulated refinery wastewater.
2. In presence of *Curcuma* extract, the inhibition efficiency values generally increased with the inhibitor concentration, but decreased with rise in $MgCl_2$ %wt at constant temperature. It is suggested that the absorption process was more favored at lower $MgCl_2$% concentration.
3. The Langmuir adsorption isotherm provided a formal description of the adsorptive behavior of the curcuma extract on mild steel surface. The values of $K_{ads.}$ indicated that inhibitor molecules occupied effective sites on the metal surface.

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