المجلة العراقية
لبحوث السوق وحماية المستهلك

المجلد (11) العدد (1)
لسنة 2019

STUDY THE ANTIBACTERIAL ACTIVITY AND INHIBITION EFFECT OF REACTIVE RED (31) DYE FOR THE CORROSION OF CARBON STEEL IN CORROSIVE MEDIA

http://dx.doi.org/10.28936/jmracpc11.1.2019.(10)

Dunya Edan Al-Mammar1, Saba Zuhair Hussein2 , Rawaa Abbas Mohammed3
[1]Department of Chemistry, Collage of Science, University of Baghdad, Baghdad, Iraq. Dunya.almamar@yahoo.com
[2]Department of Chemistry, Collage of Science, University of Baghdad, Baghdad, Iraq. sa78ba@yahoo.com
[3]Department of Chemistry, Collage of Science, University of Baghdad, Baghdad, Iraq. rawaa.abbas.mo@gmail.com

تاريخ استلام البحث: 2019/3/10 تاريخ قبول النشر: 2019/4/21

ABSTRACT

The inhibitive action of Reactive Red (RR31) dye against corrosion of carbon steel in 1M acetic acid solution has been studied using gravimetric method at temperature ranged (288-318)K. The antibacterial activity for the different concentrations of RR31 dye against different bacterial species was studied. The experimental data indicates that this dye acts as a potential inhibitor for carbon-steel in acetic acid medium and the protection efficiency increase with increasing (RR31) dye. The adsorption of (RR31) dye on the carbon steel surface was found to follow Langmuir adsorption isotherm. Thermodynamic data for the adsorption process such as Gibbs free energy change ΔG_{ads}, enthalpy change ΔH_{ads}, and entropy change ΔS_{ads} were estimated. The results showed that the different concentrations of RR31 dye has antibacterial ability.

Keywords: Reactive red dye, Carbon steel, Inhibition efficiency, Antibacterial activity.

دراسة الفعالية البايولوجية والفعل التثبيطي للصبغة الحمراء الفعالة (31) عند تآكل الحديد الكاربوني في وسط أكال

دنيا عيدان المعمار[1] ، م.د. صبا زهير حسين[2]، م.م. رواء عباس محمد[3]
[1]أستاذ. قسم الكيمياء، كلية العلوم، جامعة بغداد، بغداد، العراق. Dunya.almamar@yahoo.com
[2]مدرس دكتوره، قسم الكيمياء، كلية العلوم، جامعة بغداد، بغداد، العراق. sa78ba@yahoo.com
[3]مدرس مساعد، قسم الكيمياء، كلية العلوم، جامعة بغداد، بغداد، العراق. rawaa.abbas.mo@gmail.com

الخلاصة:

الفعل التثبيطي للصبغة الحمراء الفعالة (31) لمنع تآكل الحديد الكاربوني في وسط من (1مولاري) حامض الخليك باستعمال الطريقة الوزنية وبمعدل درجات حرارية من(288-318) كلفن. تمت دراسة الفعالية البايولوجية للتراكيز المختلفة من الصبغة الحمراء الفعالة (31) ضد الانواع البكتيرية المختلفة. اوضحت النتائج التجريبية ان الصبغة تعمل كمثبط محتمل لمنع تآكل الحديد الكاربوني في وسط حامض الخليك وتزداد فعالية التنشيط بزيادة تركيز الصبغة. ان عملية امتزاز الصبغة على سطح الحديد الكاربوني تتبع متساوي درجة الحرارة لنكماير. تم حساب الدوال الثرموديناميكية لعملية الامتزاز مثل التغير في طاقة كبس الحرة والتغير في الانثالبي والتغير في الانتروبي. كما أظهرت النتائج أن التراكيز المختلفة من الصبغة لها قدرة مضادة للبكتيريا .

الكلمات المفتاحية: الصبغة الحمراء الفعالة، الحديد الكاربوني، كفاءة التثبيط، الفعالية المضادة للبكتريا.

INTRODUCTION:

Alloys and metals are widely used in manufacturing gas and oil in various media. Acidic solution used in many industries including; descaling, pickling, degreasing and the petro-chemical industry **(Abiola & James, 2010)**. The effect of the acid on alloys and metals are destructive and leads to metal corrosion. To minimize the metal corrosion and reduce the effect of the acids and to control the corrosion process, many inhibitors are used **(Abdallah, 2003)**.

The inhibitors is organic compounds containing aromatic cycles and functional atom like sulfur (S), Oxygen (O) nitrogen (N) was applied to prevent the corrosion of the metals in aggressive medium **(El-Naggar, 2007)**. The inhibition efficiency of the inhibitor depends on chemical structure of the inhibitor and the ability of these compound to adsorbed on the surface of the metal and protect it **(Mahalakshmi *et al.*, 2016)**.

Many studies on the corrosion inhibition performance of using dyes leads to that dyes are quiet effective in retarding the corrosion of carbon steel in base and acid environment **(Tang Limu & Lin, 2003)**.

The inhibitive action of the organic dye for the carbon steel corrosion in acid solutions was the object of many studies, such as; Thymol blue, Methyl green, Alizarin yellow (AYGG), Red Alizarin ARS, colocid dye and Indigo dye **(Saqalli *et al.*, 2017)**.

Therefore an attempt was made to employ an organic dye as inhibitor for decreases the rate of corrosion in acetic acid media. Reactive Red (RR31),Single azo dye class, the molecular formula $C_{30}H_{15}Cl\ N_7Na_5O_{15}S_4$ the molecular weight (99214 g/mol). The molecular structure for RR31 dye is shown in (Figure, 1).

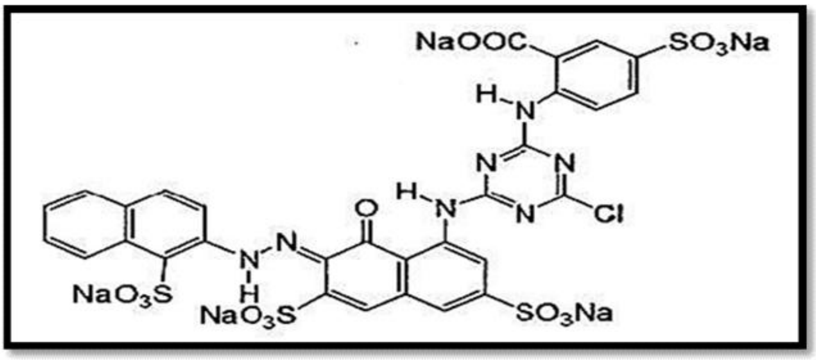

Figure (1): Molecular structure of Reactive Red (RR31) dye.

In the present work we attempt to study the antibacterial activity and the effect of reactive red (RR31) dye as inhibitor for carbon steel in different concentrations of acetic acid and at different temperatures.

MATERIALS AND METHODS:

Materials

Carbon steel type (AISI) with following composition (by weight %): P: 0.035, C: (0.38-0.44), S: 0.035, Si: (0.15-0.35), Cr: (0.9-1.2) and Mn (0.5-0.8) was used.

The analytical grade 99.8% acetic acid with molecular weight of (60.05 g/mol) was used to prepare the acidic solutions.

Methods

The thickness of the test spices about 7mm and diameter 17mm. The species were abraded throw run tap water using the following emery paper grades (400, 230, 220) and washed by distilled water, dried with acetone and then kept dry over silica gel. 1M acetic acid solution was prepared using distilled water and different concentrations of (RR31) dye were prepared (0.005, 0.0015 and 0.0025 M).

Each experiment was used 25ml of the acidic solution. After each test, the metal samples were cleaned, washed with tap water then with distilled water, dried with tissue, immersed in analar acetone. Weight losses were determined in absence and presence different dye concentrations at temperature range (288-318K).

The antibacterial was observed for the different concentrations of (RR31) dye using strain of gram positive (*Staphylococcus aureus*) and gram negative (*Escherichia coli*). The antibacterial activity was studied by disc diffusion method, 6mm diameter wells were made in the agar plate. The bacterial dish was incubated at 37 ºC for 24 hours. The inhibition zone was evaluated in (mm) **(Mythili & Kalyani, 2015)**.

RESULTS AND DISCUSSION:

Weight loss measurements:

The corrosion of carbon steel in acetic acid solution with various concentration of (RR31) ranged (0.005, 0.0015 and 0.0025 M) at different temperatures (288-318 K) was calculated by weight loss measurements. The immersion time for the measurements was 2h.

The corrosion rate R of carbon steel was determined as:

$R_{(wt.loss)} = \Delta W/\Delta T$ …………….(1)

Where ΔW is weight loss of the carbon steel in acetic acid solution, ΔT is time of immersion of the species.

Table (1) shows the corrosion rate using different RR31 concentrations and temperature range (288-318K).

The percentage of corrosion inhibition efficiency was determined by employing the expression **(Zaferani & Shishesaz, 2014)**:

$IE\% = W_a - W_p / W_a \times 100$ ………… (2)

Where W_a and W_p are weight loss of carbon steel in the absence and presence of RR31 respectively in acetic acid media.

The percentage of corrosion inhibition efficiency is shown in (Table, 1).

Table (1): Corrosion rate, protection efficiency and the degree of coverage at different temperatures and concentrations of inhibitor.

C (M)	T (K)	ΔW (g)	Rate (g/h)	Log Rate	IE (%)	θ
Blank	288	0.0910	0.0455	-1.342	-	-
	298	0.0050	0.0025	-2.602	-	-
	308	0.0240	0.0120	-1.921	-	-
	318	0.0300	0.0150	-1.824	-	-
0.005	288	0.0064	0.0032	-2.490	92.9	0.929
	298	0.0040	0.0020	-2.699	20.0	0.200
	308	0.0190	0.0095	-2.023	21.0	0.210
	318	0.0241	0.0120	-1.919	19.7	0.197
0.0015	288	0.0017	0.0007	-3.154	98.1	0.981
	298	0.0022	0.0011	-2.957	55.8	0.558
	308	0.0159	0.0079	-2.099	33.7	0.337
	318	0.0110	0.0055	-2.259	63.3	0.633
0.0025	288	0.0029	0.0014	-2.838	96.8	0.968
	298	0.0031	0.0015	-2.809	38.0	0.380
	308	0.0176	0.0088	-2.055	26.0	0.260
	318	0.0141	0.0070	-2.152	53.0	0.530

(Table, 1) shows, that the best values of inhibition efficiencies was obtained at temperature of 288 K and the highest value was obtained with 0.0015 M of (RR31) dye inhibitor concentration at the same temperature.

Adsorption isotherm:

The action of the organic inhibitor ascribed to the adsorption action of organic molecules on the surface of metal through its polar function. In aqueous solution the adsorbed water dipoles always covered the metal surface. Therefore, the adsorption process is a quasi substitution process **(Hamdy & El-Gandy, 2013)**. According to the interaction between the organic compound and the metal surface there are two types of adsorption: physisorption and chemisorption. These types related to many factor as the structure of the organic compound used as inhibitor, nature and the charge of the metal surface. In physisorption there is weak Vander-waal‘s interaction while in chemisorption charge-transfer or sharing between the organic compound (inhibitor) to the vacant (d-orbitals) related to the metal surface that leads to form a coordinate bond link **(Noor & Al-Moubaraki, 2008)**.

Addition of RR31 molecule adsorbs on the carbon steel and the interaction between adsorbent and adsorbat can be expressed by the adsorption isotherm **(Hosseini *et al*., 2003)**.

The degree of surface coverage θ of the metal surface by RR31was calculated using the formula:

$\theta = IE/100$ …………(3)

The correlation between θ and concentration $C_{(In)}$ of RR31 dye as inhibitor can be represented by Langmuir adsorption isotherm as follows:

$$\frac{C_{(In)}}{\theta} = \frac{1}{K_{ads}} + C_{(In)} \quad ……………(4)$$

Where K_{ads} is Langmuir constant.

Figure (2) shows the relation between the ratio $C_{(In)}$ / □ as a function of $C_{(In)}$ of RR31.

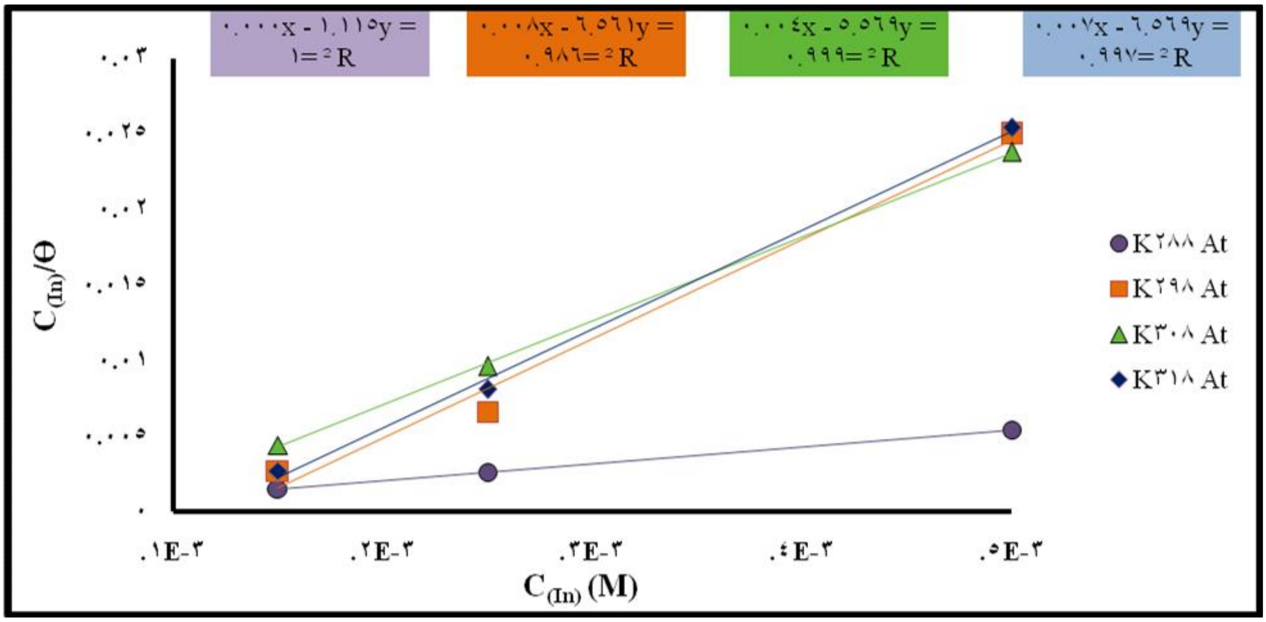

Figure (2): Langmuir adsorption isotherm plots for the adsorption of (RR31) dye on carbon steel surface at different temperatures.

The value of K_{ads} represents the power of adsorption or the binding strength of the RR31 molecule on the carbon steel surface. The values of K_{ads} are shown in (Table, 2).

Table (2): Langmuir adsorption isotherm data.

T (K)	K_{ads}	R^2
288	5,000	1
298	120.481	0.9865
308	243.902	0.9996
318	131.578	0.9974

The values of R (correlation coefficient) close to unity ranged (0.9865-1), since the adsorption process obeys Langmuir adsorption isotherm which suggest the formation of monolayer. The values of slope are slightly deviate from the unity, this deviation may be attributed to the interaction force between adsorbed (RR31) species **(Fouda & Badr, 2013)**.

Thermodynamic parameters ΔS_{ads}, ΔH_{ads}, can be evaluated using the following equation **(Abbas, 2016)**:

$$\text{Log } K_{ads} = \frac{-\Delta H_{ads}}{2.303RT} + \frac{\Delta S_{ads}}{2.303R} + \text{Log}\frac{1}{55.55} \quad \ldots\ldots\ldots (5)$$

The value 55.55 is the concentration of water in the solution in mol/L.

To determine the Gibbs free energy for the adsorption ΔG_{ads}, following relation is used **(Okafor *et al*., 2008)**:

$\Delta G_{ads} = \Delta H_{ads} - T\Delta S_{ads}$ ………… (6)

Figure (3) shows the plot of log K_{ads} vs. 1/T, in which the value of ΔH_{ads} and ΔS_{ads} are obtained from the slope and the intercept respectively.

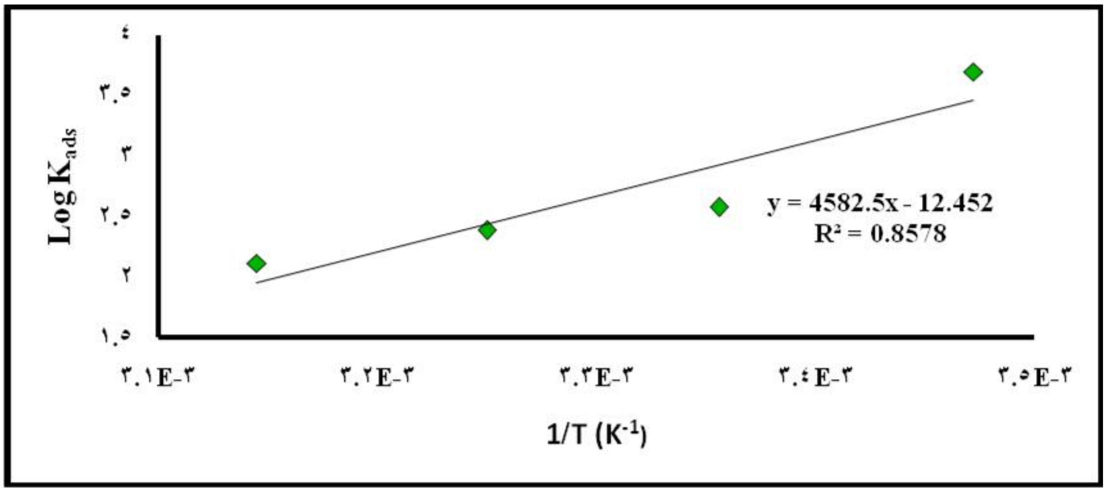

Figure (3): Plot of log K_{ads} versus 1/T.

The calculated thermodynamic parameters for the different temperatures are listed in (Table, 3).

Table (3): Thermodynamic parameters: ΔH_{ads}, ΔS_{ads} and ΔG_{ads} for the adsorption of (RR31) dye inhibitor on the carbon steel surface.

T (K)	$\Delta H/kJ.mol^{-1}$	$\Delta S/kJ.mol^{-1}.K^{-1}$	$\Delta G/kJ.mol^{-1}$
288	-87.741	-0.205	-28.701
298			-26.651
308			-24.601
318			-22.551

The negative sign of the change in enthalpy (ΔH_{ads}) reflect that the dissolution process of carbon steel in acetic acid solution is exothermic in nature. The entropy change (ΔS_{ads})of the adsorption of RR31 dye onto metal surface is negative. This meaning that the adsorption process occurs with decrease in randomness going from reactants to a metal adsorbed species reaction complex **(Bouklah *et al*., 2006)**.

The negative signs of the change in the Gibbs free energy (ΔG_{ads}) indicate the spontaneous adsorption process occurred.

Generally, when the value of -ΔG_{ads} less than (20 kJ.mol^{-1}) signifies physisorption while, if the values more than (40 kJ.mol^{-1}) signifies chemisorptions **(Ikpi *et al*., 2012)**, since the values of ΔG_{ads} are approaching to 20 kJ.mol^{-1}, physisorption adsorption of RR31 dye inhibitor on carbon steel surface was assumed.

Corrosion Kinetic study:

The values of apparent activation energy E_A over different concentrations and at different temperatures was determined using the relation **(Zhang & Hua, 2010; Khadom *et al*., 2018)**.

Rate = A exp (-E_A/RT) …………(7)

Where R: universal gas constant (8.314 J.K^{-1} .mol^{-1}) and T : absolute temperature (K), the values, A: pre exponential factor were calculated from the slope and intercept of the linear plots between log Rate and (1/T) K^{-1}, these values were given in (Table, 4).

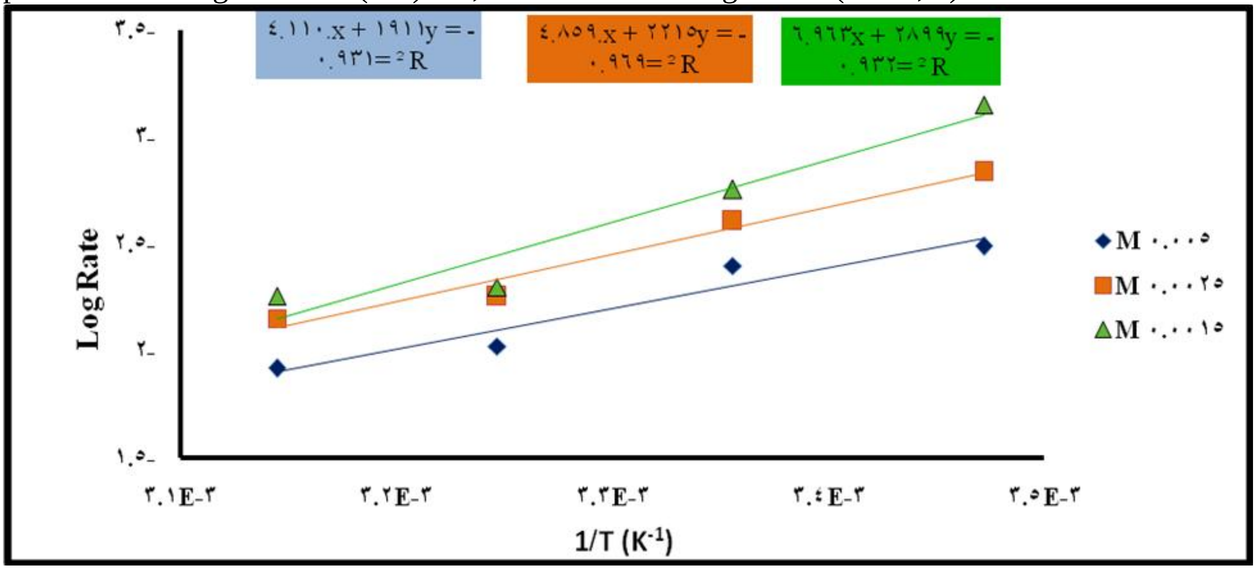

Figure (4): Plot of log rate versus 1/T for the carbon steel corrosion in acetic acid with additives solution containing various (RR31) dye inhibitor concentrations.

Table (4): The apparent activation energy E_A and pre-exponential factor for the corrosion of carbon steel in acetic acid solutions.

C (M)	A	Log A	E_A J/mol	R^2
0.005	0.6138	4.1104	2899.0	0.9317
0.0015	0.8428	6.9632	1911.8	0.9321
0.0025	0.6848	4.8396	2215.9	0.9691

In general, E_A tend to increase as the concentration of RR31 increased, furthermore, the value of E_A is less than (40 $kJ.mol^{-1}$) this proposed that the adsorption of the RR31 is physisorption process **(El- Etre, 2006)**.

Antibacterial activity:

In current study, the antibacterial activity of three concentrations of dye (0.005, 0.0015 and 0.0025 M), were evaluated against two bacterial isolates (*Escherichia coli* and *Staphylococcus aureus*). Table (5) showed the effect of different concentrations of dye in terms of diameter of inhibition zone on the bacterial isolates. The highest effect of different concentrations of dye was observed at the high concentrated (0.005 M) dye against *Staphylococcus aureus*.

Table (5): Antibacterial activity of RR31 dye. The inhibition zone measured by (mm).

Sample No.	Concentration (M)	*S. aureus (mm)*	*E. coli (mm)*
1	0.005	35	18
2	0.0015	31	19
3	0.0025	32	-

The antibacterial effect of different concentrations of dye was tested against two strains of Gram positive (*S. aureus*) and Gram negative (*E.coli*) which showed that Gram positive to be more susceptible compare to Gram negative (Table, 5). This may be related to that halogen group and N═N showed important roles in antibacterial activities **(Saeed *et al.*, 2009)**, and these group interacts with active site on the enzyme of *E.coli* and *S.aureus* through a chemical bond thus inhibit the growth of bacteria **(Ngaini & Kui, 2017)**.

CONCLUSIONS:

In this study, the highest inhibition efficiency was obtained at concentration of 0.0015 M of RR31 dye inhibitor at 288 K which equal to 98.1%. The adsorption of RR31 dye as inhibitor on carbon steel surface obeys Langmuir adsorption isotherm. The negative values of ΔH_{ads} and ΔS_{ads} indicated that the adsorption process is an exothermic process and occur with decreasing in randomness. The negative value of ΔG_{ads} indicated that the adsorption process is spontaneous and the adsorption type is a physisorption. The highest value of activation energy is 2899 $J.mol^{-1}$ at 0.005 M concentration of RR31 dye inhibitor. The different concentrations of dye exhibit greater antibacterial activity against (*S. aureus*) as compared to the (*E.coli*).

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