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Anodic Corrosion of Steel Pipeline in Presence of Novel Compounds

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***Abstract*— Preventing the corrosion of steel pipeline has played an important role in various industries. The problem of finding an inhibitor that has little or no impact on the environment has recently motivated numerous studies. Chemical inhibitors are often used for these processes, primarily to control the metal dissolution and acid consumption. Use corrosion inhibitors to prevent metal dissolution and minimize acid consumption. The rates of anodic corrosion of steel pipeline plates in different concentration of phosphoric acid (6, 8, 10, 12 and 14 mol) were determined by measuring the limiting current of anodic dissolution. The rates of corrosion in absence and in presence of acid derivatives have been measured. The corrosion rate depends on the types of inhabitations and its concentrations. The rate of corrosion decreases by amount ranging from 4.05 to 77.88 % in the case of divided cell and undivided cell depending on acid compounds and its concentrations. Those compounds verify Flory- Huggins isotherm. Thermodynamic parameters also given. Antimicrobial activity were examined for the two compounds used as chemical inhibitors. The results indicated that tested compounds did not show high activity against bacteria under test (Escherichia coli and Bacillus subtilis) while compounds revealed high activity against fungi. All new compounds were active against the microorganisms. The acid derivatives have been examined to show its Antitumor Activity. The results showed that compounds I & compound II possess the highly significant effect against breast cancer cell line (MCF7). These results show that using (.Compound I: 2-{3-[2-(4-Oxo-2-phenylquinazolin-3(4H)-ylamino) acetyl] thioureido}-benzoic acid) &. (Compound II: 2-[2-(4-Oxo-2-phenylquinazolin-3(4H)-ylamino) acetylcarbamo-thioylthio] acetic acid) as inhibitors for the corrosion of steel pipeline did not harmful on human health.**

***Index Terms*— Electrodeposition; Corrosion Inhibit; Limiting Current; Mass Transfer; Thermodynamic Parameters; Acid derivatives.**

I. INTRODUCTION

Studies on preventing the corrosion of steel pipe line in acidic environments and the problematic chemical processes that arise have attracted the attention of researchers from a wide range of industrial sectors [1]. Preventing the corrosion of steel pipe line has played an important role in various industries, especially in the chemical and petrochemical processing industries that employ the use of steel pipe line. A number of studies have been conducted to investigate effective methods for preventing corrosion. Acids are widely used in industrial processes, such as pickling, cleaning, descaling, etc. Inhibitors are effective in reducing the dissolution rate of metals [2–6]

The most of corrosion inhibitors can eliminate the undesirable destructive effect and prevent metal dissolution. Electropolishing is the electrolytic metal finishing process currently widely used in several high applications such as cardiovascular and orthopedic body implants, pharmaceutical and semiconductor installations. The process provides a very clean, smooth layer, resistant surface. Currently, all metal, alloy and intermetallic compound can be electropolished [7]

It is generally accepted that acid molecules inhibit corrosion via adsorption at the metal-solution interface [8] were two primary mechanisms of adsorption chemical or physical are associated with acid compounds acts firstly by blocking the reaction sites or generating a physical barrier to reduce the diffusion of corrosion species to the metal surface.

One of the most important methods in the protection of steel pipeline against corrosion is the use of organic inhibitors [**9**]. Acid derivatives compounds containing polar groups including nitrogen, sulfur, oxygen [**10-16]** and heterocyclic compounds with polar functional groups and conjugated double bonds have been reported to inhibit steel pipe line corrosion .The inhibiting action of these acid compounds is usually attributed to their interactions with the steel pipe line surface via their adsorption. The Polar functional groups can be regarded as the reaction center that stabilizes the adsorption process [**18**].

In this study, the effect of acid derivatives compounds on the inhibition of steel pipeline corrosion in 8M H_3PO_4 at different condition has been investigated. The rate of steel pipeline corrosion was determined by measuring the anodic limiting current, i.e. at which polishing take place.

II. EXCREMENTAL PROCEDURE

2.1. Materials

Analar grade of H_3PO_4 (85% w/w) supplied by BDH Chemicals Ltd., was used for the preparation of the electrolyte solution. Doubly distilled de-ionized water with a measured resistivity > 18 MΩ/cm was used in the preparation of solutions.

2.1.1. Compound I: *2-{3-[2-(4-Oxo-2-phenylquinazolin-3(4H)-ylamino)acetyl]thioureido}-benzoic acid.*

2.1.2. Compound II: *2-[2-(4-Oxo-2-phenylquinazolin-3(4H)-ylamino)acetylcarbamo-thioylthio]acetic acid*. Supplied by BDH Chemicals Ltd., were used as organic additives (chemical inhibitors).

2.1.3. Solution Composition

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Solution consists of 8M H_3PO_4 (100 ml) and different concentrations of acid derivatives materials. The concentrations of acid derivatives (.Compound I: 2-{3-[2-(4-Oxo-2-phenylquinazolin-3(4H)-ylamino)acetyl]thioureido}-benzoic acid) &.(Compound II: 2-[2-(4-Oxo-2-phenylquinazolin-3(4H)-ylamino)acetylcarbamo-thioylthio] acetic acid were used as organic additives cover range from $1x10^{-6}$M to $1x\ 10^{-3}$M. while the blank solution consists of 8M H_3PO_4

2.2. Apparatus and Techniques

Fig (1) represents the cell and the electrical circuit that has been used in this work. The cell consisted of a rectangular plastic container having the dimensions (5.1×5.0×10.0 cm) with electrodes fitting the whole section. Two electrodes, each as rectangular steel pipeline plate of 10 cm height and 5 cm width, are located 5.1 cm apart. A porous poly vinyl chloride diaphragm is used to prevent the effect of H_2 bubble. The electrical circuit during this work consisted of 6 Volt D.C. power supply of 6 volt with a voltage regulator and multi-range ammeter was connected in series with cell. Potential differences were obtained by increasing the cell current stepwise and measuring the steady state anode potential against a reference electrode, which consisted of wire, immersed in a cup of Luggin probe filling with phosphoric acid solution containing organic compound at concentration similar to that in the cell. The tip of Luggin probe is placed 0.5 - 1 mm tube from the anode surface. Ortho-phosphoric acid concentration is prepared from analar Ortho-phosphoric acid and distilled water. The anode height is 2 cm. before each run the block part of the anode is insulated with poly-styrene lacquers and the active surface of the anode is polished with fine emery paper, degreased with trichloroethylene, Washed with alcohols and finally rinsed in distilled water. Electrode treatment is similar to that used by Wilke. The rate of steel pipeline corrosion under different conditions is determined by measuring the limiting Current at 25°C.

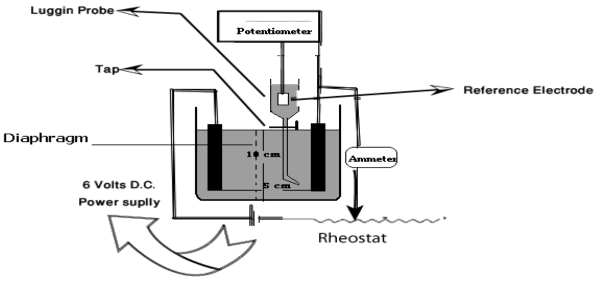


Fig (1). Schematic diagram of the apparatus [19]

2.3. Antimicrobial Activity

The agar diffusion method by Cruickshank *et al* [20] studded for the screening process. The bacteria and fungi maintained on nutrient agar and Czapek's - Dox agar media, respectively. The assay medium flasks containing 50 mL of nutrient agar for bacteria and Czapek's - Dox agar medium for fungi respectively allowed to reach 40-50 ^{o}C to be inoculated with 0.5 mL of the test organism cell suspension. The flasks were mixed well, poured each into a Petri dish (15 x 2 cm), and allowed to solidify. After solidification, holes (0.6 cm diameter) were made in the agar plate by the aid of a sterile cork poorer (diameter 6 mm). The synthesized target compounds dissolved each in 2 mL DMSO. In these holes, 100µl of each compound placed using an automatic micropipette. The Petri dishes left at 5° C for 1 h to allow diffusion of the samples through the agar medium and retard the growth of the test organism.

2.4. In vitro Antitumor Activity

Measurement of Potential Cytotoxicity by SRB assay:

The newly synthesized compounds have been evaluated for their Potential Cytotoxicity testing against breast cancer (MCF7) using the method of Skehan and Storeng[21]. Cells plated in 96-multiwell plate (10^4 cells / well) for 24 hrs before treatment with the compounds to allow attachment of cell to the wall of the plate. Different concentration of the compound under test (0, 1, 2.5, 5 and 10 µg/ml) were added to the cell monolayer triplicate wells prepared for each individual dose. Monolayer cells incubated with the compounds for 48 h at 37°C and in atmosphere of 5 % CO_2. After 48 h, cells fixed, washed and stained with Sulfo-Rhodamine-B stain. Excess stain washed with acetic acid and attached stain recovered with Tris EDTA buffer. Color Intensity measured in an ELISA reader. The relation between surviving fraction and drug concentration plotted to get tumor survival curves of each cell line. The IC_{50} percent control of infected and uninfected response values calculated for the various active compounds was in Table 7 Doxirubsin (DOX) used as positive standard. Compounds having IC_{50} < 5 µg/ml considered potentially active and exposed to further in *vivo* studies

3. RESULTS AND DISCUSSION

3.1. Effect of Electrode Height on Limiting Current density.

Figs (2.-5) and table (1) are showing that the limiting current density decreases with the increase in height

The average limiting current density decreases with increase in the height according to the following equation

$$I_L = C / (H)^{(a)} \qquad (1)$$

Where C is constant. H is the height of electrode.

Height(cm)	Potential (m V)	100	200	300	400	500	600	1000	2100	2200
divided cell	1	100	200	250	300	350	400	410	420	430
	2	200	300	350	400	450	520	525	535	550
	3	300	400	450	500	600	720	730	740	750
	4	400	450	550	700	800	900	910	920	930
	5	500	600	700	800	1000	1100	1120	1300	1500
undivided cell	1	160	190	240	290	340	390	400	410	420
	2	180	285	285	385	425	495	500	520	525
	3	200	300	350	400	500	620	630	635	645
	4	250	300	400	550	650	750	750	760	775
	5	340	490	520	660	785	835	850	865	870

Table (1): The relation between the potential and current at different anode height, in (8 M) H_3PO_4, using divided& undivided cell.

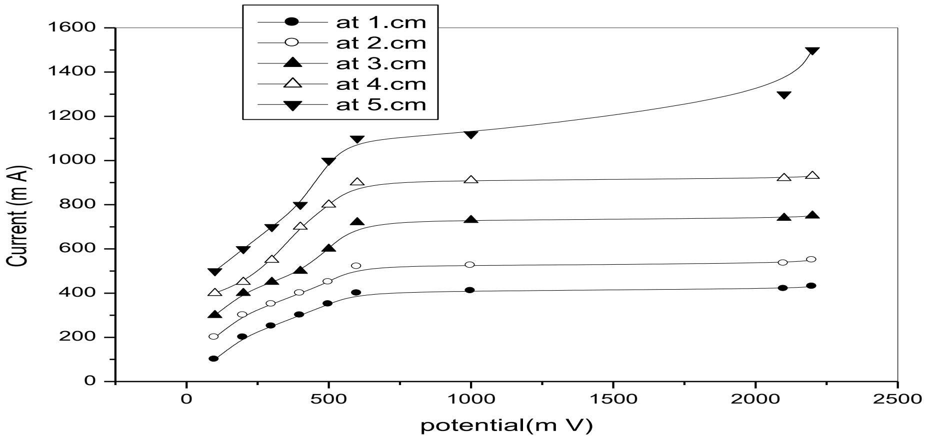


Figure (2.): The relation between the potential and current at different anode height, in(8 M) H_3PO_4, using divided cell.

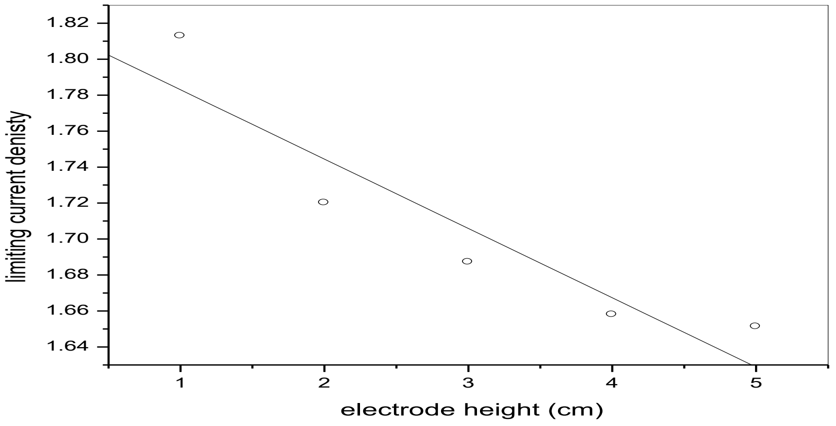


Figure (3): Give the effect of anodic height on the limiting current density using divided cell.

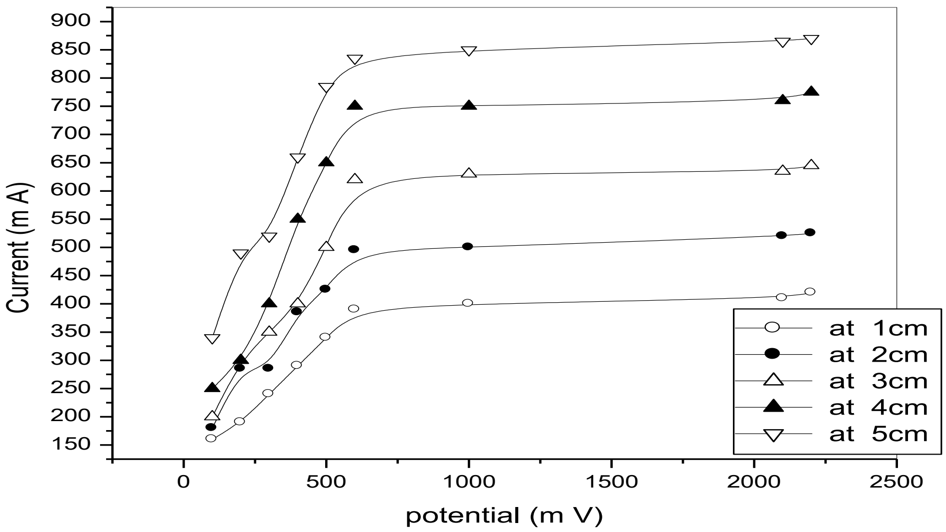


Figure (4): The relation between the potential and current at different anode height, in (8 M) H_3PO_4, using un divided cell

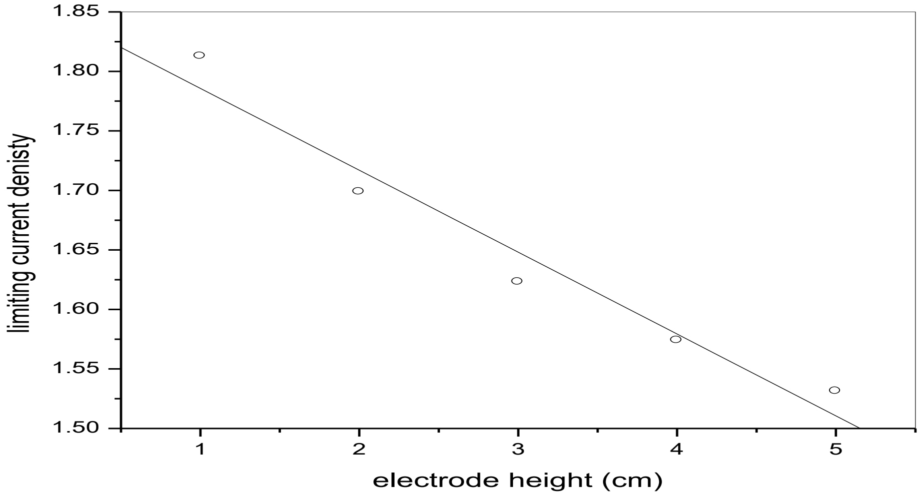
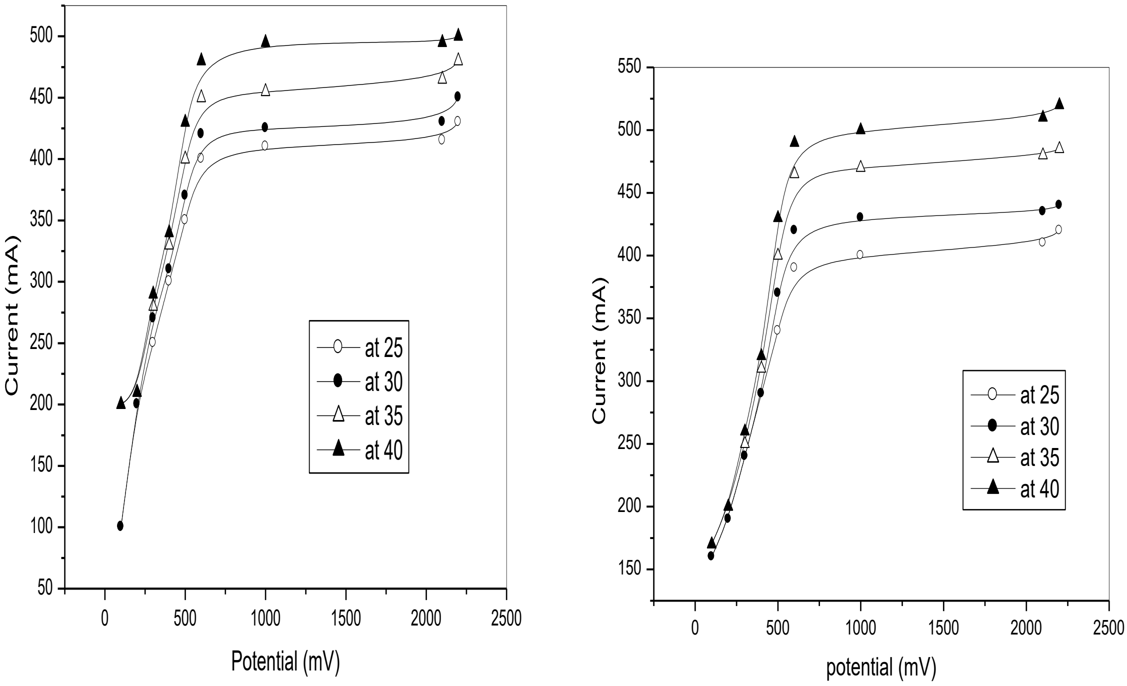


Figure (5): Give the effect of anodic height on the limiting current density using un divided cell.

3.2. Electropolishing using Divided and Undivided Cell.

Potential T ˚C Height(cm)		100	200	300	400	500	600	1000	2100	2200
divided cell	25	100	200	250	300	350	400	410	415	430
	30	100	200	270	310	370	420	425	430	450
	35	200	210	280	330	400	450	455	465	480
	40	200	210	290	340	430	480	495	495	500
undivided cell	25	160	190	240	290	340	390	400	410	420
	30	160	190	240	290	370	420	430	435	440
	35	170	200	250	310	400	465	470	480	485
	40	170	200	260	320	430	490	500	510	5290

Table (2): The variation of the current and voltage at different temperatures, at (1 cm) electrode height and in (8M) H_3PO_4 using divided and undivided cell



Divided cell **Undivided cell.**

Figure (6.): The relation between the current and volt at different temperatures, in (8 M) H_3PO_4, and the height of anode (1 cm).

3.3. Effect of Acid Derivatives Concentration on the Limiting Current for Steel Pipeline:

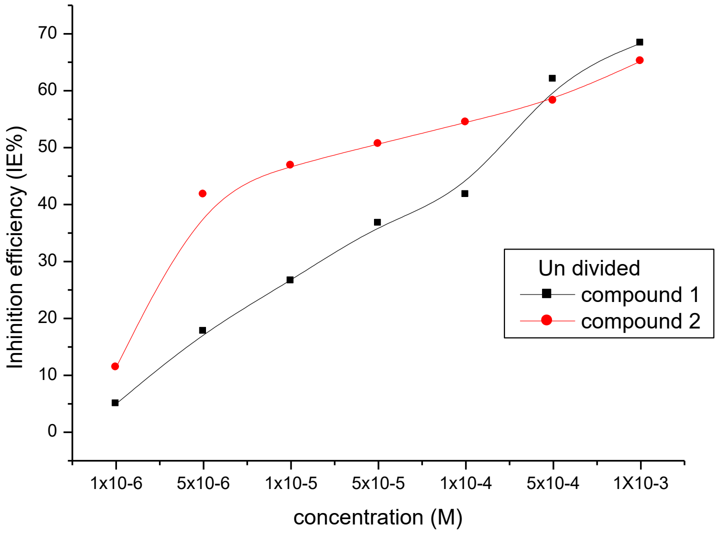
The observed limiting current density, which represents the rate of steel pipeline metal corrosion in phosphoric acid at 25ºC, decreases with increasing the concentration of the acid derivatives under test. It found that the limiting current decreases with increasing the concentration of acid derivatives. From the practical point of view and based on results obtained the used acid derivatives, studied in the concentration 10^{-6} mol/l, inhibit the corrosion of steel pipeline metal in 8 M H_3PO_4 acid

If the values of limiting current in absence of acid derivatives (I blank), and in the presence of acid derivatives (I organic), the percentage inhibition calculated from the following equation:

$$\% \text{ inhibition} = \frac{I_{\text{blank}} - I_{\text{organic}}}{I_{\text{blank}}} \times 100 \qquad \text{..............................(2)}$$

	Status	Concentration, M	Limiting current density, A.cm^{-2}			
			25°C	30°C	35°C	40°C
Compound I	Divided	0	740	800	860	950
		1x10^{-6}	710	770	830	880
		5x10^{-6}	680	740	800	850
		1x10^{-5}	650	710	770	820
		5x10^{-5}	620	680	740	780
		1x10^{-4}	590	650	710	750
		5x10^{-4}	570	620	680	720
		1x10^{-3}	540	605	640	690
	Undivided	0	790	880	940	1050
		1x10^{-6}	750	820	900	950
		5x10^{-6}	650	750	860	890
		1x10^{-5}	580	680	780	850
		5x10^{-5}	500	520	700	750
		1x10^{-4}	460	450	670	700
		5x10^{-4}	300	400	590	620
		1x10^{-3}	250	350	420	550
Compound II	Divided	0	740	800	860	950
		1x10^{-6}	670	710	770	860
		5x10^{-6}	640	680	740	830
		1x10^{-5}	620	650	710	800
		5x10^{-5}	600	630	690	780
		1x10^{-4}	580	610	670	750
		5x10^{-4}	560	590	650	720
		1x10^{-3}	540	560	630	690
	Undivided	0	790	880	940	1050
		1x10^{-6}	700	720	840	860
		5x10^{-6}	460	670	720	760
		1x10^{-5}	420	550	570	660
		5x10^{-5}	390	420	500	530
		1x10^{-4}	360	390	470	500
		5x10^{-4}	330	360	440	480
		1x10^{-3}	275	310	380	440

Table (3): The effect of temperature on the limiting current for divided and undivided cells at different concentrations of the acid derivatives using divided and undivided cell.



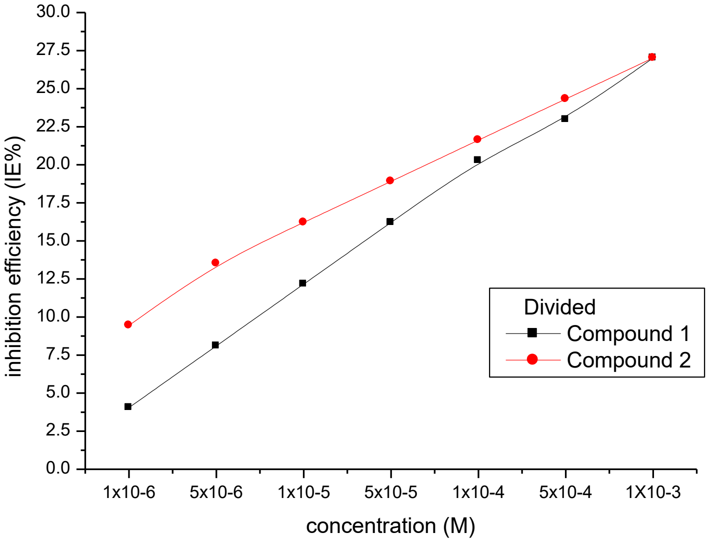


Figure (7): The relation between the percent efficiency of inhibition for different and concentration for divided cell & undivided cell.

3.4. Application of Thermodynamic Parameters

Straight lines are obtained with a slope X and intercept log x K. The experimental data fit the Flory-Huggins adsorption isotherm, which represented by

$$\log \Theta / C = \log x\, k + x \log (1- \Theta) \qquad (3)$$

Where x is the number of water molecules replaced by one molecule of the inhibitor.
The kinetic adsorption isotherm may written in the form

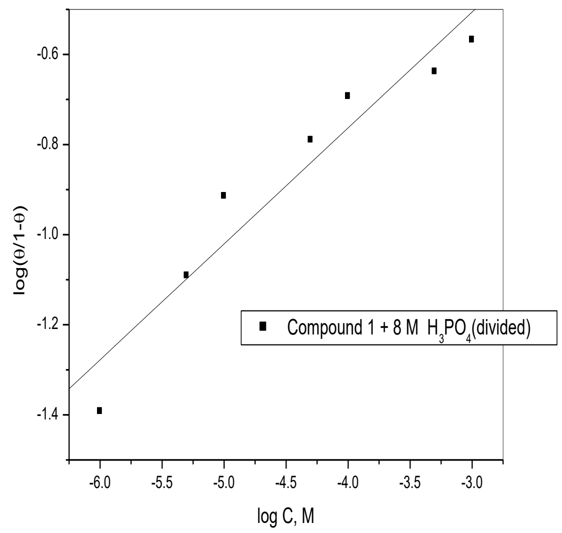
$$\log \theta / 1- \Theta = \log k' + y \log C \qquad (4)$$

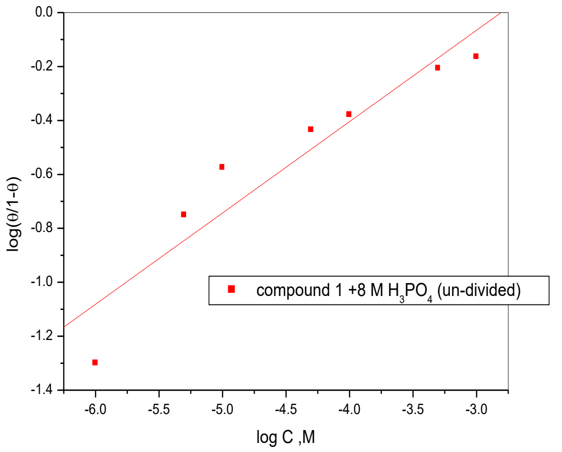
The free energy of adsorption (G_{ads}). At different concentrations of the organic materials as calculated from the following equation:

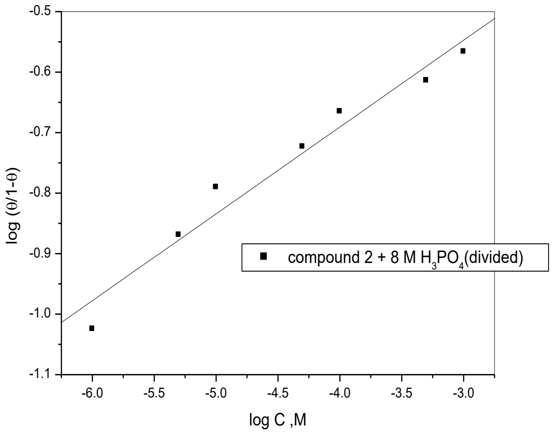
$$\Delta G_{ads} = -RTIn\,(55.5K) \qquad (5)$$

Where the value 55.5 is the concentration of water in the solution mol/1

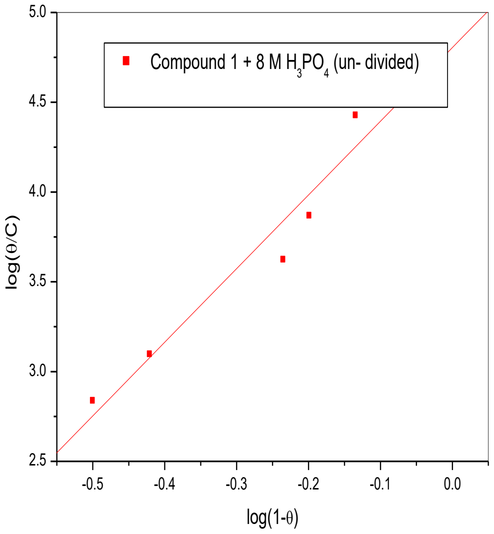
kinetic adsorption isotherm

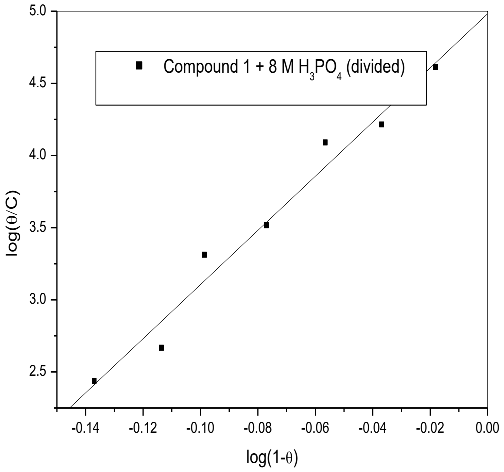


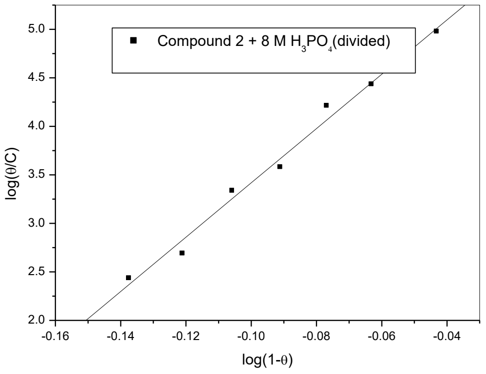




Flory-Huggins adsorption isotherm







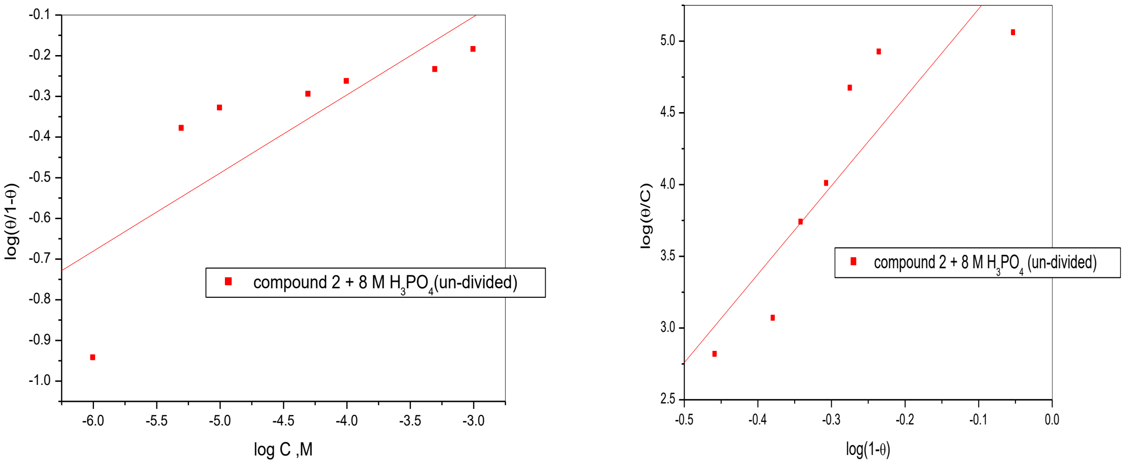


Figure (8) kinetic &Flory-Huggins adsorption isotherm

Compound	**Type**	**Flory - Huggins**	**Kinetic Adsorption Isotherm**
		-ΔG ads	**-ΔG ads**
I	**Divided**	48.12	36.16
	Un divided	49.17	34.01
II	**Divided**	46.80	38.83
	Un divided	50.62	37.01

Table (4) the calculated values of free energy of adsorption, ΔG_{ads}, (K.J. mol $^{-1}$) of the adsorbed organic materials.

3.5. Thermodynamic Treatment of the Results

From the integrated form of Arrhenius equation:

$$\mathbf{Ln\ I = - Ea / RT + ln\ A} \qquad \mathbf{(6)}$$

Where R is the gas constant (8.314 k. J. mol -1), Ea is the activation energy (k.J.mol.-1) and A is the frequency factor. It seen that the gradient is given by

– Ea/R and intercept by lnA. Table (4) give the values of Ea for the compounds used. The values of enthalpy ΔH*, entropy ΔS*, and energy of activation ΔG * obtained by the equations:

$$\Delta H^* = Ea - RT \qquad (7)$$

$$\Delta S^* / R = \ln (k\,Te / h) \qquad (8)$$

$$\Delta G^* = \Delta H^* - T \Delta S^* \qquad (9)$$

Where k is Boltzmann’s constant, e = 2.7183, h is Plank’s constant, T is absolute temperature and R is the universal gas constant. The values of the calculated thermodynamic parameters for different concentrations of organic materials in H_3PO_4 using divided and undivided cell.

Compo	**parameter**	**Thermodynamic parameters.**

	C(mol / l)		Ea* (K.J.mol^{-1})	H*Δ (K.J.mol $^{-1}$)	S * -Δ (J.mol^{-1}. K^{-1})	G*Δ (K.J.mol^{-1})
	0	divided	14.11	11.57	-156.96	58.22
	1x10^{-6}		15.20	12.66	-157.47	59.46
	5x10^{-6}		13.55	11.01	-163.50	59.66
	1x10^{-5}		13.47	10.93	-164.45	59.87
	5x10^{-5}		14.57	12.03	-161.56	60.09
	1x10^{-4}		15.89	13.35	-158.04	60.32
	5x10^{-4}		19.48	16.95	-147.20	60.61
	1x10^{-3}		19.87	17.32	-148.24	60.65
	0	Un divided	15.65	13.11	-146.60	57.90
	1x10^{-6}		14.87	12.33	-152.71	58.98
	5x10^{-6}		13.31	10.77	-158.51	59.20
	1x10^{-5}		14.20	11.67	-156.12	59.36
	5x10^{-5}		15.23	12.69	-153.34	59.54
	1x10^{-4}		16.42	13.88	-150.07	59.72
	5x10^{-4}		17.81	15.27	-146.19	59.93
	1x10^{-3}		17.65	15.11	-146.60	57.90
Compound II	0	divided	13.11	10.57	-155.96	58.22
	1x10^{-6}		11.15	8.61	-167.08	59.65
	5x10^{-6}		8.60	6.06	-176.07	59.85
	1x10^{-5}		7.90	5.36	-179.01	60.04
	5x10^{-5}		4.15	1.61	-191.82	60.22
	1x10^{-4}		14.56	12.02	-158.87	60.56
	5x10^{-4}		20.76	18.22	-139.71	60.91
	1x10^{-3}		14.11	17.57	-155.96	58.22
	0	Un divided	15.65	13.11	-146.60	57.90
	1x10^{-6}		10.93	8.39	-166.55	59.27
	5x10^{-6}		10.73	8.20	-167.79	59.46
	1x10^{-5}		11.91	9.37	-164.48	59.62
	5x10^{-5}		11.36	8.82	-167.04	59.85
	1x10^{-4}		12.37	9.83	-164.44	60.06
	5x10^{-4}		13.08	10.54	-162.93	60.32
	1x10^{-3}		14.65	12.11	-146.60	57.90

Table (5) give the values of Ea for the compounds.

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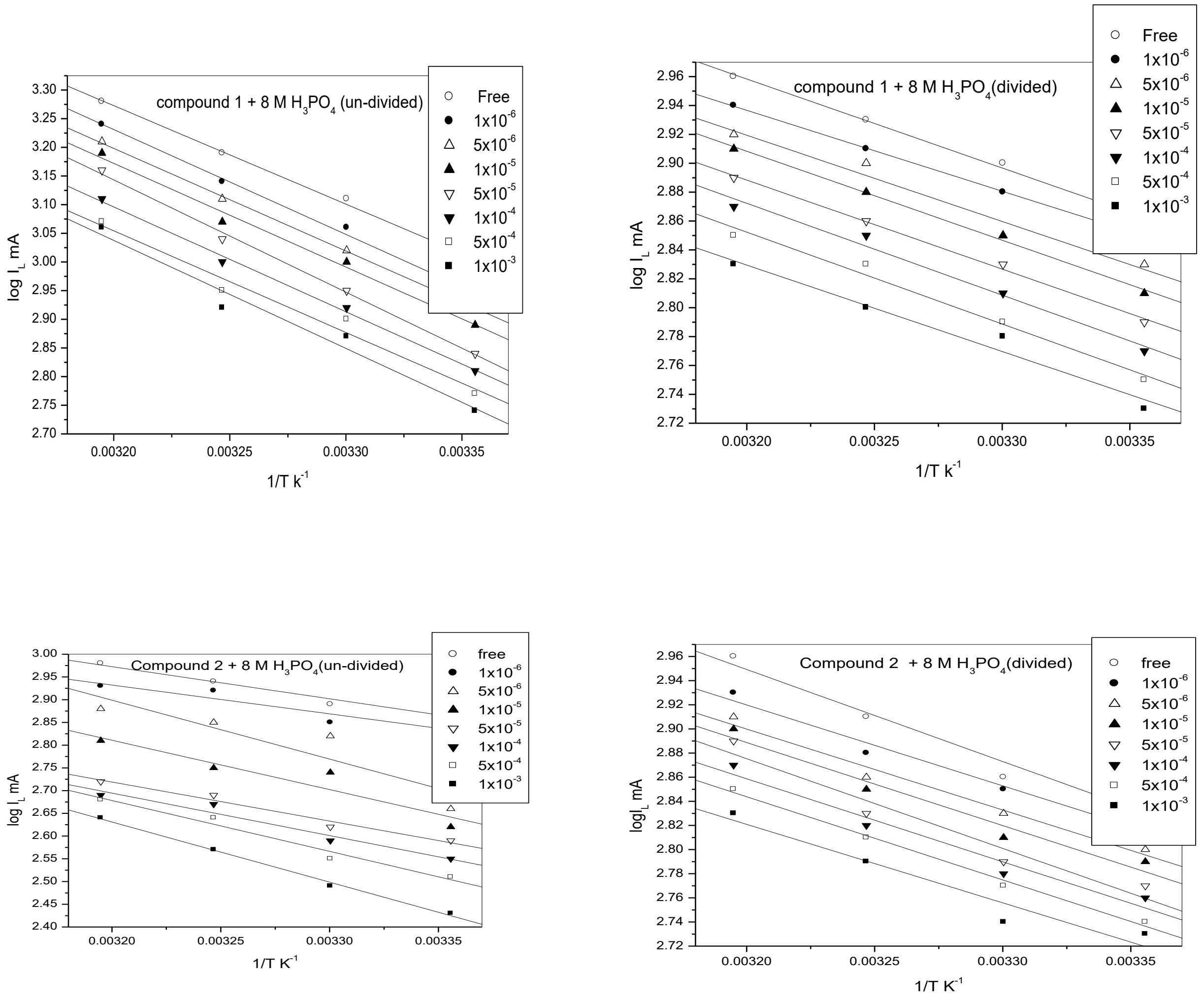
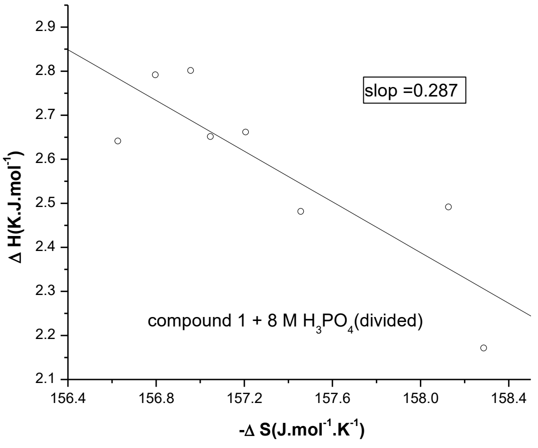
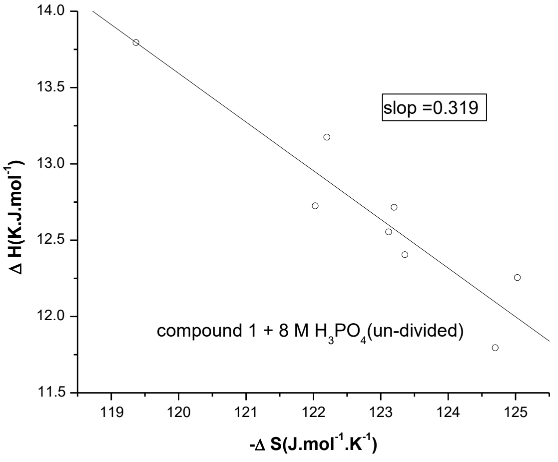
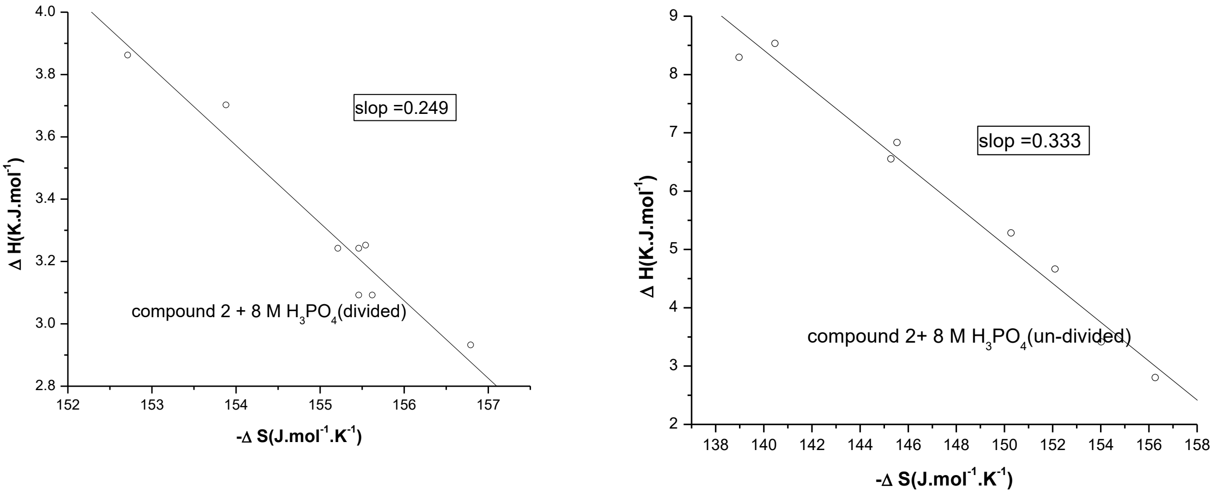


Figure (9): The relation between the logarism of the limiting current and 1/T for all at different concentration using divided cell and undivided cell.







Figures (10): The relation between Δ H *(K .J. mol $^{-1}$) and Δ S * (J. mol $^{-1}$ K^{-1}) for different concentrations .

3.6. Biological Activity

The plates incubated at 30^{o} C for 24 h for bacteria and 72 h of incubation at 28^{o} C for fungi. DMSO showed no inhibition zones. The diameters of zone of inhibition measured and compared with that of the standard, the values were tabulated. Ciprofloxacin[**22 - 23**] (50 µg/mL) and fusidic acid[**24**] (50 µg/mL) used as standard for antibacterial and antifungal activity respectively. The observed zones of inhibition presented in Table 6.

Compound No.	Zone of Inhibition (mm) of Microorganisms			
	Bacillus subtilis	*Escherichia coli*	*Candida albicans*	*Aspergillus flavus*
Penicillin	50	45	17	46
Compound **I**	30	29	18	35
Compound **II**	40	30	17	40

Table (6): In vitro antimicrobial activity by agar diffusion method of the tested compounds.

The synthesized compounds were screened *in vitro* for their antimicrobial activities against *Escherichia coli* NRRL B-210 (Gram -ve bacteria), *Bacillus subtilis* NRRL B-543 (Gram +ve bacteria), *Aspergillus flavus* and *Candida albicans* NRRL Y-477 (Fungi). The diameters of zone of inhibition measured and compared with the standard, the values were tabulated. Tetracycline used as standard for the antimicrobial activity and the observed zone of inhibition presented in Table 6.

The results indicated that tested compounds did not show high activity against bacteria under test (*Escherichia coli* and *Bacillus subtilis*) while compounds revealed high activity against fungi. All new compounds were active against the microorganisms.

3.7. Structure Activity Relationship (SAR) Studies:

The antimicrobial activity results and structure activity relationship indicated that the five-membered heterocyclic rings attached to quinazolines moiety resulted in increase of antimicrobial activity.

In conclusion, the antimicrobial screening suggests that the newly synthesized compounds showed moderate to good activity against the tested organisms. Hence the compounds prepared in this study are chemically unrelated to the current medication, suggests that further work with similar analogues is clearly warranted.

3.8. Antitumor Activity

The results obtained in table 7 showed that compounds **(I& II) possess** the highly significant effect against breast cancer cell line **(MCF7)** and this might be due to the five-membered heterocyclic rings attached to quinazolines moiety.

Compound	**IC_{50} µg/ml**
DOX	2.97
Compound **I**	4.00
Compound **II**	5.50

Table (7): The IC50 (µg/mL) of some of the selected new compounds against Breast cancer cell line (**MCF7**)

CONCLUSION

The value of the limiting current which represents the rate of corrosion is found to decrease by increasing the height of the anode and by increasing the phosphoric acid concentration. The anodic limiting current density takes higher values for undivided cell than that of the divided cell. Adsorption of these organic compounds (I&II) is founded to obey Flory – Huggins and Kinetic adsorption Isotherms but not Langmuir Isotherm. The limiting current density in presence of the added organic compounds (I&II) decreases with increasing concentration using both the divided and undivided cells and depends on their component and solution temperature. All the values of the activation energies are less than 40 K J. mol $^{-1}$ indicating that the reaction is diffusion controlled. The results indicated that tested compounds (I &II) did not show high activity against bacteria and The results obtained showed that compounds (I &II) **possess** the highly significant effect against breast cancer.

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