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Zinc corrosion in HCl in the presence of aqueous extract of *Achillea fragrantissima*

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Abstract
The effect of *Achillea fragrantissima* on the corrosion of zinc in 0.5 M HCl has been studied using weight loss, hydrogen evolution and polarization measurements. The inhibition efficiency was found to increase with increasing concentration and decrease with increasing temperature. Inhibition effect was explained on the basis of adsorption of *Achillea fragrantissima* components on the metal surface through the active centers contained in their structures. It was found also that adsorption of *Achillea fragrantissima* on zinc surface follows Langmuir adsorption isotherm. Thermodynamic and kinetic parameters for zinc corrosion and inhibition processes were calculated and interpreted.

Keywords: Zinc; polarization; corrosion inhibition; natural product.

1. Introduction
Zinc is an important metal with numerous industrial applications and is mainly used for the corrosion protection of steel. Due to these applications and economic importance of zinc metal, its protection against corrosion has attracted much attention. In modern industry acids are used for the chemical cleaning of metals and alloys. Zinc is highly susceptible to attack by acids. Hence for scale removal and cleaning of zinc surfaces with acidic solutions, it becomes necessary to use inhibitors. The use of inhibitors is one of the most practical methods for protection against corrosion, especially in acidic media. Most of the well known acid inhibitors are organic compounds containing nitrogen, sulphur and oxygen atoms. Such compounds contain electron donating groups, which decreases the corrosion rate by increasing the hydrogen overpotential on the corroding metal.
In recent years a great attention paid for trying many naturally occurring substances as corrosion inhibitors for defferent metals and alloys[1-19]. Naturally occurring substances are renewable, low cost and have no dangerous effects on human or environment. Among these substances the extracts of various parts of plants represent the most of these applications. In the present work we tested the aqueous extract of *Achillea fragrantissima* (Lavender cotton) as inhibitor for acid corrosion of zinc. Lavender cotton is a small perennial herb belongs to the family Asteraceae. It grows in Middle East countries and used in folk medicine. Weight loss, hydrogen evolution and polarization techniques were used in the study.

2. Materials and methods
Zinc metal with purity of 99.3% provided by Qaha Co. for chemical industries is used in the present study. The company uses it in manufacturing of dry cell batteries.

2.1. Weight loss measurements
Zinc sheets with surface area of 1 cm^2 were used for weight loss and hydrogen evolution measurements. The specimens were polished with emery papers (grade 320-400-800-1000), degreased with acetone and rinsed by distilled water then weighed before introduced in the test solution. A new test specimen was used in each experiment. The weight loss was taken as the average of three separate experiments.

The corrosion rate was expressed in $mg.cm^{-2}.hr^{-1}$. The inhibition efficiency (IE%) was calculated from weight loss using the following equation:

$$IE\% = \left[\frac{w_f - w_i}{w_f} \right] x100 \qquad (1)$$

Where w_f and w_i are the weight loss in absence and presence of the extract. The fraction of zinc surface covered by the adsorbed extract molecules (θ) was calculated as:

$$\theta = \left[\frac{w_f - w_i}{w_f} \right] \qquad (2)$$

2.2. Hydrogen evolution

Zinc sheets with dimension of (1.0 – 1.0 – 0.1 cm) were used for the experiments of hydrogen evolution. Prior to each experiment, the surface of zinc specimens were mechanically polished with different grades of emery papers degreased with acetone and rinsed by bi-distilled water. The specimen was inserted in a beaker having a capacity of 100 ml. evolved hydrogen gas was collected through a side arm connected by flexible polyethylene tubing to a gas burette standing in a beaker filled with water. It allowed measurement of the variation of the volume of hydrogen evolved during dissolution of the metal as a function of time. The experiments were carried out in absence and presence of the different inhibitors.

The corrosion rate (r) was taken as the slope of straight line obtained from the relation between volume of evolved hydrogen and time. The inhibition efficiency (IE%) was calculated as following:

$$IE\% = \left[\frac{r_f - r_i}{r_f} \right] x100 \qquad (3)$$

where r_f and r_i are the corrosion rates in absence and presence of the extract.

2.3. Polarization technique

For potentiostatic studies, a cylindrical rod embedded in araldite with exposed surface area of 0.5 cm^2 was used. The electrode was polished with different grades of emery papers, degreased with acetone and rinsed by distilled water before introduced in the test solution. The electrode was left in the test solution for 10 min. until it acquired the steady state potential. The potential was swept during the experiment at scan rate of 10 mV/sec. The corrosion rate was calculated by polarization method as the current corresponds to the intercept between cathodic and anodic lines. Inhibition efficiency was calculated from the equation:

$$IE\% = \left[\frac{I_f - I_i}{I_f} \right] x100 \qquad (4)$$

Where I_f and I_i are the corrosion rates in absence and presence of the extract.

2.4. Extract preparation

Stem, leaves and flower of *Achillea fragrantissima* were dried and crushed to powder. The powder was boiled in distilled water for three hours. The solution was then filtered and the filtrate was evaporated to dryness by keeping it in a drying oven at 80^{o}C. The solid residue was then used for preparing a stock solution of high concentration (in ppm). The desired concentrations were then prepared by dilution of the stock solution. All chemicals used for preparing the test solutions were of analytical grade and the experiments were carried out at room temperature; 30 ^{o}C ± 1 ^{o}C.

3. Results and discussion

3.1. Weight loss measurements

The loss of weight of zinc strips in 0.5 M HCl solution in absence and presence of different concentrations of *Achillea fragrantissima* extract, for 24 h, was determined. The inhibition efficiency was calculated and represented in Table 1. The rate of corrosion was tabulated as ($mg.cm^{-2}.hr^{-1}$) and the concentration of the extract was expressed as part per million (ppm). Inspection of the data of Table 1 reveals that *Achillea fragrantissima* extract acts as a good inhibitor for corrosion of zinc in hydrochloric acid solution. The inhibition efficiency increases with the increase of extract concentration. A parameter (θ) which represents the part of the metal surface covered by the inhibitor molecules was calculated for different inhibitor concentrations and represented also in Table 1.

Table 1: Corrosion parameters of zinc in 0.5 M HCl devoid of and containing different concentrations of *Achillea fragrantissima* extract.

Conc., (ppm)	Corr. rate. ($mg.cm^{-2}.hr^{-1}$)	IE%	θ
Free	6.9875	-	-
50	5.5875	20	0.20
100	4.6583	33	0.33
200	3.4916	50	0.50
400	2.3291	66	0.66
800	1.2416	82	0.82

The composition of water distilled essential oils of Achillea species was analysed by GC and GC/Ms. More than fifty-eight compounds were identified in the aqueous extract of *Achillea fragrantissima* [20]. α-Thujone (60.9%), β-Thujone (9.1%), sabinene (4.1%) and camphor (3.7%) were characterized as the main constitutes (Fig 1). The extract acts as inhibitor due to adsorption of its components on the metal surface. Therefore, one can conclude that the major component; Thujone may be responsible for the inhibitive action of the extract. The other components may act in synergism with the major one.

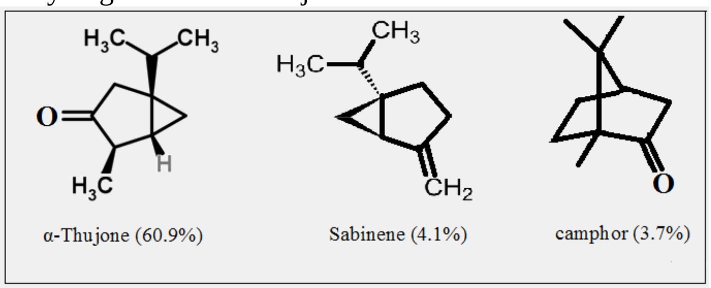

Fig 1: Major constituents of *Achillea fragrantissima* extract.

3.2 hydrogen evolution measurements

The dissolution reaction of zinc in 0.5M HCl devoid of and containing different concentrations of *Achillea fragrantissima* was studied using hydrogen evolution method. The relationship between the volume of hydrogen evolved during the corrosion reaction and the reaction time is represented in Fig. 2.

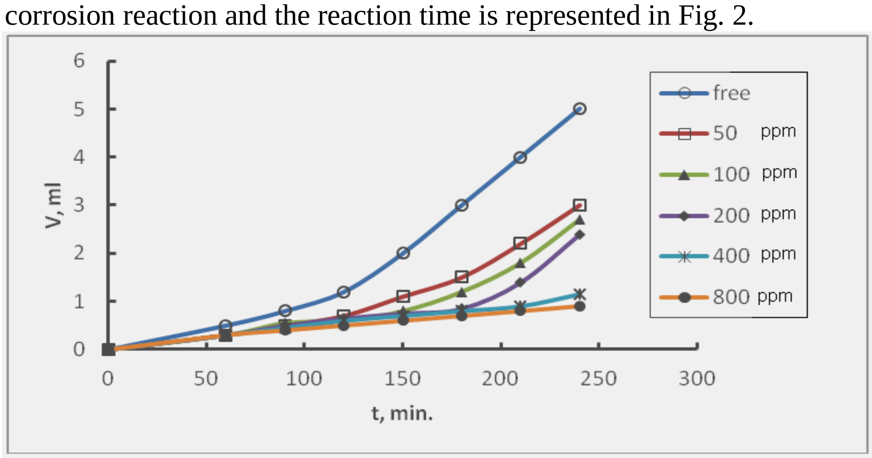

Fig 2: hydrogen evolution during corrosion of zinc in free and inhibited 0.5 M HCl.

Inspection of the figure reveals that, there is a linear relation between hydrogen volume and time. The rate of hydrogen evolution is small at the beginning of the reaction then after certain time it increases markedly. The initial time interval, through which the rate of reaction is small, is the incubation period. During this incubation period, the breakdown of the pre-immersed oxide film on the metal surface takes place before the start of metal attack. Since zinc is readily soluble in aqueous acidic solutions with the liberation of hydrogen the rate of hydrogen liberation corresponds to zinc corrosion rate. So, the slopes of the straight portions of the curves, after the incubation period, were taken as a measure of the corrosion rates of zinc in free and inhibited acid solutions.

Further inspection of the curves of Fig 2 reveals that the addition of *Achillea fragrantissima* reduces the rate of hydrogen evolution as the *Achillea fragrantissima* concentration is increased. The values of inhibition efficiency of different concentrations of *Achillea fragrantissima* are given in table 2. These values show that the IEs of the *Achillea fragrantissima* are very high at high concentrations and comparable with those obtained from weight loss technique.

Table (2): Inhibition efficiencies as revealed from hydrogen evolution measurements.

Conc. (ppm)	50	100	200	400	800
IE (%)	22	44	52	77	82

3.3 Potentiostatic polarization

The effect of addition of *Achillea fragrantissima* extract on the anodic and cathodic polarization curves of zinc in 0.5 M HCl solution at 30 ^{o}C was studied. The potentiodynamic polarization curves of zinc in 0.5 M M HCl in absence and presence of of various concentrations of *Achillea Fragrantissima* extract is shown in Fig 3. Inspection of Fig 3 reveals that both the anodic and cathodic polarization curves shift toward less current densities values upon addition of the extract. This result suggests the inhibitive action of *Achillea Fragrantissima* extract toward zinc corrosion in the acidic medium.

The polarization parameters; anodic Tafel slope (β_a), cathodic Tafel slope (β_c), corrosion potential (E_{corr}), corrosion current (I_{corr}) and inhibition efficiency (IE) are presented in table 3. Inspection of Table 3 reveals that the corrosion potential shows slight shifts to less negative values as the concentration of the added extract is increased. Moreover, both anodic and cathodic Tafel constants decrease with increasing additive concentration. These findings suggest that the additive acts as mixed inhibitor. This means that the inhibitor retards both anodic and cathodic electrochemical reactions.

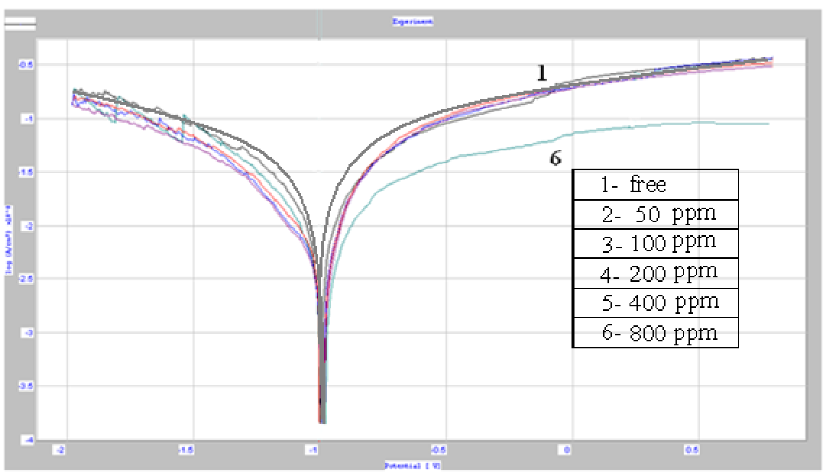

Fig 3: Polarization curves of zinc in 0.5 M M HCl in absence and presence of various concentrations of *Achillea Fragrantissima* extract.

Table (3): Polarization parameters of zinc in 0.5 M HCl containing and devoid of different concentrations of *Achillea fragrantissima* extract.

Conc. (ppm)	E (mV)	β_a (mV/decade)	- β_c (mV/decade)	I_{corr} (mA/cm^{-1})	IE (%)
0	-1015	85	100	3.364	-
50	-1003	79	109	2.869	14.7
100	-999	64	92	2.523	25
200	-992	96	122	2.075	38.3
400	-996	65	76	1.371	59.2
800	-996	58	69	1.000	70.2

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On the other hand, the corrosion current density is markedly decreased upon addition of the extract. This may be ascribed to adsorption of the inhibitor molecules on the metal surface.

3.4. Adsorption behaviour

To study the adsorption behaviour of *Achillea fragrantissima* on zinc surface in the given medium, the adsorption isotherm must be defined. Therefore, the relation between the concentration of extract (C) and the fraction of zinc surface covered by the adsorbed compounds (θ) was obtained. Because the inhibition action is postulated as a result of the adsorption process, (θ) is directly related with the inhibition efficiency (IE). The best fit was obtained for the relation between (C/θ) and C, which represented in Fig 4. A straight line was obtained with almost unity slope indicating that the adsorption process follows Langmuir adsorption isotherm. This isotherm postulates that there is no interaction between the adsorbed molecules and the energy of adsorption is independent on the surface coverage (θ). Langmuir adsorption isotherm could be represented using the following equation:

$$\frac{C}{\theta}=\frac{1}{K}+C \tag{5}$$

Where K is the adsorption constant and:

$$\ln K = \ln\frac{1}{55.5}-\frac{\Delta G_{ad}^{o}}{RT} \tag{6}$$

The standard free energy of adsorption could be calculated using equation (6) where one molecule of water is replaced by one molecule of inhibitor [21]. The numerical value (1/55.5) in equation (6) stands for molarity of water.

It is unsafe to determine the value of free energy of adsorption for an extract contains much variety of compounds. All the constituents of the extract are expected to take a part in the inhibition process. Therefore, it is impossible to define a molarity to be used in the isotherm graph and then use eq (6).

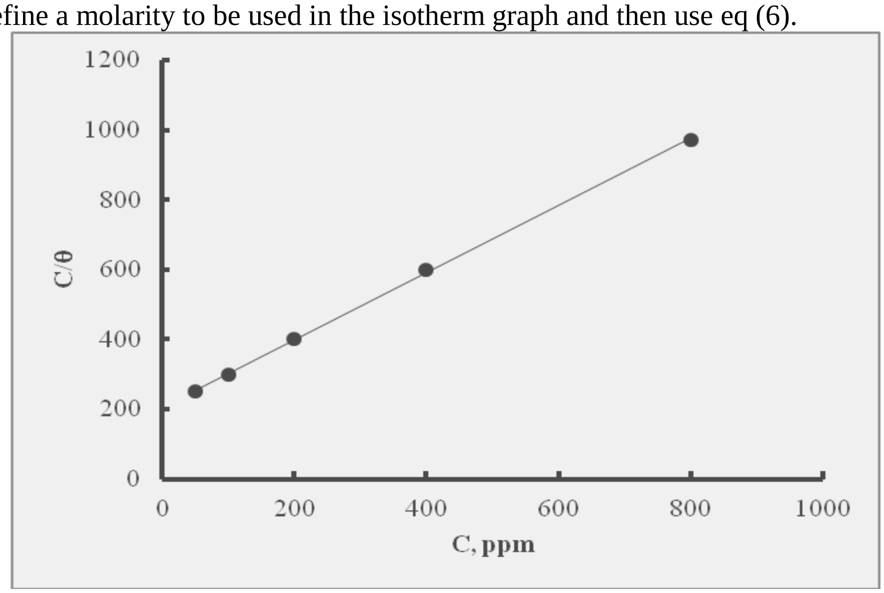

Fig 4: Langmuir adsorption isotherm

3.5. Effect of temperature

The effect of temperature on the corrosion parameters of zinc in free and inhibited solutions of 0.5 M HCl was studied using polarization technique in a temperature range 40 - 70 ^{o}C. The acid solutions were inhibited by addition of 800 ppm of *Achillea fragrantissima* extract. The variation of temperature has no effect on the general shape of the polarization curves. The obtained corrosion parameters are given in table 4.

Inspection of table 4 reveals that the corrosion rate of zinc increases with increased temperature. On the other hand, the inhibition efficiency of *Achillea fragrantissima* extract decreases as the temperature was increased.

The activation energy of corrosion process in free and inhibited acid can be calculated using Arrhenius-type equation:

$$\log I_{corr} = \log A - \frac{E_a}{2.303RT} \qquad (9)$$

Where E_a is the activation energy, A is the frequency factor, T is the absolute temperature, R is the gas constant and I_{corr} is the rate of corrosion reaction.

Table (4): corrosion parameters of zinc in 0.5 M HCl containing 800 ppm of *Achillea fragrantissima* extract at different temperatures.

Temp. (K)	E (mV)	β_a (mV/decade)	- β_c (mV/decade)	I_{corr} (mA/cm^{-1})	IE (%)
313	-988	63	76	2.211	51
323	-989	80	98	4.252	39.8
333	-977	66	66	3.302	33.4
343	-984	85	99	4.302	33.6

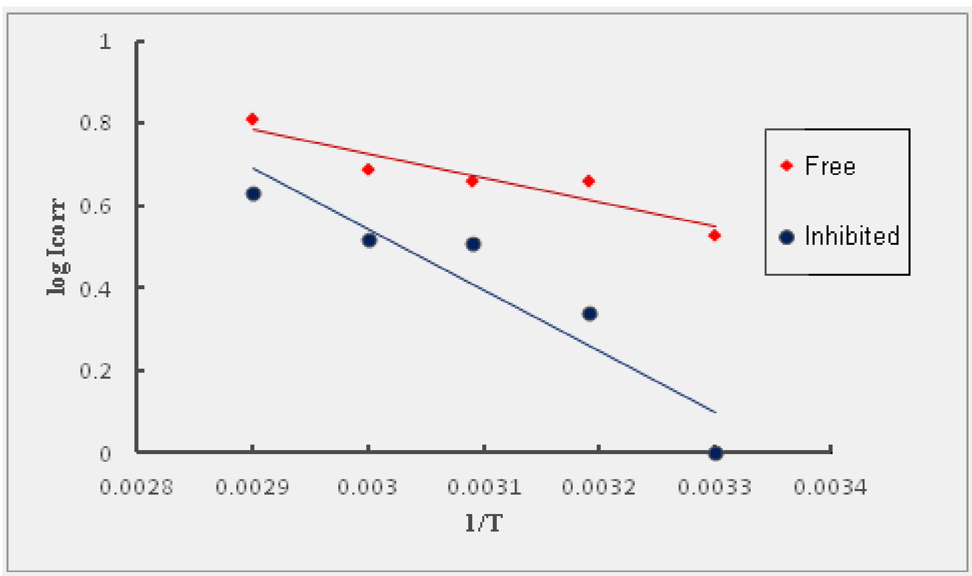

Fig 5: Arrhenius plot for corrosion of zinc in free and inhibited 0.5 M HCl solutions.

Fig 5 represents the relationship between log I_{corr} and $\frac{1}{T}$. The values of activation energy calculated using the curves of Fig 5 are listed in table 5 for free and inhibited acid solutions. The obtained results suggest that *Achillea fragrantissima* extract inhibits the corrosion reaction by increasing its activation energy. This could be done by adsorption on the zinc surface making a barrier for mass and charge transfer. However, such types of inhibitors perform a good inhibition at ordinary temperature with considerable loss in inhibition efficiency at elevated temperatures [22].
The enthalpy of activation (ΔH*) and entropy of activation (ΔS*) for the corrosion of zinc in HCl solutions, devoid of and containing 800 ppm of *Achillea fragrantissima* extract, were obtained by applying the transition-state equation [23]:

$$\log \frac{I_{corr}}{T} = \left[\left(\log \frac{R}{hN}\right) + \left(\frac{\Delta S^*}{2.303R}\right)\right] - \frac{\Delta H^*}{2.303RT} \qquad (10)$$

where h is the Planck's constant and N is the Avogadro's number. Fig 6 represents a plot of log (I_{corr}/T) versus (1/T). Straight lines were obtained with slopes equal to $\left(\frac{-\Delta H^*}{2.303R}\right)$. The values of ΔS* were calculated from the intercepts of log (I_{corr}/T)-axis. Table 5 contains the calculated values of ΔH* and ΔS*.

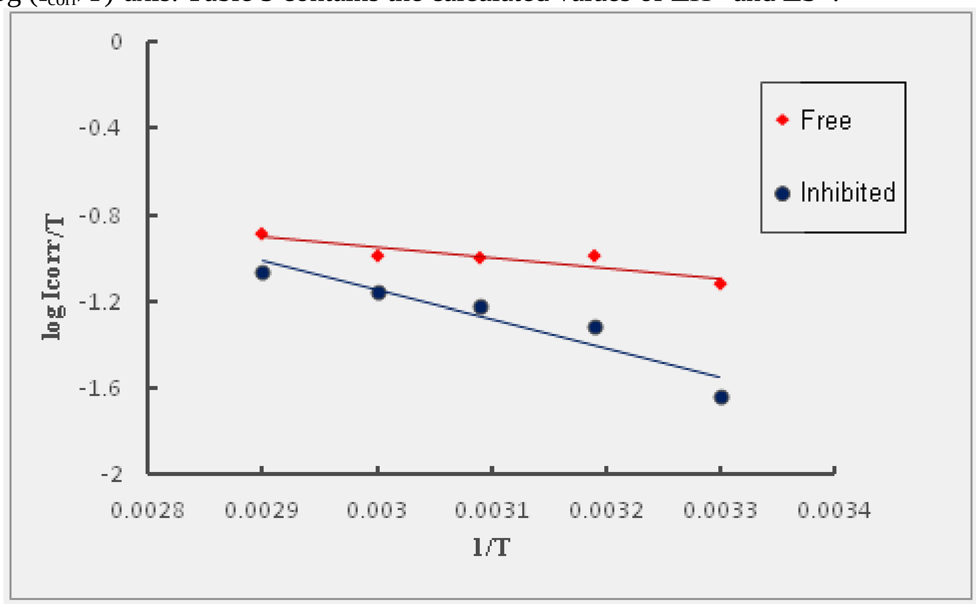

Fig 6: Plot of log (I_{corr}/T) versus (1/T).

Table (5): Activation parameters of zinc corrosion in free and inhibited 0.5 M HCl solutions.

Solution	E_a (kJ.mol^{-1})	ΔH* (kJ.mol^{-1})	ΔS* (J.mol^{-1}.K^{-1})
Free	11.46	8.89	-188
Inhibited (800 ppm)	28.21	25.61	-142

All the values of E_a are larger than those of corresponding values of ΔH* by about 2.6kJ.mol^{-1}. This value is almost equal to the average value of RT (2.5 kJ.mol^{-1}) at room temperature; 30^{o}C. This value verifies the known thermodynamic relation between E_a and ΔH* characterizing unimolecular reaction [24]:

$$E_a - \Delta H^* = RT \quad (11)$$

The negative values of activation entropies show that the activation complex in the rate determining step represents an association rather than dissociation step. This means that a decrease in disordering takes place on going from reactants to the activated complex [25].

Conclusions

1- The aqueous extract of *Achillea fragrantissima* leaves acts as a good inhibitor for corrosion of zinc in 0.5M HCl.
2- The inhibition efficiency was found to increase by increasing the inhibitor concentrations and decrease with increasing temperature.
3- The inhibitive action of the extract takes place through the adsorption of its constitutes on the metal surface.
4- The adsorption of *Achillea fragrantissima* constitutes on a zinc surface followed Langmuir adsorption isotherm.

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