

Effect of Creatinine Extracted from the Bovine Urine on the Corrosion of Mild Steels in 0.5 M HCl (Environmental Aspect)

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■ Abstract:

Bovine farm waste, which includes urine, is typically thrown away and pollutes the environment. In the current study, bovine urine has been employed as a primary component to create an inhibitor extract that will prevent mild steel from corroding and prevent livestock waste from contributing to issues in the community such environmental pollution and poor air and water quality. The corrosion rate, inhibitor efficiency, adsorption and thermodynamic study has been experimentally investigated using weight loss technique. The outcome has demonstrated that the creatinine extract is an effective mild steel corrosion inhibitor in 0.5 M HCl at room temperature. The creatinine extract dosage ranged from 0.396 to 4.420 M. The corrosion rate and inhibitor efficiency ranged from 23.99 to 241.38 mpy and 58.16 to 90.06 % respectively. The weight loss calculations showed that the corrosion rate of mild steel in HCl media decreases with increasing the inhibitor concentration. So, it was concluded that the Creatinine has excellent inhibition effect on the corrosion of mild steel in HCl medium. The thermodynamics parameters reveals that the mechanism of inhibitor adsorption was spontaneous and physisorption. The Creatinine inhibitor which extracted from bovine urine obeying to all applied adsorption isotherm models. Thus, it has a great adsorption on the surface of mild steel.

● **Keywords:** Mild Steel, HCl Corrosion, Bovine Urine, Creatinine Extract, Adsorption Isotherms.

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■ المستخلص:

نفايات مزارع الأبقار، التي تشمل البول، عادة ما تُلقى في القمامة وتلوث البيئة. في هذه الدراسة، تم استخدام بول الأبقار كمكون أساسي لإنشاء مستخلص مثبط يمنع تآكل الفولاذ الطري ويحول دون مساهمة نفايات الماشية في مشاكل المجتمع مثل تلوث البيئة ورداءة جودة الهواء والماء. تم دراسة معدل التآكل وكفاءة المثبط، بالإضافة إلى الدراسة الامتزازية والديناميكية الحرارية، تجريبيًا باستخدام تقنية الوزن المفقود. أظهرت النتائج أن مستخلص الكرياتينين هو مثبط فعال لتآكل الفولاذ الطري في محلول HCl 0.5 عند درجة حرارة الغرفة. تراوحت جرعة مستخلص الكرياتينين من 0.396 إلى 4.420 م. تراوحت معدلات التآكل من 23.99 إلى 241.38 مل/سنة وكفاءة المثبط 58.16 إلى 90.06 %. أظهرت حسابات فقدان الوزن أن معدل تآكل الفولاذ الطري في وسط HCl ينخفض مع زيادة تركيز المثبط. لذلك، تم الاستنتاج بأن الكرياتينين له تأثير مثبط ممتاز على تآكل الفولاذ الطري في وسط HCl. تكشف بارامترات الديناميكية الحرارية أن آلية امتصاص المثبط كانت تلقائية وامتزازا فيزيائيًا. يمثل مثبط الكرياتينين المستخرج من بول الأبقار لجميع نماذج الإيزوثيرم الامتزازية المطبقة. وبالتالي، فإنه يمتلك قدرة كبيرة على الامتزاز على سطح الفولاذ الطري.

● **الكلمات المفتاحية:** الفولاذ الطري، تآكل، HCl، اليورين البقري، مستخلص الكرياتينين، إيزوثيرم، الامتزاز.

1. Introduction

For the processing of acid, alkali, and salt solutions, one of the main building materials used in the chemical and related industries is mild steel (1). HCl is the most challenging of the common acids to work with corrosion. Even in relatively diluted quantities of hydrochloric acid, the choice of materials to handle the acid alone must be made with extreme caution. The majority of popular metals and alloys are severely corroded by this acid (2). All species, but especially humans, depend on good health and reliable access to food. Both are primarily mental and bodily states, and if one is neglected, a person may eventually pass away (3). When it comes to environmental issues related to cow urine, heavy metals can move from irrigation water to agricultural soils, posing a risk to human health due to direct contact with the metals in

the soil and the translocation and bioaccumulation of metals in forages, which contaminates animal products and, in both cases, can cause cancer and non-cancerous diseases (4). It is generally known that urine is a metabolic waste that is produced in enormous amounts and is made by the filtration of plasma at the renal level. Metals are thought to be a sign of contamination from long-term exposure in this matrix (5), making them a crucial diagnostic tool. On the other hand, in some parts of the world, pee is utilised as a product in the manufacturing of food, the pharmaceutical sector, and the management of bee problems (6), making knowledge of urine's level of contamination crucial. The analysed cows' urine had a Pb content of 0.028 mg L^{-1} , which was lower than the $50\text{--}124 \text{ mg L}^{-1}$ range reported by Raghu (2015) (7). The excretion of Cd in urine is thought to represent the body load of this element because, on the other hand, high excretion levels indicate serious kidney impairment (8). Particularly during the winter, urine significantly reduces clovers' ability to fix nitrogen. According to Richards & Wolton's distribution statistics from 1976, when dairy production is extensive (three cows per ha), urine impacts around 40% of the grazed area. A minimum 10% annual reduction in nitrogen fixing must result from such an addition (9). There have also been reports of using cow urine to create nanoparticles (10). The green approach is always necessary because organic solvents are poisonous and hazardous to the environment (11). Due to its pH level or acid-base potency, cow urine may one day be useful in other organic synthesis as a solvent or catalyst to potentiate a reaction or for a particular transformation (12). The economic growth of a poor country might be greatly aided by the use of cannabis and cow urine (13). Copper, silver, and palladium nanoparticles with numerous medicinal applications have recently been created using cow urine (14). Healthy bovine urine ranges in volume from 17 to 45 ml/kg/day and has a specific gravity of 1.025 to 1.045. Seasonal changes affect its pH, which ranges from 7.4 to 8.4. The daily ranges for urea nitrogen and total nitrogen are 23–28 ml/kg and 40–45 ml/kg, respectively. Protein, glucose, and haemoglobin are not present

in the urine of healthy cows (15). Other important constituents are given in Table (1) below.

Table (1) Bovine Urine Chemical Composition (15).

Ammonia Nitrogen	1-1.7ml/kg/day
Allantoin	20-60ml/kg/day
Calcium	0.1-1.4ml/kg/day
Chloride	0.1-1.1mmol/kg/day
Creatinine	15-20mg/kg/day
Magnesium	3.7mg/kg/day
Potassium	0.08-0.15mmol/kg/day
Sodium	0.2-1.1mmol/kg/day
Sulphate	3-5mg/kg/day
Uric Acid	1-4mg/kg/day
Leucocyte	15micro It>

In the urine of healthy cows, there is no protein, glucose, or haemoglobin. The current study's focus, creatinine, functions as an antibacterial (15). A substance called creatinine is created when nonenzymatic water is removed from creatine phosphate, a crucial energy source for the metabolism of muscle tissue (16). Degradation of creatine phosphate happens naturally and very often. Every day, the body converts about 2% of its stored creatine to creatinine (17). Blood and urine both contain creatinine. However, since the animal is no longer using the creatinine in the blood, the kidneys filter and eliminate it through the urine (18). Since the balance of the creatinine molecule (creatine & creatinine) in vitro is largely dependent on temperature and pH, with creatine being favoured at basic pH and low temperature,

and creatinine having an increase in its concentration when there are high temperatures and acidic environments, the increase in relative creatinine concentrations in the cow urine may be linked to the excretion of creatine in the urine (19). The metabolism of creatine and creatinine are illustrated in Figure (1). Creatinine, 2-imino-1-methylimidazolidin-4-one and its tautomer, 2-amino-1-methylimidazoline-4-one, is the anhydride of creatine, that is, a lactam obtained by cyclocondensation of creatine, N-methyl-N-guanylglycine which is present in muscular tissue of many vertebrates (20).

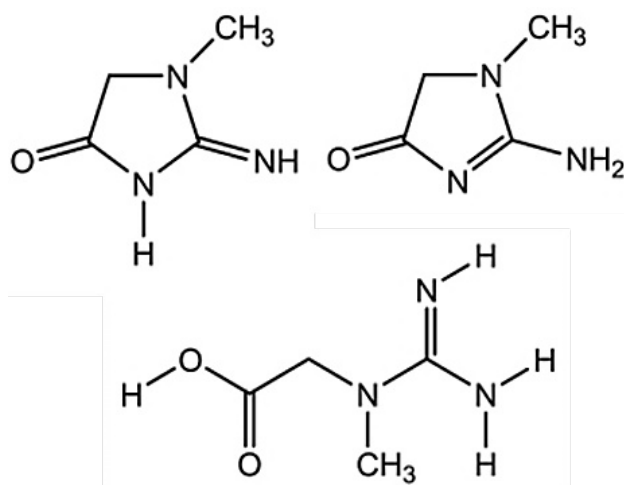


Figure (1) Chemical Structure for Creatine and Creatinine (20).

The phenomena governing the retention (or release) or mobility of a chemical from aqueous porous media or aquatic habitats to a solid phase at a constant temperature and pH is generally described by an adsorption isotherm, which is a valuable curve (21). When an adsorbate-containing phase has been in contact with the adsorbent for enough time for its adsorbate concentration in the bulk solution to be in a dynamic balance with the interface concentration, adsorption equilibrium (the ratio between the adsorbed amount with the remaining in the solution) is established (22). The mathematical correlation, which is typically shown visually by plotting the solid-phase against its residual concentration, plays a significant part in the modelling analysis,

operational design, and practical application of adsorption systems (23). Its physicochemical features and the underlying thermodynamic presumptions shed light on the adsorption mechanism, surface characteristics, and level of adsorbent affinities (24).

Over the years, a wide variety of Models of equilibrium isotherms include those by Langmuir, Temkin, Frumkin, Freundlich, Flory-Huggins, Adejo Ekwonchi, El-Awadi, Hill Deboer, Fowler-Guggenheim, etc (25). The aim of the present research work is to evaluate the corrosion of mild steel in the absence and the presence of creatinine extracted from bovine urine in 0.5 M HCl. The corrosion inhibition is studied firstly by weight loss method and then thermodynamics parameters including; adsorption constant () and adsorption free energy (). Finally, the adsorption of the inhibitor on the surface of mild steel using various isotherm models was discussed.

2. Research Methodology

2.1 Bovine Urine Sample Collection

A one liter of bovine sample was collected from Cow farm at FedEx in Tamiya Al-Fayoum Governorate – Egypt. During spontaneous bovine urinating, samples were taken. In accordance with Chen and Gomes' instructions, the urine samples were diluted in 160 mL of distilled water to prevent uric acid precipitation and had their pH values lowered to levels below 3 to prevent microbial destruction of purine and creatinine derivatives (26). Immediately after sampling, dilution, the bovine urine was kept in a refrigerator at a temperature of -20 to -40 degrees Celsius to prevent any change in the concentration of creatinine (27).

2.2 Creatinine Extraction from Bovine Urine

(a) A creatine solution was introduced to the diluted bovine urine to test the creatine to creatinine conservation. The urine pH was adjusted to a value lower than 3 using sulfuric acid drops; (b) In order to assess the preservation of creatine to creatinine, a creatine solution was added to the diluted bovine urine. After 30 days of storage under refrigeration (4 °C), the presence of

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creatinine in the urine results in an increase in the creatinine content (27). Six different creatinine concentrations were prepared in order to investigate their effects on the corrosion of mild steel in 0.5 M of hydrochloric acid solution. The different inhibitor concentrations were (0.396, 0.884, 1.768, 2.652, 3.536 and 4.420 M).

2.3 Mild Steel Samples Preparation

A mild steel sheet was cut in order to prepare 14 metal coupons. The dimension of mild steel coupons was (4x2x0.2cm). The composition of mild steel material used in the current research is showing in Table (2)

Table (2) Chemical Composition of Mild Steel.

Constitute	Mn	Cu	Si	C	Ni	Cr	S	P	Mo
(%)	0.37	0.27	0.27	0.21	0.039	0.08	0.03	0.02	0.01

2.4 Weight Loss Measurements

In a double glass cell, gravimetric measurements were conducted. The testing took place in aerated solutions for 6 hours at 25°C. The samples were meticulously cleaned after each test, and then weighed. In each instance, duplicate trials were run, and the average weight reduction was recorded. Losing weight made it possible to calculate the mean corrosion rate in mpy. The corrosion rate (CR) with and without creatinine inhibitor different concentrations in 0.5 M HCl, the inhibitor efficiency (IE%) and inhibitor surface coverage (θ) were calculated as the follows (28):

$$CR \text{ (mpy)} = \left(\frac{534 W}{DAT} \right) \quad (1)$$

$$IE\% = \left(\frac{W_1}{W_2} \right) \times 100 \quad (2)$$

$$\theta = 1 - \left(\frac{W_1}{W_2} \right) \quad (3)$$

Where, 534 is the unit's conversion, W is the mild steel coupon weight (mg), D is the mild steel density (g/cm³), A is the area of the mild steel coupon (in²),

T is the exposer time (hour), W_2 is the weight of mild steel coupon after exposer (mg), W_1 is the weight of mild steel coupon before exposer (mg).

3. Results and Discussion

3.1 Corrosion Rate, Inhibitor Efficiency and Inhibitor Surface Coverage

Table (3) showing the results of the corrosion tests for mild steel coupons in 0.5 M HCl with and without creatinine corrosion inhibitor. According to the results, it can be noticed that the corrosion rate (CR) of the mild steel coupons decreases with gradually increasing the creatinine inhibitor concentration, the maximum (CR) was 241 mpy at the un-treated mild steel coupon, while the minimum (CR) was 23.99 mpy at creatinine inhibitor concentration () 4.420 M. This was the first indication that the creatinine inhibitor which extracted from the bovine urine was effective in protecting the mild steel surface against corrosion. In other hand, the efficiency of the inhibitor (IE%) increases with with gradually increasing the creatinine inhibitor concentration, the maximum (IE%) was about 90% at inhibitor concentration () 4.420 M, while the minimum (IE%) was about 58% at () 0.884 M. The increasing of () from 0.884 M to 4.420 M, causing decreasing in corrosion rate (CR) with about 77% and that's causes increasing in inhibitor efficiency (IE%) with about 35%. The high inhibitor efficiency (IE%) about 90% was another premovement that the creatinine inhibitor is fit in decreasing the corrosion of mild steel materials in HCl medium.

3.2 Adsorption Thermodynamic Parameters

In order to understand the inhibitive process, thermodynamic factors are crucial. It was determined that the free energy of adsorption, ΔG_{ads} , which can describe the interaction between adsorbed molecules and metal surfaces, is equal to $RT \ln (55.5 \times K_{ads})$. Where, K_{ads} is the adsorption equilibrium constant; R is the gas constant ($8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$), T is the absolute temperature in Kelvin, and 55.5 is the water content in solution reported in $\text{mol} \cdot \text{L}^{-1}$ (29). The equilibrium constant of adsorption, K_{ads} , and the free energy of adsorption can be

determined using the following equation (4):
$$K_{\text{ads}} = \frac{\left(\frac{\theta}{1-\theta}\right)}{I_{\text{inh}}} \quad (4)$$

Whether the sorption process follows physisorption or chemisorption is determined by the thermodynamic behaviour of the sorption of inhibitor ions onto adsorbents from aqueous solution. In physisorption, a surface and adsorbate (metal ion) exhibit a weak Van der Waals attraction. Chemisorption, on the other hand, took place when chemical bonds were formed between the surfaces of the solid (adsorbent) and the metal ion. Because it is difficult to get the heavy metal out of the adsorbent in this situation, chemisorption is irreversible (30). Table (4) provides the thermodynamic parameters for the adsorption of creatinine inhibitor on the surface of mild steel material in HCl aqueous media. The stability of the absorbed layer on the electrode surface is ensured by the negative value of ΔG° . In general, the values of ΔG° up to -20 KJ/mol are constant with the electrostatic interaction between the charged molecules and charged metal (physisorption), whereas those negative values higher than -40 KJ/mol involve sharing or transfer of electrons from the inhibitors to the metal surface to form a covalent type of bond (31). The predicted value of ΔG° was discovered to be negative less than -40 KJ. mol⁻¹ based on the experimental data shown in Table (4). Creatinine's values range from -12.499 KJ. mol⁻¹ to -10.930 KJ. mol⁻¹, which shows that a powerful physisorption process is taking place to adsorb the components to the metal surface.

Its significant corrosion IE% is explained by the relatively large and negative free energy value, which shows a strong and spontaneous adsorption of the creatinine components on the metal surface. As a result, physisorption is most likely the basis for the mechanism that will be suggested for the creatinine inhibitor system. In general, the inclusion of hetero atoms, such as N, O, and S atoms with a lone pair of electrons, in the inhibitor molecules may increase the adsorption, causing the inhibitor to become electrostatically adsorbed on the metal surface, producing insoluble stable coatings and reducing metal dissolution (32).

Table (3) Corrosion Rate, Inhibitor Efficiency and Inhibitor Surface Coverage Calculations.

Coupon No.	Weight Before Exposer (W_1) (mg)	Weight After Exposer (W_2) (mg)	Weight Loss (W) (mg)	Area (A) (cm^2)	Corrosion Rate (CR) (mpy)	Inhibitor (Concentration) (I_{inh}) (M)	Inhibitor Efficiency (IE%)	Inhibitor Surface Coverage (θ)
1	12560.32	12524.30	36.02	8.0	241.38	Un-treated	-	-
2	12559.68	12543.37	16.31	8.0	105.00	0.396	58.16	0.5816
3	12561.02	12550.34	10.68	8.0	072.95	0.884	69.78	0.6978
4	12560.63	12551.87	08.87	8.0	055.76	1.768	77.00	0.7700
5	12560.27	12552.50	07.77	8.0	044.16	2.652	81.71	0.8171
6	12559.88	12553.76	06.12	8.0	038.44	3.536	84.07	0.8407
7	12561.22	12557.20	04.02	8.0	023.99	4.420	90.06	0.9006

3.3.1 Introduction

The kind, quantity of active sites on the metal surface, charge density, molecule size, interactions between the metal and the inhibitor, and creation of metallic complexes all affect how effective the inhibition is. Adsorption isotherms provide details on the interactions between metal inhibitors (33). The surface coverage measurements were theoretically fitted into various adsorption isotherms in order to obtain insight into the manner of inhibitor adsorption on carbon steel surfaces, and the values of correlation coefficient (R^2) were utilised to select the best – fit isotherm (33). The most often utilised adsorption isotherms are those of Lungmir, Temkin, Freundlich, Adejo Ekwenchi, El-Awady and etc.

3.3.2 Langmuir Adsorption Isotherm

The Langmuir isotherm compares and measures the adsorptive capacities of various adsorbents and describes gas-solid phase adsorption (34).

$$= \frac{I_{\text{inh}}}{\theta} = \frac{1}{K_{\text{ads}}} + I_{\text{inh}} \quad (5)$$

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The above equation is how the Langmuir isotherm, which represents the relationship between surface coverage and inhibitory concentration of a material, is stated. Figure (2) illustrates a linear relationship between ($\log I_{inh}/\theta$) and ($\log I_{inh}$).

Table (4) Adsorption Parameters for Adsorption of Creatinine on the Mild Steel Surface.

Coupon No.	Surface Coverage (θ)	$\log I_{inh}$ (M)	$\log \frac{I_{inh}}{\theta}$ (M)	$\frac{\theta}{1 - \theta}$	Adsorption Constant (K_{ads}) (mg^{-1})	Adsorption Energy (ΔG°_{ads}) (kJ. mol^{-1})
1	0.5816	- 0.40230	- 0.16693	1.233270	2.790204	- 12.499
2	0.6978	- 0.05355	+ 0.10272	2.309067	2.612067	- 12.336
3	0.7700	0.24748	+ 0.36099	3.347861	1.893587	- 11.539
4	0.8171	0.42357	+ 0.51130	4.467469	1.684566	- 11.249
5	0.8407	0.54851	+ 0.62387	5.277464	1.481186	- 10.930
6	0.9006	0.64542	+ 0.69089	9.060362	2.049856	- 11.735

The parameters of Langmuir isotherm are presented in Table (4). The R^2 value of 0.9994 indicate strong adherence to Langmuir adsorption isotherm (34). The application of Langmuir isotherm to the adsorption of Expired Esomeprazole on surface of mild steel indicated that there is no interaction between the adsorbate and adsorbent (35). Lungmir, Temkin, Frumkin, Freundlich, Adejo Ekwenchi, and El-Awady, etc.

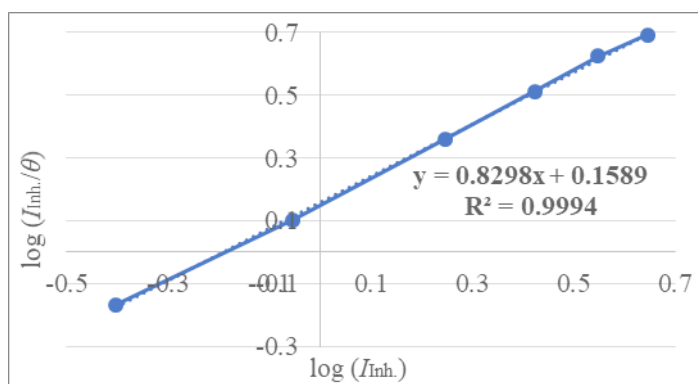


Figure (2) Langmuir Isotherm for Adsorption of Creatinine on the Mild Steel Surface.

3.3.3 Temkin Adsorption Isotherm

This isotherm has a component that explicitly accounts for the interactions between the adsorbent and adsorbate. The model makes the assumption that the heat of adsorption (function of temperature) of all molecules in the layer will drop linearly rather than logarithmically with coverage by disregarding the extremely low and high concentration values (35). According to equation (6), the Temkin adsorption isotherm shows a relationship between inhibitor concentration () and surface coverage (θ) (36):

$$\exp (-2 a \theta)=K_{\text {ads }} I_{\text {inh }} \quad(6)$$

Plots of θ against $\log ()$, as presented in Figure (2). The value is 0.9890. Since the value of 0.9 and it close to unity, that indicating the experimental data is fit well into the Temkin adsorption isotherm (37). The Temkin is a little bit obeying comparing with Langmuir adsorption isotherm.

Table (5) Temkin Parameters for Adsorption of Creatinine on the Mild Steel Surface.

Coupon No	Logarithm Surface (θ) Coverage (θ) log		log (θ)
1	-	-	
2	0.23538 -	0.71940 -	0.14303 -
3	0.15627 -	0.43308 -	0.36343 -
4	0.11351 -	0.29870 -	0.52476 -
5	0.08772 -	0.22384 -	0.65006 -
6	0.07536 -	0.18948 -	0.72244 -
7	0.04547 -	0.11037 -	0.95715 -

3.3.4 Frendlich Adsorption Isotherm

The Frendlich adsorption isotherm model has been selected as the third option for assessing the adsorbant solution’s adsorption potential. The

following equation (7) yields the Freundlich isotherm (38):

$$\log \theta + \log n \log \quad (7)$$

Where, n is the parameter for the interaction. Table (5) displays the Freundlich isotherm's parameters. Figure (3)'s plot of $\log (\theta)$ vs. $\log$ reveals a linear relationship with a R^2 value of 0.9861, demonstrating that adsorption of creatinine on the mild steel outer surface is highly compatible with the Freundlich isotherm adsorption model, since R^2 value is > 0.90 .

3.3.5 Adejo Ekwenchi Adsorption Isotherm

The Adejo Ekwenchi isotherm establishes an inverse relationship between the amount of adsorbate uptake from the bulk concentration and the difference between the total amount of surface area on the adsorbent surface and the fraction that is covered by the adsorbate at a specific temperature, prior to reaching the maximum value of surface cover (39).

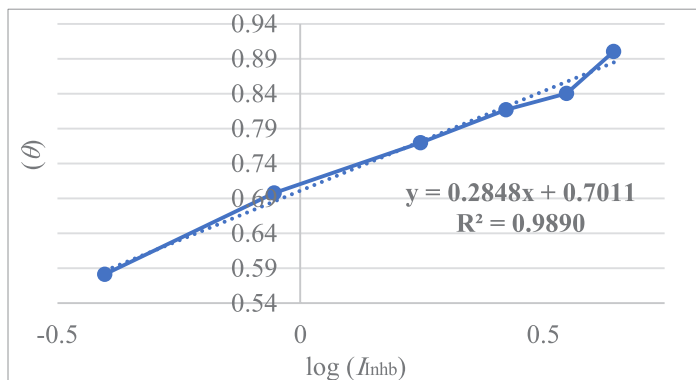


Figure (3) Temkin Isotherm for Adsorption of Creatinine on the Mild Steel Surface.

It is given by the equation: $\log (1/(1 - \theta)) = \log K_{ads} + b \log I_{inh}$. (7)

The mechanism of adsorption of an inhibitor on the metal surface is identified by the b parameter in this case. Table (5) displays the Adejo Ekwenchi isotherm's parameters. A plot of $\log (1/(1 - \theta))$ vs. $(\log)$ as shown

in Figure (5) which gives a linear relation with value 0.9510 which indicated that the adsorption of creatinine inhibitor on the outer surface of mild steel is highly obeying to the Adejo Ekwenchi isotherm model.

3.3.6 El-Awady Adsorption Isotherm

The El-Awady adsorption isotherm model was fitted to the experimental data. The equation (8) below represents the model’s characteristic (39):

log (θ /1- θ) = logK_{ads} + y logI_{inh} . (8)

Where, y represents the number of active sites. If the 1/y is less than one indicates multilayer adsorption, if 1/y greater than one implies inhibitor occupies more than one active site. El-Awady isotherm parameters are given in Table (4). A plot of log (θ /1- θ) vs. (log).

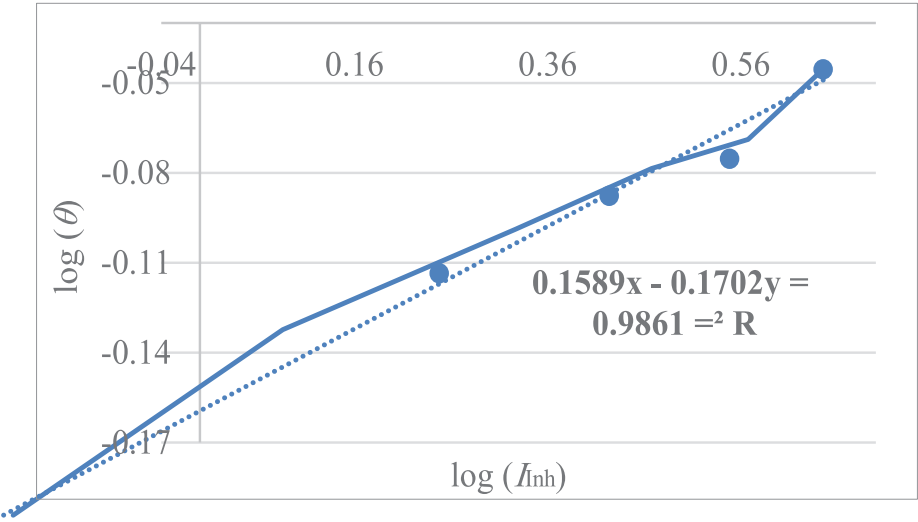


Figure (4) gives a linear relation with value 0.9320 which indicated that the adsorption of creatinine inhibitor on the mild steel surface is highly obeying to El-Awady adsorption isotherm model.

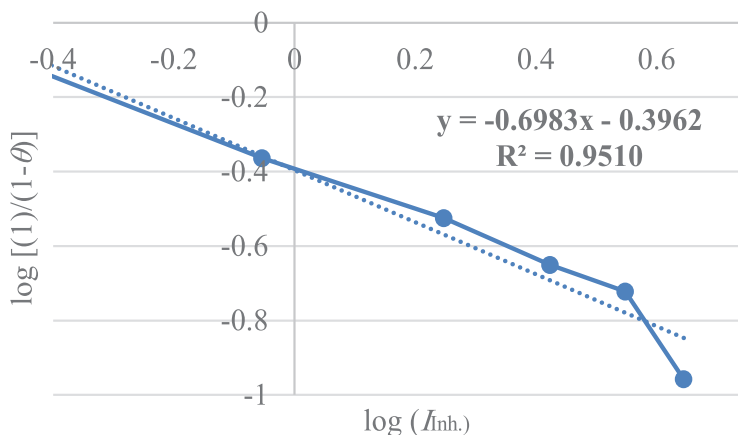


Figure (5) Adejo Ekwenchi Isotherm for Adsorption of Creatinine on the Mild Steel Surface.

4. Conclusions

In this paper, regards the environmental pollution of the bovine urine, an investigation of the corrosion inhibition of creatinine compound which extracted from the bovine urine was carried out on the surface of mild steel in HCl aqueous solution at 25 °C, the corrosion rate of the different creatinine inhibitor concentration was evaluated using the weight loss method. The results reveal that the corrosion rate decreases with increasing the inhibitor concentration, the maximum inhibitor efficiency was found about 90%. In order to investigate the mechanism of creatinine inhibitor adsorption on the surface of mild steel, the adsorption thermodynamic parameters including the free adsorption energies were calculated, the results showed that the mechanism was spontaneous and physisorption. Five adsorption isotherm models were studied. The adsorption data fitted into Langmuir, Temkin, Freundlich, Adejo Ekwenchi and El-Awady isotherms out of which Langmuir Adsorption model was found to be have the highest regression value and hence the best fit. It could be concluded that creatinine extracted from the bovine urine is a potential and active biosorbent for inhibition of the mild steel corrosion in HCl medium.

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