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Unification of the Quadratic Model Equations of the Inhibition Characteristics of Acidified Ocimum Basilicum on the Corrosion Behaviour of Mild Steel

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ABSTRACT

An attempt has been made at unifying the resulting quadratic models from the study of the correlation behavior of the inhibition characteristics of acidified ocimum basilicum on conventional mild steel. Weight-loss corrosion technique was employed in obtaining the corrosion penetration rate using the equation: $cpr = \dfrac{87.6\Delta w}{\rho At}$. Subsequently, the quadratic models were developed by using a computer-aided statistical modeling technique (International Business Machine (IBM)'s SPSS version 17.0). The results obtained showed a nearly perfect positive correlation with a correlation coefficient in the range of $0.986 \leq R \leq 0.996$ which depicts that $R \geq 1$. Also, the coefficient of determination fell within the range of $0.972 \leq R^2 \leq 0.992$ showing that approximately 97% to 99% of the total variation in passivation rate was accounted for by corresponding variation in exposure time, leaving out only between 3% and 1% to extraneous factors that are not incorporated into the model equations. The equations were further unified into a generalized form using MathCAD 7.0 and the resulting equation was $y = 1.032 - 0.002t + 1.899 \times 10^{-6} t^2$ with a R^2 value of 0.935 indicating a well-correlated relationship. With this, a new frontier on corrosion studies has emerged typifying a classical departure from previously long-held assumption that corrosion behaviours at room temperature were only logarithmic.

Keywords: Corrosion; Inhibition; Ocimum Basilicum; Correlation; Quadratic Models; Passivation

1. Introduction

Corrosion has been defined from the individual perspectives of several authors. However, most authors insist that the definition of corrosion should be restricted to metals. More often than not, though, corrosion engineers must consider both metals and nonmetals for solution of a given problem. Accordingly, polymers (plastics, rubbers, etc.), ceramics (concrete, brick, etc.) or composites (mechanical mixtures of two or more materials with different properties) and other nonmetallic materials are generally included as materials that can corrode [1].

Reference [2] defined corrosion as the environmentally induced degradation of a material that involves a chemical reaction. Degradation implies deterioration of physical properties of the material. This can be a weakening of the material due to a loss of cross-sectional area;

it can be the shattering of a metal due to hydrogen embrittlement; or it can be the cracking of a polymer due to sunlight exposure.

The deleterious effects of corrosion are well-known and include among others: poor outward appearance of material surfaces, high maintenance and operating costs, frequent plant shutdowns, contamination of end products, loss of valuable products, hazardous effects on safety and reliability and burdensome product liabilities. As a result of these, huge financial losses have always been recorded annually as resulting from corrosion damage. As an instance, in 1998 alone, the United States reported an estimate of the cost of corrosion to be around $276 billion: a figure that is however realistically put at $30 billion [1]. In fact, [3] has gone further to project that this figure would reach $993 billion by March 2013, with a still

further increase to $1 trillion by June of the same year.

It is against this backdrop of financial losses that corrosion engineers over the years have had to rely on the concept of materials selection and economics to mitigate corrosion. However, even with the proper selection of base metals and well-designed systems or structures, there is no absolute way to eliminate all corrosion. Therefore, corrosion protection methods are used to additionally mitigate and control the effects of corrosion. Corrosion protection can be in a number of different forms or strategies with perhaps multiple methods applied in severe environments [4]. The various forms of corrosion protection include among others the use of inhibitors, surface treatments, coatings and sealants, cathodic protection and anodic protection.

In recent times, however, the hazardous consequences of the somewhat traditional or conventional methods of corrosion control, has made it imperative to source for cost-effective and environmentally-friendly corrosion control measures to eliminate or at least reduce these effects. In this respect, the use of natural plants as corrosion inhibitors has expectedly become the current frontiers of most research activities in corrosion engineering. Inhibitors are chemicals that react with the surface of a material decreasing the material's corrosion rate, or that interact with the operating environment to reduce its corrosivity [4]. They can be added into the corrosion medium as solutions or dispersions to form a protective film, or as additives in coating products, or further still into waters used for washing vehicle, system or component. When added, they interact with the metal, thus slowing the corrosion process by shifting the corrosion potential of the metal's surface toward either the cathodic or anodic end; preventing permeation of ions into the metal; or increasing the electrical resistance of the surface [4].

Africa, and particularly Nigeria, with her favourable tropical climatic conditions is home to a vast number of natural plants that are continuously been investigated as profitable alternatives to synthetic inhibitors because of their inherent advantages amongst which are their ready availability, biodegradability, non-toxicity, non-pollutancy and eco-friendliness [5,6]. It is on the strength of these that ocimum basilicum was chosen for this work.

Ocimum basilicum is itself a vegetable plant believed to be of Indian origin [7-9]. It belongs to a popular plant species called basil. There are several varieties of basil in existence, some of which have been used in previous works [10-13]. However, basilicum species have not been investigated previously in relation to mild steel to the best of the authors' knowledge.

Reference [14] used statistical tools (particularly regression analysis) as a novel approach in corrosion studies. Since then, several other works have been done to develop models for predicting the corrosion behavior of engineering materials using specific parameters [15-18]. The findings from these works show that corrosion profiles correlated better in the quadratic models than the logarithmic models at room temperatures.

This work therefore is an attempt to reinforce the findings of [14] with regards to the regression behavior of corrosion rates at room temperatures; and then unifying the resultant regression equations into a single model equation that would satisfy the conditions as a framework for futuristic corrosion predictions particularly during design considerations.

2. Experimental Techniques

2.1. Materials/Equipment

The materials and equipment used for the work include 10mm diameter mild steel rods sourced from a local steel stockiest in Enugu, Nigeria, beakers, digital weighing balance, tetraoxosulphate (VI) acid, leaves of ocimum basilicum, acetone, nylon strings, emery cloth, distilled water, hacksaw, vernier caliper, measuring cylinder, and volumetric flask.

2.2. Materials Preparation

The mild steel rods were cut to sizes, each averaging 94.5 cm^2 in surface area. They were thoroughly brushed with emery cloth to reveal the metal surface. Thereafter, they were washed with distilled water and rinsed with acetone.

The tetraoxosulphate (VI) acid was prepared to 0.5 M and 1.0 M concentrations using standard procedures.

The ocimum basilicum leaves were washed with cold tap water, dried under room temperature after which they were subjected to soxhlet extraction process in ethanol for about 80 hours to obtain the extract.

2.3. Experimentation

The mild steel coupons were tied with nylon strings and then suspended in beakers containing the acid and the acidified extracts. Each beaker contained 5 coupons and the entire set up were allowed to stand for 30 days. After 6 days a coupon was withdrawn from each beaker, rinsed in distilled water and swabbed in acetone. Thereafter, they were weighed for weight loss determination and corrosion rate calculation using the formula:

$$cpr = \frac{87.6\Delta w}{\rho At}.$$

The pH value of the ocimum basilicum extract was evaluated and noted.

2.4. Unification of the Model Equations

Using MathCAD 7.0, the model equations were plotted

and the best line of fits was taken. The equation corresponding to this line was then noted with all of its necessary parameters.

3. Results

Tables 1-6 show the corrosion penetration rate values obtained from weight loss measurements; while **Figures 1** and **2** are the quadratic model fits from regression analysis of the corrosion penetration rates. Table 8 is the quadratic model equations obtained from the regression analysis.

4. Discussion

4.1. Corrosion Trends

Looking at **Tables 1-6**, the corrosion rates obtained depict those of passivating metals: beginning with an initial steep rise, peaking at a maximum and then subsequently decreasing as exposure time increased. On interaction with the corrosion medium, the metal surface normally reacts swiftly with it, forming an oxide film that coats the entire surface acting as a barrier, thereby preventing further reactions [19].

Table 1. Corrosion penetration rates of mild steel sample in 0.5 m H_2SO_4.

Exposure time (hrs)	Initial weight (g)	Final weight (g)	Weight loss (g)	Corrosion rate (mm/yr)
144	26.76	20.46	6.30	0.5178
288	26.34	19.59	6.75	0.2774
432	26.87	19.77	7.10	0.1945
576	26.51	19.00	7.51	0.1543
720	27.01	15.93	11.11	0.1826

Table 2. Corrosion penetration rates of mild steel sample in 0.5 m H_2SO_4 with 25 cm³ of ocimum basilicum.

Exposure time (hrs)	Initial weight (g)	Final weight (g)	Weight loss (g)	Corrosion rate (mm/yr)
144	25.14	19.04	6.10	0.5013
288	28.82	22.29	6.53	0.2683
432	28.36	21.80	6.56	0.1767
576	27.61	20.67	6.94	0.1422
720	26.90	17.80	9.10	0.1596

Table 3. Corrosion penetration rates of mild steel sample in 0.5 m H_2SO_4 with 50 cm³ of ocimum basilicum.

Exposure time (hrs)	Initial weight (g)	Final weight (g)	Weight loss (g)	Corrosion rate (mm/yr)
144	28.02	22.46	5.56	0.4560
288	27.24	21.05	6.19	0.2544
432	27.93	21.63	6.30	0.1745
576	27.41	20.36	7.08	0.1444
720	27.38	17.38	10.00	0.1454

Table 4. Corrosion penetration rates of mild steel sample in 1.0 m H_2SO_4.

Exposure time (hrs)	Initial weight (g)	Final weight (g)	Weight loss (g)	Corrosion rate (mm/yr)
144	25.70	14.84	10.86	0.8926
288	25.64	12.69	12.95	0.5322
432	25.50	12.35	13.15	0.3603
576	24.47	9.82	14.65	0.2900
720	26.63	10.63	16.00	0.2630

Table 5. Corrosion penetration rates of mild steel sample in 1.0 m H_2SO_4 with 25 cm³ of ocimum basilicum.

Exposure time (hrs)	Initial weight (g)	Final weight (g)	Weight loss (g)	Corrosion rate (mm/yr)
144	26.58	17.03	9.55	0.7849
288	26.40	16.36	10.04	0.4126
432	26.81	15.53	11.28	0.3090
576	24.80	12.69	12.11	0.2488
720	25.10	6.08	17.02	0.2305

Table 6. Corrosion penetration rates of mild steel sample in 1.0 m H_2SO_4 with 50 cm^3 of ocimum basilicum.

Exposure time (hrs)	Initial weight (g)	Final weight (g)	Weight loss (g)	Corrosion rate (mm/yr)
144	27.71	18.42	9.29	0.7635
288	27.22	16.85	10.37	0.4261
432	26.86	15.29	11.57	0.3170
576	25.19	12.97	12.22	0.2318
720	24.73	10.63	14.10	0.2511

$$0.793 - 0.002 \cdot x + 1.998 \cdot 10^{-6} \cdot x^2$$

$$0.771 - 0.002 \cdot x + 1.922 \cdot 10^{-6} \cdot x^2$$

$$0.682 - 0.002 \cdot x + 1.567 \cdot 10^{-6} \cdot x^2$$

$$1.302 - 0.003 \cdot x + 2.647 \cdot 10^{-6} \cdot x^2$$

$$1.155 - 0.003 \cdot x + 2.588 \cdot 10^{-6} \cdot x^2$$

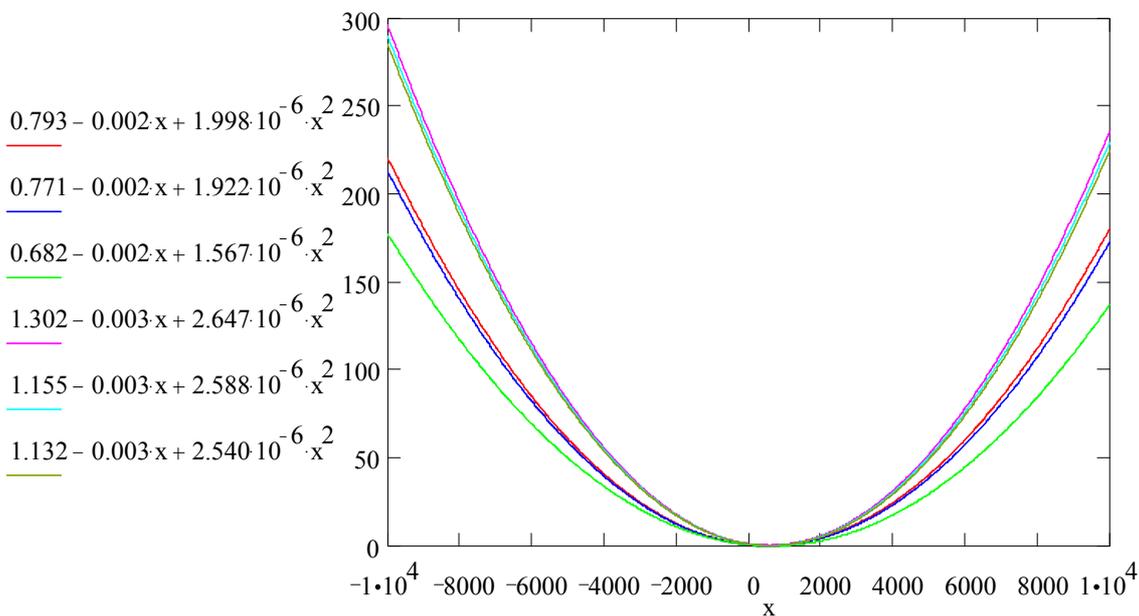$$1.132 - 0.003 \cdot x + 2.540 \cdot 10^{-6} \cdot x^2$$

Figure 1. Graphical plots of the quadratic model equations using mathcad 7.0.
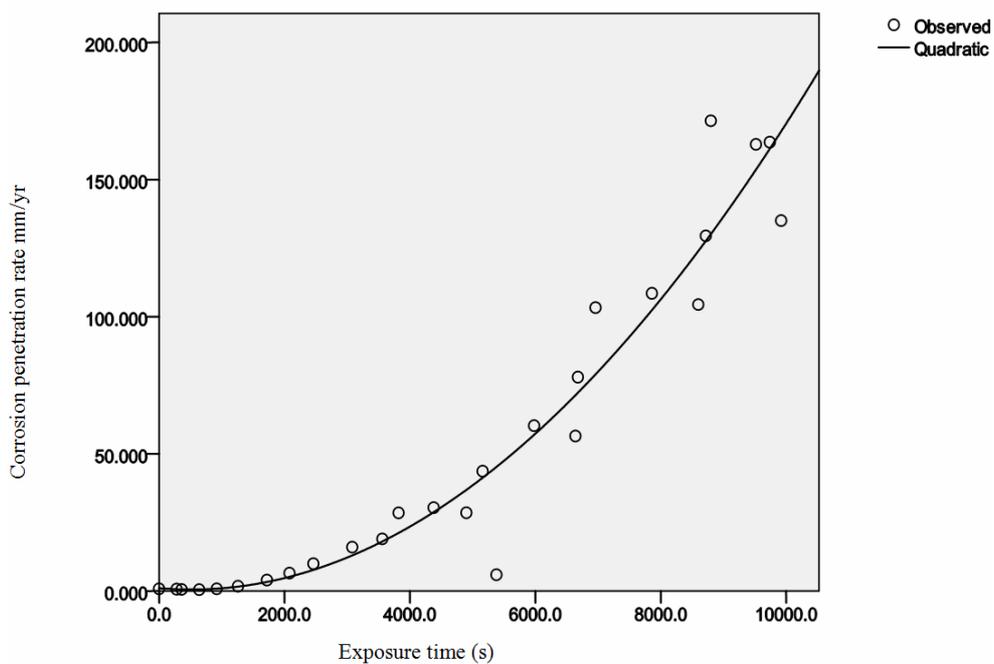

Figure 2. Line of best fits from the model equations.

4.2. Model Summary

From **Table 7**, it can be seen that R (coefficient of correlation) values ranged from 0.986 to 0.996 showing that $R \geq 1$, which is a near-perfect correlation; while the R^2 (coefficient of determination) values ranged from 0.972 to 0.992, implying that approximately between 97% to 99% of the entire variation in passivation rate is dependent on exposure time, leaving only a maximum of 3% to extraneous sources such as errors of measurements, experimental procedures and test locations.

Also, the standard error of estimation fell between 0.021 - 0.054 which is significantly less than 0.1. The implication of this very narrow error margin is that the use of quadratic models to characterize corrosion rates at room temperature is justifiable and therefore could be employed. That being the case, a classical departure from the long-held assumptions that corrosion rate behaviours are only logarithmic at room temperatures has been established.

These claims are corroborated by the line patterns of **Figure 1** where the lines of best fits agree with the near perfectness of the correlation data obtained.

4.3. Model Equations

From **Table 8**, the model fit equations show that each had a non-negligible quadratic element that must be accounted for during corrosion rate evaluation. Since time and media are critical considerations in corrosion monitoring, for a given medium therefore the exposure time becomes the overriding factor for corrosion progression, hence our time-dependent quadratic models subsist in this present study.

Furthermore, looking at the equations in the order in which they appeared, both the constant term and the coefficient of t^2 decreased as the volume of the extracts increased in each of the acid molarities. This confirms further that inhibition has taken place and that an increase in the inhibitor concentration caused a decrease in corrosion penetration rate.

4.4. Unified Model Equation

From **Figure 2** we see the best line of fits from the plots of all the model equations represented in **Table 8** and as plotted in **Figure 1**. The model parameters in **Table 9** clearly show that the coefficient of determination, R^2 of 0.935 is very high indicating in similar manner that about 94% of the determining factors are dependent on exposure time of the corrosion process, whilst 6% is accounted for by extraneous factors which in this case may include errors of mathematical measurements and evaluations. Based on the foregoing, the unified model equation

$$cpr = 1.032 - 0.002t + 1.899 \times 10^{-6} t^2$$

is adjudged a suitable and correct corrosion predictor for the present study.

Table 7. Model equations of the various quadratic fits.

Corrosion medium	Model equations
0.5 M H_2SO_4 only	$0.793 - 0.002t + 1.998 \times 10^{-6} t^2$
0.5 M H_2SO_4 + 25 cm^3 ocimum basilicum	$0.771 - 0.002t + 1.922 \times 10^{-6} t^2$
0.5 M H_2SO_4 + 50 cm^3 ocimum basilicum	$0.682 - 0.002t + 1.567 \times 10^{-6} t^2$
1.0M H_2SO_4 only	$1.302 - 0.003t + 2.647 \times 10^{-6} t^2$
1.0 M H_2SO_4 + 25 cm^3 ocimum basilicum	$1.155 - 0.003t + 2.588 \times 10^{-6} t^2$
1.0 M H_2SO_4 + 50 cm^3 ocimum basilicum	$1.132 - 0.003t + 2.540 \times 10^{-6} t^2$

Table 8. Model parameters.

Corrosion Medium	Parameters			
	R	R^2	Adjusted R^2	Standard Error of Estimation
0.5M H_2SO_4	0.994	0.988	0.976	0.023
0.5 M H_2SO_4 + 25 cm^3 Ocimum basilicum	0.995	0.990	0.980	0.021
0.5 M H_2SO_4 + 50 cm^3 Ocimum basilicum	0.994	0.988	0.975	0.021
1.0M H_2SO_4	0.996	0.992	0.984	0.033
1.0 M H_2SO_4 + 25 cm^3 Ocimum basilicum	0.986	0.972	0.944	0.054
1.0 M H_2SO_4 + 50 cm^3 Ocimum basilicum	0.993	0.986	0.972	0.037

Table 9. Model summary and parameter estimates of the unified equation.

	Model Summary					Parameter Estimates		
Equation	R Square	F	df1	df2	Sig.	Constant	b1	b2
Quadratic	0.935	171.551	2	24	0.000	1.032	−0.002	1.889E-6

Dependent Variable: Y

The independent variable is T.

Regression Equation: $y = 1.032 - 0.002t + 1.899 \times 10^{-6} t^2$.

5. Conclusion

The conclusion that can be drawn from the foregoing discussions is that ocimum basilicum is a good corrosion inhibitor since its pH value of 6.7 falls within the region in which passivation occurs in the Poubaix diagram [20]. Again the quadratic model which fits each with a nearly perfect correlation suggest in strong terms that room temperature corrosion progression can no longer be said to be only logarithmic but also has a significant quadratic part that must be accounted for during corrosion characterizations. Additionally, the unification of the model equations into a single generalized form also shows that it is henceforth possible and accurately so, to use the equation to make futuristic computations of corrosion penetration rates for engineering mild steel in acidic environments with ocimum basilicum serving as a veritable inhibitor.

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