

Central Composite Design Foroptimizing Katemfe Seed Extracts as Green Inhibitor on Galvanized Steel in 0.5 M HCL Acidic Media

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Abstract: The effect of Katemfe Seed Extract as inhibitor for Galvanized steel in 1M HCl acidic media was investigated in this study. The combination of the concentration of inhibitor (0.2-1.0 g L⁻¹), time (1-5 h) and temperature (30) on corrosion rate was investigated using optimization. The optimum conditions obtained were temperature 54.55; time 2.28 h and inhibitor concentration of 0.20 g L⁻¹. The obtained optimal value of 85.9% predicted agreed closely with the 86.5% obtained from the experiment. The micrographs result of Scanning Electron Micrographs analysis showed that the passive layer of film was formed on the surface. This study showed that Katemfe seed extract is a good inhibitor for Galvanized steel in 0.5 M HCl.

Key words: Corrosion, inhibitor, katemfe seed extract, response surface methodology (RSM), weight loss

INTRODUCTION

The investigation of metallic corrosion is a subject of immense conceptual and practical concern and has thus received a substantial amount of interest. Furthermore, oil well acidizing operations, industrial acid cleaning, pickling, descaling and acid solutions are widely employed on metal substrates to achieve the intended purpose (Ajayi *et al.*, 2011). It is thus essential that these metallic structures are protected. The cost implication of corrosion has not yet been surveyed in Nigeria; however, the Central Intelligence Agency, stated that it was estimated at 3.2 billion USD annually (Omosho, 2016). He stated that the increase in corrosion control measures is required in every area of human life and industry. Several means are available for preventing or protecting metallic structures in service. The major methods for combating corrosion of metals are: Materials selection, coatings, cathodic/anodic protection and use of corrosion inhibitors has grown in popularity over the years. There exist two major types of inhibitors; which are organic and inorganic/chemical inhibitors. The inorganic inhibitors contaminate the environment after use and cause a lot of

problems like the disposal and destruction of plant and animal life. Restrictions have been on the use of chemical inhibitors because of their toxicity. Furthermore, according to Rani and Basu, (2012), research had been tailored to the use of plants being environmentally friendly. However, extracts of plants also known as green inhibitors on metals in various acidic media. Mango bark and leaves extract (Loto, 2001); Spirulina platensis (Kamal and Sethiraman, 2012); Cola Acuminata and Camellia Sinensis (Loto *et al.*, 2013), Neolamarckiacadamba alkaloids (Raja *et al.*, 2013), Vernonia Amygdalina (Loto *et al.*, 2013), Litchi Chinensis peels, Jatropha stem (Olamide *et al.*, 2016), Orange peels extract, Orange Seed (Olawale *et al.*, 2018), Groundnut husk (Olawale *et al.*, 2018), Pterolobiumhexapetalum and Celosia argentea plant extracts (Kumar and Mohana, 2013), leaves and stem extracts of Sidaacuta (Eduok *et al.*, 2012) had been worked on as inhibitors. The Katemfe leave is diagonal in shape and has a dark red/brown colour when matured. Itsfruit contains three black, extremely hard seeds. The seeds are covered with a sticky thin, pale yellow basal aril which contains the sweetening protein,

thaumatin. Katemfe leaves are used as covering for: Beans pudding (moi-moi); beans (adalu), locust beans (iru), ofada rice (Wiersema and Leon, 1999). Katemfeseed back extract as an eco-friendly corrosion inhibitor for Galvanized steel in 0.5 M HCl solution was investigated in this research.

MATERIALS AND METHODS

Materials: Materials used for the study was Galvanized Steel Coupons and Katemfe seed back Extract which was collected from Ekiti State, Nigeria.

Experimental design and data analysis: The Design Expert Software (version 8.0.7.1) was used for the statistical design of experiments and data analysis. In this study, Central Composite Design (CCD) and RSM was applied to optimize the three operating variables which were; Time (3-5 days), Concentration of Kafemfe extract (0.2-1.0 g l⁻¹) and Temperature (30-60°C), respectively. The experimental range of the variables is as shown in Table 1; while the Central Composite Design factors and levels is shown in Table 2.

Preparation of metal specimen: Experiments were performed using Galvanized steel coupons. Coupons' surface area of 2×2×2 cm were obtained and hole was drilled in the middle with the 0.2cm diameter to enable

hanging of the coupons in the corrosion media that was prepared. These coupons were further treated to expose shining surface using emery paper. The coupons were then, washed using distilled water and cleansed with acetone and later stored in the desiccator.

Phytochemical analysis: Katemfe Seed Back Extract (KSE) was subjected to phytochemical analysis to determine the bioactive constituents such as tannin; alkaloids, flavonoids and saponin that might be present in it. This was to ascertain the suitability of the KSE as a corrosion inhibitor.

Corrosion medium: The corrosion medium of 0.5 M HCl was used throughout the experiments. Different concentrations of the extracts were prepared to range from 0.2-1.0 g L⁻¹ in the 0.5 M HCl solution.

Weight loss measurements: Weight loss measurements were conducted under total immersion using 250 mL capacity beakers containing the various concentration of test solution at a temperature range of 30-60°C in 100 mL test solutions. Weight loss Experiment was carried out by weighing the specimens before and after immersion in 0.5M HCl in the presence and absence of inhibitor. The experimental readings were determined using the equations:

$$\Delta w_u = W_u - W_i \tag{1}$$

Table 1: Experimental range of the independent variables, with factor levels for the inhibition of KatemefeSeed Extract on Galvanized steel in HCl solution

Independent variables	Range and levels			
	Symbols	-1	0	+1
Time (h)	X ₁	1	3	5
Temperature (°C)	X ₂	30	45	60
Inhibition concentration (g L ⁻¹)	X ₃	0.2	0.6	1.0

Table 2: Showed the central composite design factors and levels

Block 1	Time (h)	Temp (°C)	Conc. Inh (g L ⁻¹)
Block1	5	45	0.6
Block1	3	45	0.6
Block1	1	45	0.6
Block1	5	60	0.6
Block1	3	60	0.2
Block1	5	60	0.6
Block1	5	60	1.0
Block1	3	30	0.2
Block1	1	45	0.6
Block1	3	60	0.2
Block1	5	45	0.2
Block1	3	30	0.2
Block1	3	45	0.6
Block1	3	30	1.0
Block1	1	60	1.0
Block1	3	30	0.6
Block1	5	45	0.6
Block1	3	30	0.6
Block1	3	45	1.0
Block1	3	30	1.0

$$CR = \frac{\Delta W_u - \Delta W_i}{A t} \quad (2)$$

Where:

Δw = The weight loss

W_u = Initial weight

W_i = Final weight

CR = Corrosion rate

Regression model for the corrosion rate: Weight loss and corrosion rate is as shown in Table 4.

The Design Expert Software derived a polynomial quadratic regression equation of the form:

$$Y = B_0 + B_1 X_1 + B_2 X_2 + B_3 X_3 + B_4 X_{12} + B_5 X_2^2 + B_6 X_3^2 + B_7 X_1 X_2 + B_8 X_1 X_3 + B_9 X_2 X_3$$

The model in terms of the coded values of the process parameters is given by:

$$Y = +0.0129.79A + 0.012B5.33C + 3.44A^2 + 3.30B^2 + 8.19C^2 + 8.21AB + 3.61AC - 3.77BC$$

Table 5 presented the analysis of variance (ANOVA). The p-value is less than 0.05, implied that the

RESULTS AND DISCUSSION

Phytochemical analysis: The qualitative analysis result of the Katemfe seed extract was done to investigate the different phytochemical in the seed. The results as shown in Table 3 which showed active organic constituents that made the Katemfe seed extract a good green inhibitor.

Table 3: Phytochemical component result of KSE

Test	Reagent	Color change	Confirmation
Alkaloids	Wager	Brown precipitate (PPT)	+++positive
Tannin	FeCl3	Greenish PPT	++positive
Flavonoid	NaOH+AlCl3+ H2SO4	Yellow PPT	++positive
Saponins	Distilled water	Formed a persistent foam	+++positive
Steroid	Acetic anhydride and 2 mL Conc.H2SO4	Reddish brown	++positive

+++ : Highly present, ++: Moderately present

Table 4: Process variables with weight loss and corrosion rate

Time (h)	Temp (Deg)	Conc (g L ⁻¹)	Intial weight (Wo)	Final weight (Wa)	Weight loss	Corrosion rate $\left(\frac{mg}{cm^2 h}\right)$
5.00	45	0.6	5.50	5.43	0.07	7.50
3.00	45	0	5.34	5.31	0.03	5.80
1.00	45	6	4.97	4.96	0.01	15.00
5.00	50	0.6	4.58	4.52	0.06	24.00
3.00	60	0.6	4.95	4.88	0.07	38.00
5.00	60	0.2	5.20	5.08	0.12	24.00
5.00	60	0.6	5.20	5.12	0.08	19.00
3.00	30	1.0	5.35	5.34	0.01	5.83
1.00	45	0.6	4.76	4.73	0.03	17.50
3.00	60	0.2	4.95	4.88	0.07	38.00
5.00	45	0.2	5.16	5.14	0.02	6.00
3.00	30	0.2	5.35	5.34	0.01	5.83
3.00	45	0.6	5.33	5.30	0.03	6.70
3.00	30	1.0	5.47	5.46	0.01	5.00
1.00	60	1.0	5.01	4.98	0.03	17.50
3.00	30	0.6	4.89	4.87	0.02	2.50
5.00	45	0.6	4.78	4.74	0.04	4.50
3.00	30	0.6	4.89	4.87	0.02	2.50
3.00	45	1.0	4.63	4.61	0.02	5.00
3.00	30	1.0	5.47	5.46	0.01	4.17

Table 5: ANOVA

Source	Sum of squares	DF	Mean square value	F	Prob>F
Model	2.265	9	2.517	88.630	< 0.0001 significant
A	8.732	1	8.732	30.750	0.0002
B	2.640	1	2.640	92.960	<0.0001
C	3.748	1	3.748	13.200	0.0046
A2	1.890	1	1.890	6.660	0.0274
B2	2.857	1	2.857	1.010	0.3395
C2	2.482	1	2.482	8.740	0.0144
AB	8.115	1	8.115	2.860	0.1218
AC	1.041	1	1.041	3.670	0.0845
BC	3.695	1	3.695	13.010	0.0048
Residual	2.84	10		2.840	
Lack of Fit	2.005	2	1.002	9.600	0.0075 significant
Pure Error	8.350	8	1.044		
Cor Total	2.293	19			

Adj R-squared: 0.9765, Pred. R-squared: 0.8623, R-squared: 0.9876

model is significant and that the quadratic model is suitable to analyze the experimental data. The Model F-value of 88.63 implied the model is significant. “Pred R-Squared” of 0.8623; in reasonable agreement with “Adj R-Squared” of 0.9765. The significant model terms from the ANOVA Table were: A B, C, A², C², BC, respectively

Results on 3D surface plots: The 3D curves are shown in Fig. 1-3. Fig 1 showed that corrosion rate decreased with an increase in inhibitor concentration and also increases with an increase in time, Fig. 2; showed that corrosion rate increased with an increase in temperature and also increased with increase with time. Furthermore, Fig. 3; corrosion rate decreases with an increase in inhibitor concentration. This assumed physical adsorption. Figure 4 showed the plot of Residuals

versus normal runs while Fig. 5 showed Normal probability versus studentized residuals. Figure 6 showed predicted versus actual.

Experimental validation: The Optimum conditions predicted with the Design Expert Software were: Inhibitor concentration (0.20 g L⁻¹), Temperature (54.55 °C) and Time (2.88); furthermore, the optimum corrosion rate at this optimum condition was predicted to be 85.9%. Experiment was carried out at these optimum conditions to validate the predicted optimum values. The experimental value of 86.4% agreed closely with the predicted corrosion rate.

Result on surface analysis: The galvanized steel surface immersed in the absence of inhibitor observed

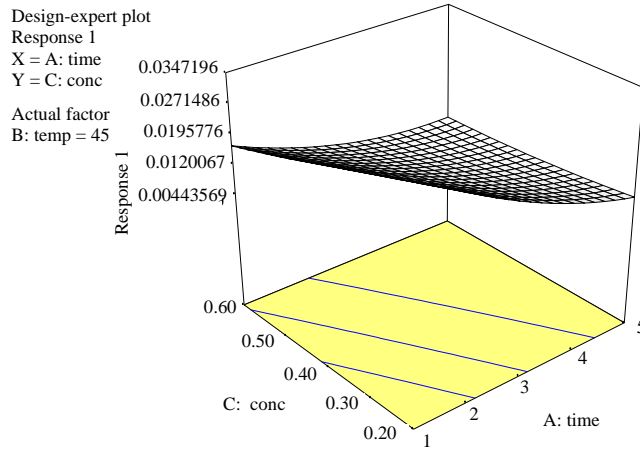


Fig. 1: Effect of time and concentration on

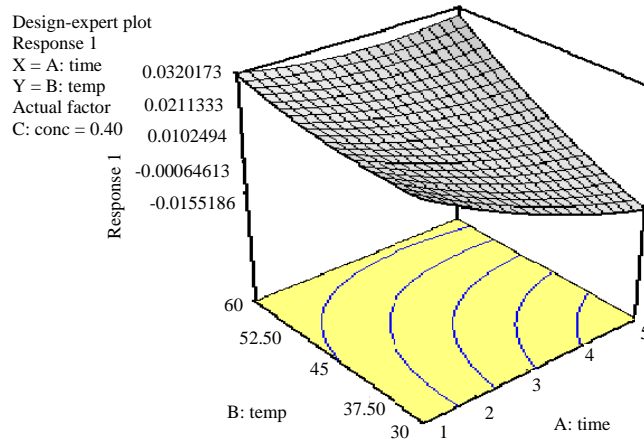


Fig. 2: Effect of time and temperature on corrosion rate corrosion rate

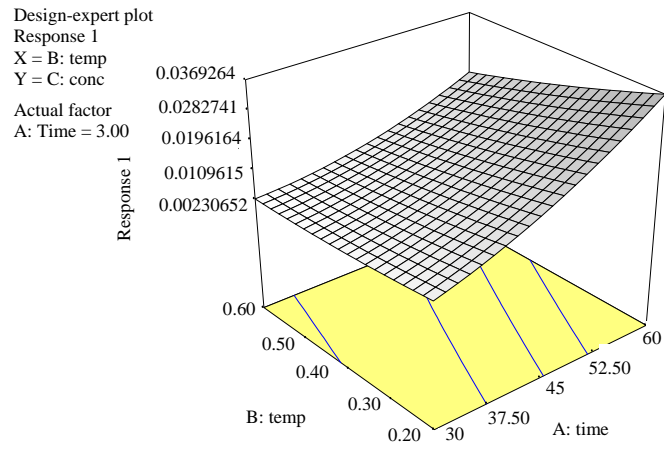


Fig. 3: Effect of temperature and

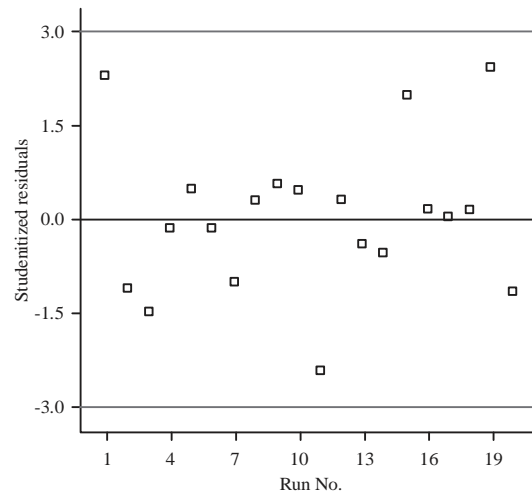


Fig. 4: Residuals vs. run; Residuals vs. run

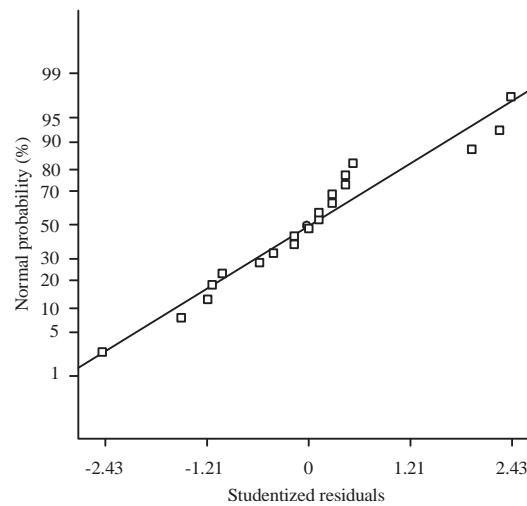


Fig. 5: Normal plot vs. studentized residuals; Normal plot of residuals

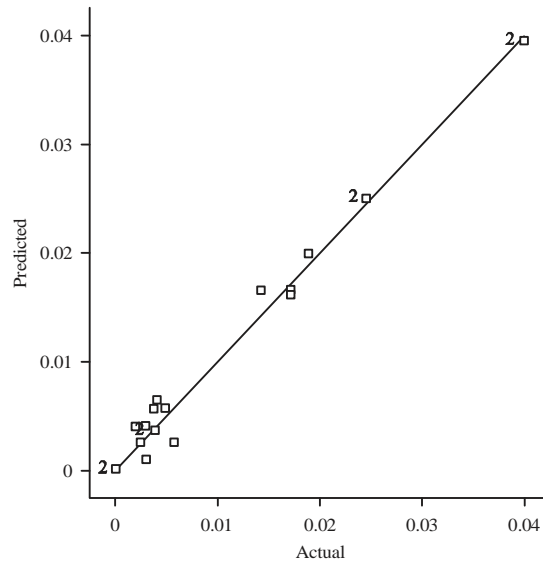


Fig. 6: Plot of predicted vs. actual

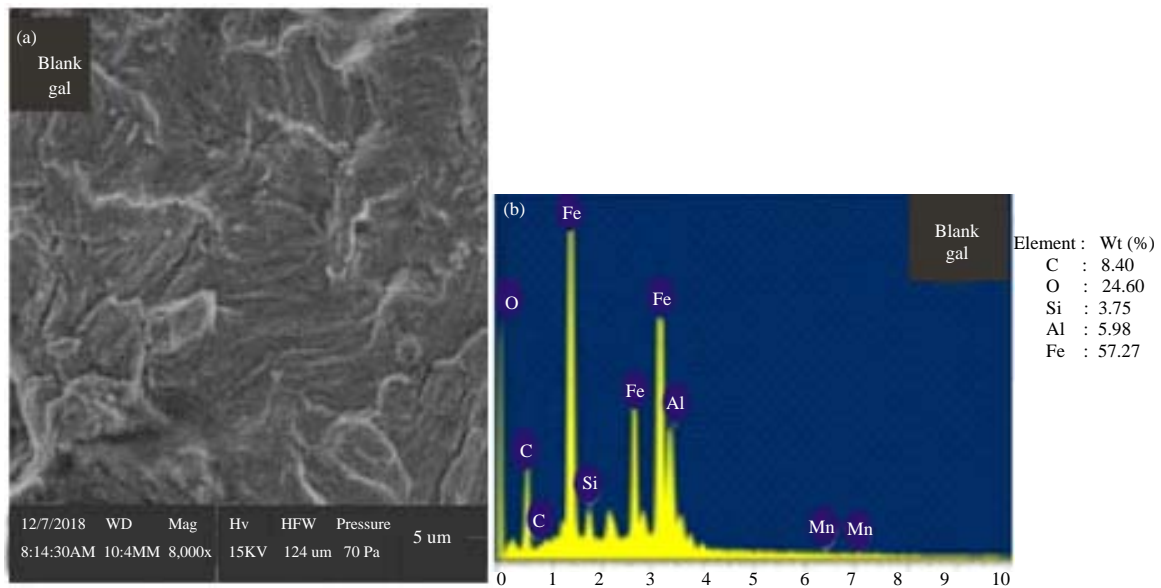


Fig. 7(a-b): (a) SEM and (b) EDX of blank galvanized coupon

clear corrosion pits on the surface. Moreover, the corrosion did not occur on Fig. 9b because it had the lowest corrosion rate as observed from the result obtained from the Design of the experiment. The shield layer is more prominent form the result of the SEM obtained from the predicted optimum level as shown in Fig. 8a.

Mechanism of inhibition: Figure 7a showed the SEM result of the blank coupon and the EDX is as shown in Fig 7b. The protective film formed was due to the

adsorption of the inhibitor constituents on the galvanized steel. Furthermore, Fig 8a, showed more film that were formed due to the optimum predicted level from the software and its EDX is shown in Fig. 8b. The protective film formed on 9a; confirmed what was reported by Olawale *et al.* (2018), that it acted as a barrier which reduces the metal atoms participating in the electrochemical process and consequently increases the corrosion effectiveness. The EDX is as shown in Fig 9b, respectively. The inhibition of the galvanized steel is mainly due to the presence of heteroatoms of organic

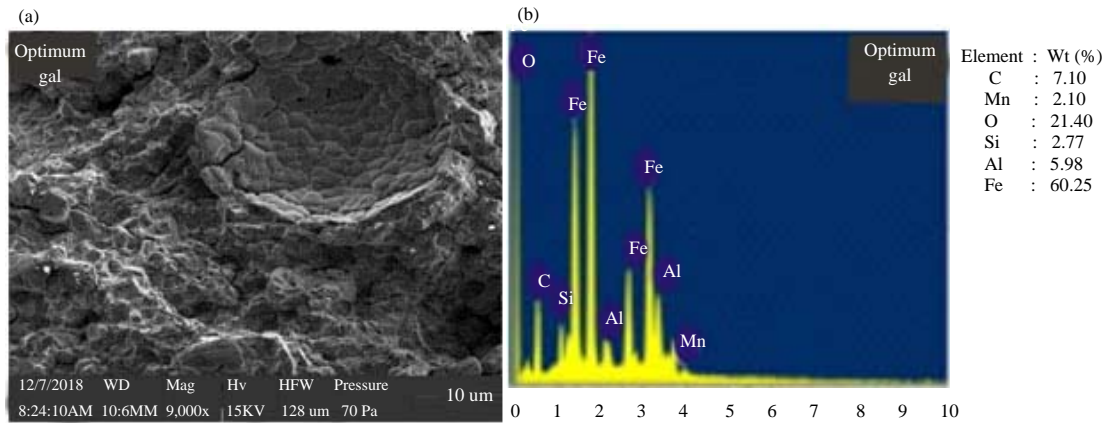


Fig. 8(a-b): (a) SEM and (b) EDX of optimum predicted level

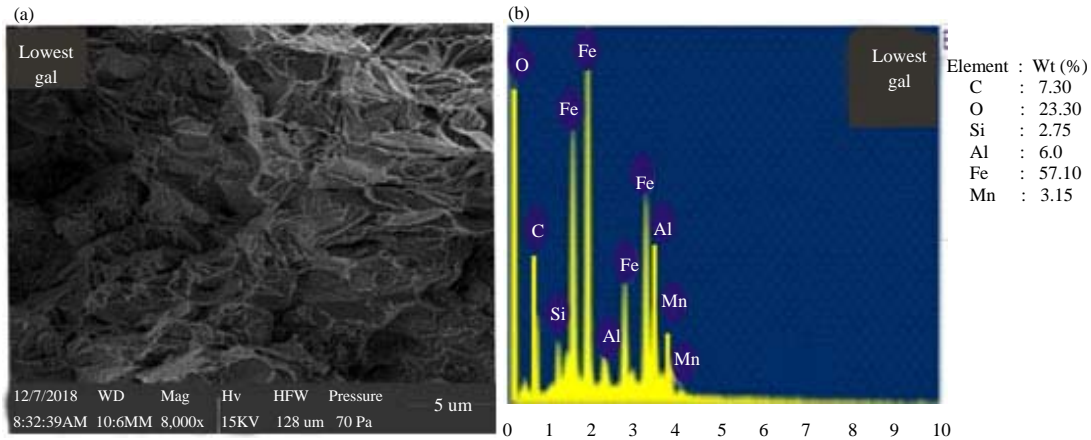


Fig. 9(a-b): (a) SEM and (b) EDX of lowest corrosion rate

chemical constituents of the KSE. The Katemfe seed extract consisted of mixtures of chemical compounds as shown from the results of the phytochemical analysis.

CONCLUSION

Katemfe Seed Extract proved to be a good inhibitor on galvanized steel in 0.5M HCl acidic medium. An optimal operating condition for corrosion rate of 85.9% was observed. The corrosion rate increased as temperature increases. The validity of the model was carried out at the optimal process conditions; time: 2.28 h, temperature: 54.55°C and inhibitor concentration: 0.20 g l⁻¹ to validate the predicted optimum value. The experimental value of 86.4% agreed closely to that getting from the Response Surface Methodology. The inhibitive ability of the Katemfe Seed Extract occurred because of the protective oxide layer formed on the mild steel by adsorption of alkaloids, tannins and steroids.

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