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Investigation Of Mechanism of Inhibition of Corrosion of Mild Steel by Fast Green

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Abstract

This research work investigated the potential of fast green ($C_{37}H_{34}N_2O_{10}S_3Na_2$) as inhibitor of corrosion for mild steel in 1M HCl. Gravimetric method was employed for the studies. The influence of concentration, time of immersion and temperature on corrosion rate were investigated. The corrosion rate was found to decrease from 3.50×10^{-4} to 1.8×10^{-4} g/cm²/h as the concentration of the fast green was increased from 1 to 5 %v/v. The inhibition efficiency (IE %) thus increased from 30 to 65 % within the concentration range (1-5 v/v %) of the inhibitor within 24 h at room temperature (30 °C). The corrosion rate also increased from 2.44×10^{-4} to 9.03×10^{-4} g/cm²/h as the experimental hours was increased from 24 to 120 h for the studies at room temperature. The adsorption studies confirmed that Langmuir isotherm was the best model to explain the adsorption characteristics of fast green on the mild steel, with a correlation efficiency (r^2) of 0.9847. The standard free energy associated with the adsorption, $\Delta G°_{ads}$, was calculated to be -25.78 kJmol^{-1}. The value being up to -20 kJmol^{-1} suggest that the adsorption of fast green molecules on to the mild steel surface is essentially by physisorption. It can concluded that the inhibitor acted as a mixed type inhibitor since the experimental data fit into the Langmuir model, which is characteristics of chemisorption.

Keywords: Corrosion, mild steel, fast green, adsorption, physisorption

INTRODUCTION

Corrosion is a process that occurs when a metal's surface gets damaged due to its interaction with environment (EL-Etre, *et al.*, 2021; Alamry *et al.*, 2023). It has been defined as the deterioration or destruction of metals and alloys in the presence of an environmental species by chemical or electrochemical means (Rafael *et al.,* 2014). Billion dollar losses annually in industries are attributable to corrosion (Ikpi *et al.*, 2017, EL-Etre, *et al.*, (2021). The global loss due to corrosion is about $2.5 trillion, which is near 3.5% of the world's GDP (Gupta *et al*, 2017).

Mild steel is a structural material with numerous uses in the industries. However, it can easily corrode in corrosive atmosphere. It is therefore a necessity to protect this valuable material from corrosion to avoid loss through metal failure.

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Cathodic protection technique and use of inhibitors have been the basic methods of protecting steel structures from corrosion. Cathodic protection is achieved by making a metal to work as a cathode in an electrochemical cell (Sastri, 2014). The approach of using a corrosion inhibitor has been acknowledged as the best methods of controlling corrosion (Ikpi *et al.*, 2017). Corrosion inhibitors are chemicals that efficiently slow the rate of corrosion of metals and alloys when used in relatively low concentrations (Al-Amiery *et al.*, 2022). The inhibitors control the metal dissolution as they form a thin protective layer. Inhibitors also interact with anodic or/and cathodic reaction sites to decrease the oxidation or/and reduction of corrosion reactions (Solomon and Umoren, 2015 and Singh *et al.*, 2016). They are therefore, generally used to reduce the corrosion rate. Most effective inhibitors are heterocyclic compounds that possessed electron donor atoms such as nitrogen, oxygen, sulfur (Al-Amiery *et al.*, 2022). Most of the corrosion inhibitors that have been used successfully are toxic and harmful to the environment (Thakur *et al.*, 2022). The discharge of such corrosion inhibitors into the environment constitute health risk to life. The search for green inhibitors is therefore on the rise.

Many dyes have shown effectiveness in inhibiting corrosion of mild steel. However, the inhibition mechanism by fast green towards mild steel has been rarely cited. Fast green ($C_{37}H_{34}N_2O_{10}S_3Na_2$) is an organic dye and associated with several applications. The molecule possess electro-active nitrogen, oxygen atoms and aromatic rings and large and flat enough to be able to block more surface area of the mild steel (Prabhu *et al.*, 2009). Moreover, it is a green reagent with no reported health concerns. It can therefore be regarded as an ecofriendly inhibitor. This research sought to study the performance of fast green as inhibitor and investigate the mechanism of protection mild steel by the inhibitor.

MATERIAL AND METHODS

Mild Steel Collection

The mild steel specimen was obtained from the Department of Metallurgy, Ahmadu Bello University, Zaria. The mild specimen has a composition of 99.552% iron. It was mechanically cut into strips of dimension 2.0 × 0.27× 1.0 cm and the surface was polished with an emery paper.

Preparation of Test Solution

Analytical grade HCl (37%) was used to prepare 1.0 M HCl solution. A 1-5 % (v/v) solution of the fast green solution were prepared in the 1.0 M HCl solution.

Gravimetric Studies

The effects of the inhibitor concentrations on the corrosion inhibition efficiency was studied by immersion of weighed coupons of the mild steel into five 100 cm^3 beakers containing varying concentration of the inhibitor (1-5 %(v/v)). HCl (1.0 M) solution was used as blank and the experimental time was 24 hours. These experiments were repeated for a time of 48-120 h using 3 % (v/v) of the fast green solution in acid medium and at 40 - 70 °C for a time period of three hours. After each experiment, the specimen were removed and washed extensively with distilled water and then acetone and air dried. The weight loss of the specimen was determined with the aid of an analytical balance. The rate of corrosion (CR), surface coverage (θ), efficiency of inhibition (IE %) and were calculated using equation 1, 2 and 3 respectively.

Corrosion rate, CR (Adejoro *et al*, 2014);

$$CR = \frac{w_o - w_i}{A \times t} \dots\dots\dots\dots\dots\dots..1$$

w_i is weight loss in presence of inhibitor and w_0 is weight loss in absence of inhibitor, A (cm^2) is area of the coupon and t (h) is the time of immersion in hour.

Surface coverage (Eddy *et al*., 2008) ;

$$\theta = \frac{w_o - w_i}{w_o} \dots\dots\dots\dots\dots\dots\dots 2$$

Inhibition efficiency (Al-Amiery *et al*., 2022) ;

$$IE\ (\%) = \frac{w_o - w_i}{w_o} \times 100 \dots\dots\dots\dots..3$$

RESULTS AND DISCUSSION

The Factor of Concentration

Figure 1 shows the plot of concentration versus inhibition efficiency. The uninhibited media (blank) has the highest weight loss and corrosion rate due to absence of inhibitor. However, in the inhibited media, a decrease in weight loss was observed as fast green concentration rises. This suggests that as the number of molecules of fast green available on the steel surface increases, the inhibition activity also increases. The observed increase in surface coverage (θ), efficiency (IE %), concentration of inhibitor per surface coverage (C/θ) and the corrosion rate (CR) (Table 4.1) as the concentration increases agreed with this deductions. Similar observation was reported by Prabhu *et al*. (2009) and Karthik and Sundarayadiyeh, (2015).

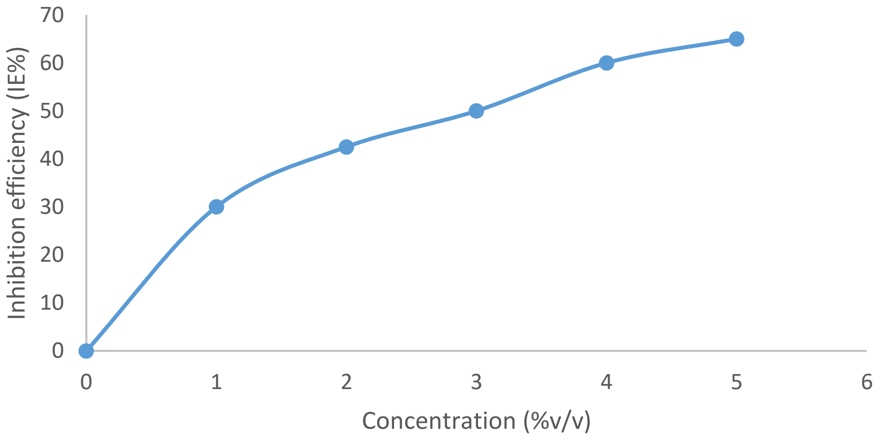

Figure 1: Plot of Inhibition efficiency vs concentration

Table 1: Variation Corrosion Parameters with inhibitor Concentration

Concentration of inhibitor(%v/v)	Surface coverage θ	Inhibition efficiency IE%	Corrosion rate (CR) $g/cm^2/h$
Blank (0)	-	-	5.0×10^{-4}
1	0.3000	30.00	3.5×10^{-4}
2	0.4250	42.50	2.9×10^{-4}
3	0.5000	50.00	2.5×10^{-4}
4	0.6000	60.00	2.0×10^{-4}
5	0.6500	65.00	1.8×10^{-4}

Impart of Time of Immersion on Weight Loss

The weight loss generally increases with time of immersion as shown in Figure 2. This implied the CR increases with material exposure time. This may reasonably be due to decomposition or depletion of fast green molecules with time, thus reducing the number of molecules of fast green available on the surface. The weight loss was generally high in each uninhibited medium than in the inhibited medium. IE (%) therefore decreases with time of immersion. Similar observation was reported by Aribo *et al*. (2017).

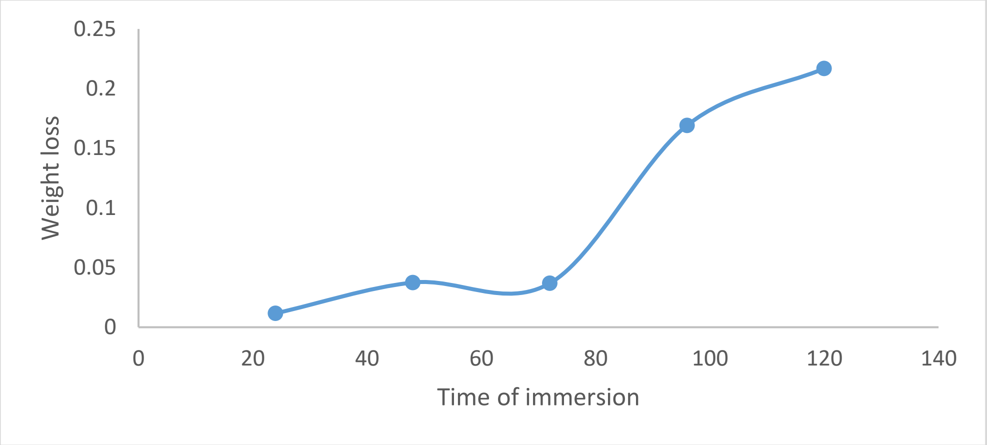

Figure 2: Changes in Weight Loss over Exposure Time

Effect of temperature on inhibition efficiency

Table 2 indicated that the CR and hence IE (%) generally increased with increased temperature. Corrosion rate was least at temperature of 40°C, and highest at 70°C. Maximum inhibition efficiency of 77.05% was observed at 60°C. Above 60°C, the IE% decreases. This observation may be due to the fact that high temperature above 60°C denatured the fast green molecules being an organic compound. Similar observation was reported in literature (Adejoro *et al*., 2014; EL-Hassouni *et al*., 2022**).**

Table 2: Impact of temperature on CR at constant concentration of inhibitor

Temperature ˚C	Coverage (θ)	Efficiency IE (%)	Corrosion rate CR (g/cm²)
40	0.4000	40	0.0008
50	0.5496	54.96	0.0018
60	0.7705	77.05	0.0027
70	0.4756	47.56	0.0048

Mechanism of corrosion inhibition

The nature of interaction of fast green molecules as inhibitor on the corroding surface during corrosion inhibition for mild steel is described in terms of adsorption characteristics of the fast green molecules. The adsorption process according to Langmuir theory, is influenced by the nature and surface charge of the mild steel, the type of aggressive electrolyte/solution and the chemical structure of the inhibitor (Refaey *et al*., 2004). The Langmuir equation is expressed as (Adejoro *et al*, 2014);

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \dots\dots\dots\dots 4$$

A plot of $\frac{C}{\theta}$ vs C is expected is presented in Figure 3. The K_{ads} is the adsorption equilibrium constant, calculated from the intercept of the plot (Table 3).

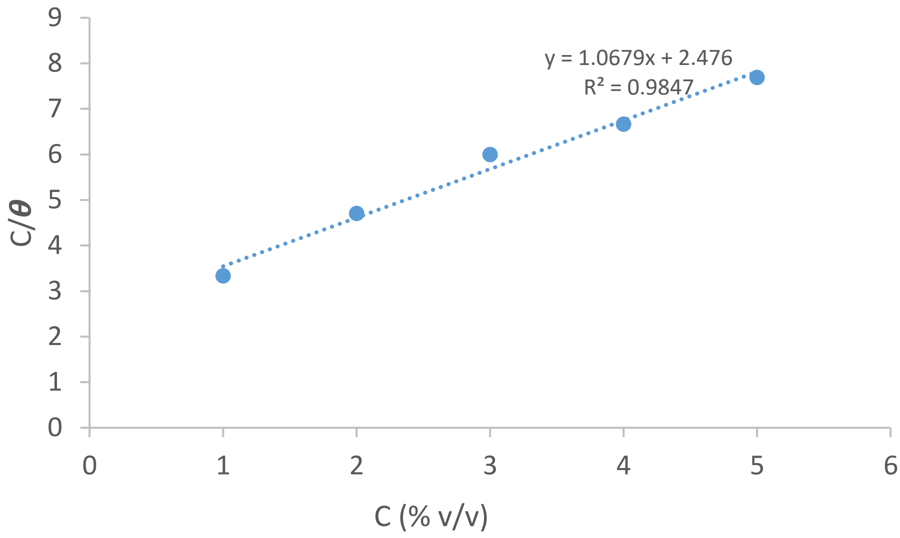

Figure 3: Langmuir adsorption isotherm

The Langmuir isotherm plot shows a linear relationship (Figure 3). The observed correlation coefficient (r^2) is 0.98. This indicated that the adsorption of fast green molecules is characteristic of Langmuir model. Adsorption isotherms are very important in determining the mechanism of corrosion reactions (Eddy *et al*., 2008).

The thermodynamics properties of the adsorption process was studied by investigating the impact of temperature on rate of corrosion. The activation energy, Ea was determined from the expression (Eddy *et al*., 2008);

$$\log\frac{CR_2}{CR_1} = \frac{Ea}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \ldots\ldots\ldots\ldots\ldots..5$$

Where CR_2 and CR_1 are the corrosion rate at temperature T_2 (333 K) and T_1 (313 K) and R is the universal gas constant, given as 8.314472 $JK^{-1}mol^{-1}$.

The heat of adsorption Q_{ads} was determined from the expression (Eddy *et al*., 2008).

$$Qads = 2.303R\log\left[\frac{\theta_2}{1-\theta_2}\right] - \log\left[\frac{\theta_1}{1-\theta_1}\right] \times \frac{T_2 \times T_1}{T_2 - T_1} \ldots\ldots\ldots\ldots\ldots 6$$

Where θ_2 and θ_1 are the surface coverage at absolute temperature T_2 and T_1 respectively. The change in free energy, $\Delta G°_{ads}$ for the adsorption process was determined from the expression (Adejoro *et al*, 2014);

$$\Delta G°_{ads} = 2.303RT\log(55.5\ K_{ads}) \ldots\ldots\ldots\ldots\ldots 7$$

Table 3 shows the activation energy Ea, which is the energy barrier that must be overcome before adsorption can occurs to be relatively high (-47.0680 $kJmol^{-1}$). This is essentially expected for the fact that corrosion process is a very slow process which takes longer time, and thus higher energy.

Table 3: Calculated thermodynamic parameters

Parameters	Ea (kJ/mol)	Q_{ads} (kJ/mol)	$\Delta G°_{ads}$ (kJ/mol)	K_{ads}
Values	-47.0680	70.0629	-25.7775	0.4038

The adsorption equilibrium constant K_{ads}, an indicator of interaction characteristics surface and the molecules of the fast green was 0.4038. The value suggests a weak interaction (physical) between the surface and the molecules of the fast green forming a film of protective monolayer in effecting inhibition of corrosion.

Generally, Q_{ads} for physical adsorption should be below 80 kJ/mol and for chemical adsorption it ranges between 80 and 400 kJ/mol (Lafia *et al*, 2022). The heat of adsorption Q_{ads} was calculated to be 70.0629 kJ/mol. This implies that the adsorption of fast green onto mild steel was by the mechanism of physisorption. The positive value suggests that adsorption process is essentially an endothermic reaction, meaning that heat is required to drive the adsorption process. It is higher than the energy barrier Ea, as expected because corrosion is a slow process and energy required to overcome activation energy (a barrier) must be in excess, otherwise adsorption will not be thermodynamically feasible.

Generally, $\Delta G°_{ads}$, the standard Gibb's free energy of adsorption values for physisorption are in the range of – 20 to 0 kJ/mol, and those for chemisorption range between – 80 and – 400 kJ/mol (Lafia *et al*, 2022). $\Delta G°_{ads}$, obtained in this study was -25.7775 kJ/mol. The value has a negative sign which indicates spontaneous adsorption of molecules of the fast green onto surface of the steel. The value being around -20 $kJmol^{-1}$ suggest that adsorption is by donor-acceptor electrostatic interaction between lone pairs and the donor atoms (N and O) pie electrons of and the aromatic rings of the fast green molecule with the vacant d-orbitals of iron atoms (Fe), thus inhibition is effected predominantly by physisorption process.

CONCLUSION

The results of the experiments show that fast green is an effective corrosion inhibitor for mild steel in 1M HCl. The inhibition efficiency of fast green increased as the concentration of the inhibitor increased. At a concentration of 5%v/v of the fast green, maximum inhibition efficiency of 65% was obtained. The corrosion rate also increased with increasing immersion time and temperature of the environment/medium. The adsorption isotherm showed that the process with which the fast green molecules adsorbed to the surface of mild steel obeys Langmuir adsorption theory. The implication is that there was a monolayer coverage, characteristics of chemisorption. However, the $\Delta G°_{ads}$ was -25.7775 $kJmoi^{-1}$. The negative sign of $\Delta G°_{ads}$ indicates spontaneous adsorption of molecules of fast green on to the surface of mild steel. The value of the free energy suggests that adsorption is by donor-acceptor electrostatic interaction and that inhibition is effected by physisorption mechanism. Evidence therefore abound to show that both chemisorption and physisorption occurred in the processes and the inhibitor acted as a mixed type inhibitor.

REFERENCES

Adejoro I.A, Ojo F.K and Obafemi S.K. (2014). Corrosion Inhibition Potentials of Ampicillin for Mild Steel in Hydrochloric Acid Solution. *Journal of Taibah University for Science.* **9**:196-202.

Al-Amiery A.A, Mohamad A.B, Kadhum A.H, Shaker L.M, Roslam W.N, Isahak W & Takrif.M.S (2022). Experimental and theoretical study on the corrosion inhibition of mild steel by nonanedioic acid derivative in hydrochloric acid solution, *Scientifc Reports* 12:4705.

Alamry K.A, Khan A, Aslam J, Hussein M.A & Aslam R (2023). Corrosion inhibition of mild steel in hydrochloric acid solution by the expired Ampicillin drug. *Scientifc Reports*, 13:6724.

Aribo, S, Olusegun. J.S, Ibhadiyi J.L, Oyetunji A, Folorunso O.D, Green inhibitors for corrosion protection in acidizing oilfield environment, *Journal of the Association of Arab Universities for Basic and Applied Sciences* (2017) 24, 34–38

Ebenso, E. E., Eddy, N. O. and Odiongenyi, A. O, (2008). Corrosion inhibitive properties and adsorption behaviour of ethanol extract of Piper guinensis as a green corrosion inhibitor for mild steel in H_2SO_4. *African Journal of Pure and Applied Chemistry* 2 (11), 107-115.

EL-Etre, A.Y. Seyam, S.M. and .Mady, M.A (2021). Corrosion inhibition of Isosorbidedinitrate drug on Carbon steel in Hydrochloric Acid solution, *Journal of Applied Sciences,(* 6) 2, 205-212.

ELHassouni. H , Elyousfi. A, Benhiba. F. Setti. N, Romane, A.. Benhadda. T, Zarrouk. A, Dafali. (2022). A. Corrosion inhibition, surface adsorption and computational studies of new sustainable and green inhibitor for mild steel in acidic medium, *Inorganic Chemistry Communications,* 143, 109801.

Gupta N.K, Gopal C.S.A, Srivastava V, Quraishi M.A, (2017). Application of expired drugs in corrosion inhibition of mild steel. *International Journal of Pharmaceutical Chemistry and Analysis*, 4(1):8-12.

Ikpi. M. E, Abeng F. E, and Okonkwo B. O. (2017) Experimental and computational study of levofloxacin as corrosion inhibitor for carbon steel in acidic media. *World News of Natural Sciences* 9 (2017) 79-90.

Karthik G and Sundaravadiveh M. (2015). Studies on the Inhibition of Mild Steel in Hydrochloric Acid Solution by Atenolol Drug. *Egyptian Journal of Petroleum. http://dx.doi.org/10.1016/j.ejpe.2015.04.003*

Lafia R, Abdellaoui L, Montasser I, Mabrouka W, Hafianea A (2022). The effect of head group of surfactant on the adsorption of methyl red onto modified coffee residues, *Journal of Molecular Structure,* 1249 (5), 131527

Prabhu, R. A, Venkatesha T.V and Shanbhang A.V (2009). Carmine and Fast green as Corrosion Inhibitors for Mild Steel in Hydrochloric Acid Solution. *J. Iran. Chem. Soc., Vol. 6, No. 2, pp. 353-363.*

Raefey, SAM, Taha F, Abd. El-Malak AM. (2004). Inhibition of Stainless Steel Pitting Corrosion in Acidic Medium by 2- mercaptobenzoxazole. *Appl. Surf. Sci.* 236: 175-185.

Sastri .V.S. (2014). Corrosion Processes and the use of Corrosion Inhibitors in Managing Corrosion in Underground Pipelines. *Underground Pipeline Corrosion: Cathodic Protection and High Efficiency Coating*, pp.127-165.

Singh P, Srivastava V and Quraishi M.A. (2016). Novel Quinoline Derivative as Green Corrosion Inhibitors for Mild Steel in Acidic Medium: electrochemical, SEM, AFM and XPS studies. *Journal of Molecular Liquids,* vol.216, pp. 164-173.

Solomon M.M and Umoren S.A. (2015). Enhanced Corrosion Inhibition Effect of Polypropylene Glycol in the presence of Iodide Ions at Mild Steel/Sulphuric Acid Interface. *Journal of Environmetal Engineering*. Vol.3. no.3, pp. 1812-1826.

Thakur, A, Kaya, S, Abousalem, A.S, Sharma, S, Ganjoo, R, Assad, H, Kumar, A (2022). Computational and experimental studies on the corrosion inhibition performance of an aerial extract of *Cnicus Benedictus* weed on the acidic corrosion of mild steel, 161: 801-818.