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Solvents Effect, Anticorrosion and Adsorptive Binding of Annatto Dye Formulations on Steel Surface

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ABSTRACT

Annatto dye was investigated as a cheap and ecologically friendly alternative steel corrosion inhibitor. Corrosion process was simulated in 1.0 M hydrochloric acid at temperatures between 30°C to 60°C by weight loss and spectroscopic techniques. The dye effectively inhibited the corrosion of mild steel in the acid at temperatures studied. Inhibition efficiency varied with temperature and concentration of the dye. Adsorption models were used to predict the nature of the dye-steel surface interaction. Thermodynamic models provided evidence of spontaneous physical and chemical adsorption mechanism with the evolution of heat. Kinetic studies revealed deepening effect on the activation potential well in the presence of the dye. The effect of solvent and synergistic metal ion intensifiers on the effectiveness of the dye was also assessed. Heavy metal ion composition in the formulation was within the limit of environmental and health safety.

Introduction

Corrosion is a phenomenon that is perhaps as old as when humans started using metallic structural materials. Failure of materials due to corrosion has resulted in spills, increased production costs and down time. To control corrosion, scientists and engineers have used corrosion inhibitors, but high cost and toxicity usually associated with imported chemical inhibitors creates more problems. This has become a driving force for active research on cheap and efficient corrosion inhibitors. Little wonder why a wide range of materials have been tested and reported as corrosion inhibitors [1-2]. Some of these substances reported or currently used for corrosion control are still very expensive or difficult to synthesize. Economically, an inhibitor produced from cheap and readily available materials would be more desirable. On the other hand, non-toxicity to environment in terms of heavy metal composition and biodegradability is also desired. Materials that best fit into these descriptions are locally sourced materials such as plant products. Some plants, including those used for food production, have been reported to possess good inhibitive properties against corrosion of different metals under different conditions [3-21]. As soon as farmers prefer to sell their produce at higher profits to industries for manufacture of corrosion inhibitors instead of food production, food scarcity is inevitable. The paradigm therefore shifted to the use of agricultural wastes and wild (non-edible) plants. In Nigeria, for instance, the transformation of local materials into products useful for industrial application (like corrosion inhibitors) within acceptable limits of health and environmental safety will keep a door to actualization of Nigerian content act of 2010 open.

Annatto (*Bixa orellana* L.), is a fruiting shrub that grows generously up to 5-10 m high as wild plant in southern Nigeria. Some are cultivated by individuals for the purpose of either folk medicine or dye extraction from the seeds, which are covered with reddish aril (Fig. 1). Phytochemical screening of this extract has revealed the presence of tannins, saponins, flavonoids, terpenoids, phenolics, anthraquinones, steroids, proteins and carbohydrates [22]. Bixin and norbixin carotenoids having molecular structures shown in Fig. 2, have been isolated from the dye extract and bixin is claimed to be the active compound in the dye [23-24]. The dye has be used locally in the manufacture of hair oil, shoe polish, floor polishes, nail gloss, furniture lacquer, domestic lipsticks, etc. The paste may also be used as a natural dye for cloth and hair and are sometimes employed in paints industries [25]. Extracts from the fruits and seeds of the plant and their extracts have been used in folk medicine as additives for treatment of malaria, fever, astringent, kidney diseases and skin diseases because of its anti-bacterial and anti-microbial activity [25-26]. The dye is also used as colourants in some foods and beverages due to its characteristic red colour. Since some dyes have been reported to efficiently inhibit corrosion [27-29], this study aims to investigate annatto dye, a natural dye from a cheap, non-toxic and renewable source as a possible replacement to these synthetic dyes used in corrosion inhibitor. It also investigates the effect of solvents on its anti-corrosive effectiveness.

Figure 1. Images of Annatto fruits and seeds.

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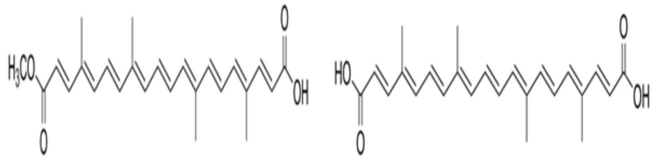


Figure 2. Molecular structures of bixin (Left) and norbixin (Right).

Materials and method

Materials preparation

Mild steel sheets (thickness = 0.46mm) used was of composition (wt. %): 0.13 C, 0.18 Si, 0.39 Mn, 0.60 P, 0.04 S, 0.025 Cu, and bal Fe) purchased from Building Materials Market, Uyo, Akwa Ibom State, Nigeria. They were mechanically press-cut into 4.0 cm × 4.0 cm dimensions, degreased in absolute ethanol, prepared according to ASTM G01 standard procedures and stored in moisture free desiccator were used for the study. Fresh *Bixa orellana* seeds were harvested from a local forest in between Ikot Ambon village in Ibesikpo-Asutan L.G.A. of Akwa Ibom State, Nigeria. The dye was obtained and prepared into different concentrations (1.0, 3.0 and 5.0 mg/L) in 1 M solution of general purpose grade HCl.

Weight loss technique

Pre-weighed mild steel coupons were totally immersed in the test solutions containing the acid in the presence and absence of the dye, retrieved after 5 hours immersion time, washed thoroughly in 20 % NaOH solution containing 200 g/L of zinc dust, rinsed in water, dried in acetone, and re-weighed using a FA2104A digital weighing balance with sensitivity ± 0.0001 g. This was conducted at temperatures 30 – 60 °C in triplicates, and the mean values of mass losses were used to estimate the corrosion rate using equation (1).

$$CR = (W_1 - W_2)/At \qquad (1)$$

where CR (gcm^{-2}h^{-1}) is the corrosion rate, W_1 and W_2 (g) are the weights before and after immersion respectively, A (cm^2) is the average surface area of the coupons and t (h) is the immersion time. The inhibitor effectiveness (%*I*) was estimated from equation (2).

$$\%I = 100\left(\frac{CR_b - CR_i}{CR_b}\right) \qquad (2)$$

where CR_b and CR_i are the corrosion rates in the absence and presence of the extract respectively. The fractional surface coverage was calculated from % *I* using equation (3).

$$\theta = 0.01\ \%I \qquad (3)$$

Intensifier blending

The highest concentration of the dye formulated with intensifiers by blending it with a mixture of 2.0 wt% KI/1.0 wt% CuI and the inhibition efficiency (effectiveness) of the resulting mixture was determined using the weight loss procedure described above.

Solvatochromic technique

To determine the effect of solvents on the inhibition efficiency, the dye with the intensifier blend was formulated in different solvents namely water (W), methanol (M), nitromethane (N) and formic acid (F). The UV-Vis spectra of the lowest concentration (1.0 mg/L) of the dye both in the acid and in the different solvents were scanned *ab initio* using UNICO-UV-Spectrophotometer (Model 2010, Made in China) at a dilution of 1:40. The metal coupons were thereafter immersed in the test solutions for 5 hours before retrieval and the absorbance and maximum wavelength of absorption of the solutions were also obtained.

These formulations in the different solvents were also subjected to weight loss measurements as earlier described.

Adsorption studies

The values of fractional surface coverage obtained were fitted into Langmuir, Temkin, Florry Huggins and Frumkin adsorption models respectively given by equations 4-7 [30-31]. These models were used to probe the responsiveness of fractional coverage on the steel surface (θ) to changes in concentrations (C) of the extract.

$$\log\left(\frac{C}{\theta}\right) = \log C + \log K \qquad (4)$$

$$e^{-2\alpha\theta} = KC \qquad (5)$$

$$\log\left(\frac{C}{\theta}\right) = \log K + \log(1-\theta) \qquad (6)$$

$$\log\left(\frac{C\theta}{1-\theta}\right) = 2.303\log K + 2\alpha\theta \qquad (7)$$

$$\Delta G_{ads} = -RT\ln(55.5K) \qquad (8)$$

where α is the lateral interaction term or interaction parameter describing the interaction in the adsorbed layer, *x* is the size parameter which measures the number of water molecules substituted by the inhibitor molecules and *K* is the adsorption-desorption equilibrium constant related to the free energy of adsorption according to equation (8), *R* is the universal gas constant and *T* is the absolute temperature.

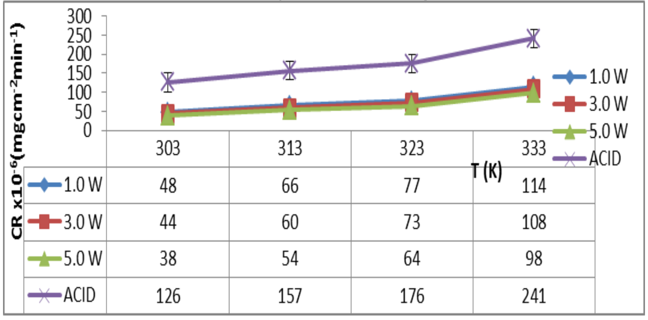
Atomic Absorption Spectrophotometric (AAS) technique

Copper ions content in the formulation was determined by Atomic Absorption Spectrophotometry using model 939/959 UNICAM Spectrophotometer with de-ionized water was used as blank.

Results and Discussion

Corrosion rate and dye effectiveness

The corrosion rates of mild steel after 5 hours of immersion in 1.0 M HCl in the absence and presence of annatto dye at 30-60°C were calculated. Corrosion rate increased with increase in temperature but decreased with increase in concentration of the extracts, which agrees findings from some other reports [31-33]. Results indicate that corrosion rate was reduced by addition of even very low concentrations of annatto dye extract (Fig. 3).



	303	313	323	333
1.0 W	48	66	77	114
3.0 W	44	60	73	108
5.0 W	38	54	64	98
ACID	126	157	176	241

Figure 3. Variation of corrosion rate with temperature.

The inhibitor effectiveness (Inhibition efficiency) increased with increase in concentration of the extract and decreased as immersion system temperature increased (Fig. 4). This effectiveness may be attributed to the presence of the electron rich phytochemicals earlier mentioned. Bixin and norbixin may be the active ingredients in the dye extract responsible for the high inhibition efficiency. The corrosion inhibition process may be due to adsorption of these phytochemicals onto the mild steel surface by interaction of ‘phyto-electrons’ from oxygen atoms and pie-functionalities of these phytochemicals with the vacant d-orbitals of iron. However, further study is recommended to help assign inhibitive effects to these phytochemicals and elucidate their contributions.

Effect of intensifier blend

The use of plant biomass as corrosion inhibitors is limited because they do not have long shelf life (they degrade with time) and their phyto-compounds at high temperatures and lose their effectiveness [33].

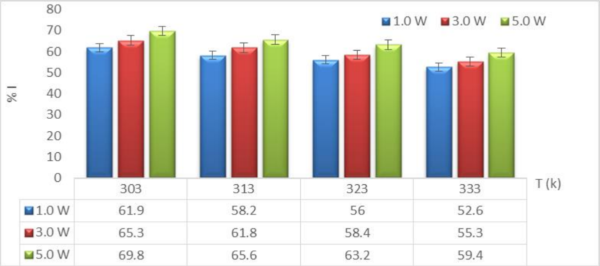


Figure 4. Variation of inhibition efficiency with concentration and temperature.

In oilfields, for instance, when the borehole temperature assumes higher values due to geothermal gradient, an inhibitor with good performance at surface conditions may not protect the steel structures in the deep. An intensifier, sometimes called an inhibitor aid [34], is usually added to enhance the performance of the inhibitor at high temperatures and long exposure time [33]. Potassium iodide has been widely reported to elicit synergistic effect to inhibitors in deep sour wells [35-36]. The dye was blended with 2.0 wt% KI/1.0 wt% CuI. Results revealed that KI/CuI blend intensified the effectiveness of the extract, even at temperatures up to 90°C (Table 1). This intensifying effect may be due to release of metal ions from the formulation and formation of coordinated or associated complexes with some of the phyto-compounds in the dye, leading to formation of protective deposits (film) on the metal surface [37].

Effect of solvents

A study was designed to determine the effect of some polar solvents on the inhibition effectiveness of the dye extract. It has been claimed that solvents function by either reducing the viscosity for ease of handling or ensuring the stability of the corrosion inhibitor formulation in various environments [33]. The effect of extracting solvents on inhibitor effectiveness has been described earlier [19], but researchers are yet to quantitatively describe the effect of solvent or co-solvent used in corrosion inhibitor formulation on its effectiveness. When a corrosion inhibitor is blended with intensifier(s) and a solvent (and sometimes with a surfactant) and co-solvent, the resulting mixture is usually called corrosion inhibitor formulation (CIF). The purpose of a solvent may sometimes be similar to that of a surfactant but with a different mechanism, i.e. to improve CIF solubility, dispersability in the acid and wettability on the acid-steel interface [33]. Solvents with polarity (methanol, nitromethane and formic acid) were selected (concentration 0.8 wt% and consisting of 50% by volume of the total test solution) to promote miscibility and enhance inhibition effectiveness.

Table 1. Inhibition effectiveness of annatto dye in the presence of blend of KI/CuI and different solvents.

T (°C)	30	40	50	60	75	90
Dye alone	69.8	65.6	63.2	59.4	38.3	21.4
Dye+KI/CuI alone	92.4	85.8	77.9	68.5	59.2	53.6
Formic acid CIF	87.9	82.3	76.1	62.9	55.3	48.6
Methanol CIF	93.6	86.8	78.6	69.1	60.8	55.4
Nitromethane CIF	95.4	89.2	80.1	72.3	61.4	56.9

Results show that the solvents affected the inhibition efficiency of the formulation. The effectiveness increased in methanol and nitomethane but decreased in formic acid (see Table 1). Nitromethane showed higher enhanced effectiveness than methanol and this may be explained in terms of the electron rich atoms (N and O) in it than ethanol. Formic acid may be thought to act antagonistic to the corrosion inhibition or even aiding to increase the corrosion rate of the system. For practical applications, methanol is more cost effective than nitromethane but may be hazardous to health like formic acid.

Solvent effect on UV-Vis absorption

In order to elucidate the effect of solvents on the adsorption of the dye molecules onto the metal surface, the uv/vis absorbance spectra of the dye in the various solvents was obtained before and after the immersion of steel. Before immersion, the dye sample showed absorbance of 1.889 (dye in water), 0.622 (in methanol), 0.646 (in formic acid) and 1.258 (in nitromethane). One wonders why the absorbance values in the different solvents were lower than that obtained in water (table 2).Introduction of the solvents lowered the absorbance of the dye molecules, but after the adsorption process, increase in absorbance was observed with nitromethane (1.274) and methanol (1.031) while formic acid (0.610) showed a decrease (table 2). The differences in absorbance before and after adsorption may be attributed to synergistic enhancement offered by the solvents. The mechanism underlying the observed phenomena is still unclear although it appears consistent with the trend of solvent effect on the inhibition efficiencies (table 1). It is believed that the complex(es) formed between Fe^{2+} and phyto-compounds in dye was/were rapidly dissolved by formic acid, thus reducing the absorbance. Further studies may be needed to understand this mechanism. In addition, shift to shorter wavelengths of absorption were also observed in all the solvents after the adsorption process (Table 2).

Table 2. Absorbance (A) and maximum wavelength of absorption (λ_{max}) of dye extract of annatto in different solvents before and after adsorption on mild steel in 1.0 M hydrochloric acid.

System	A		λ_{max}	
	Before immersion	**After immersion**	**Before immersion**	**After immersion**
CIF in water	1.991, 1.899	1.552, 1.179	249, 371	250, 371
CIF in formic acid	0.646	0.610	371	370
CIF in methanol	0.622	1.031	371	369
CIF in Nitromethane	1.258	1.274	349	337

Mechanism of inhibition

The fractional surface coverage (θ) data were fitted into the adsorption models described above by a plot of some functions of θ against those of inhibitor concentration (C). The best fit was obtained with the Temkin adsorption model ($R^2 > 0.96$), the linear form of which is given in equation 8 below:

$$\theta = -0.5\alpha (\ln K + \ln C) \qquad (9)$$

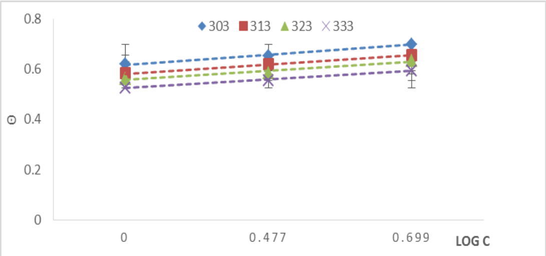


Figure 5. Temkin adsorption isotherm for the inhibition of mild steel corrosion by different concentrations of annatto dye extracts at different temperatures.

Table 3. Parameters deduced from Temkin adsorption isotherm.

T (K)	α	K_{ads} x 10^{14}	ΔG_{ads} (kJ/mol)
303	0.039	1.91	-93.25
313	0.037	5.04	-95.69
323	0.036	2.78	-94.19
333	0.034	2.41	-93.83

Negative values of ΔG_{ads} were obtained at all temperatures studied (table 3) implies spontaneous adsorption. It has been established that when $\Delta G_{ads}$is less negative than -20 kJ/mol, the mechanism is physical adsorption and if more negative than -40 kJ/mol, it is chemical adsorption [30,33]. Physical adsorption mechanism (physisorption) is usually associated with intermolecular forces which would cause preferential binding of certain phytochemicals of the dye to the metal (reversible on increase in temperature) while chemical adsorption involves chemical bond formation (coordinate covalent in nature) usually with release of heat. However, ΔG_{ads} values obtained indicate chemisorptions which may be further supported by the the exothermicity of the process and large values of K_{eq}. Chemisorption is associated with monolayer adsorption and protective film formation. However, this observation is not in agreement with the predictions usually made from the trend of inhibition efficiency with temperature. When inhibition efficiency decreases with increase in temperature as obtained in this study, physical adsorption mechanism is usually proposed which involves multilayer adsorption. The values of α and K_{eq} obtained signify strong adsorbate-adsorbent molecular attraction and great binding strength.

Thermodynamic considerations

Energetically, negative ΔG_{ads} obtained is consistent with the spontaneous nature of adsorption processes. A classical thermodynamic model called the transition state equation (equation 10) was used to deduce some energetic parameters (table 4) associated with the adsorption process:

$$CR = (RT/Nh)\ exp\ (\Delta S_{ads}/R)\ exp\ (\Delta H_{ads}/RT) \qquad (10)$$

where *CR* is the corrosion rate, h is Plank's constant, N is Avogadro's number, R is the universal gas constant and T is the absolute temperature. A plot of log CR/T against 1/T (not shown) afforded straight lines with slopes (ΔH_{ads}/2.303R) and intercepts [log(R/Nh) + (ΔS_{ads}/2.303R)]. Data obtained reveal that the adsorption process was exothermic and with higher heat of adsorption in the presence of the extracts. Negative ΔS_{ads} values obtained indicate decrease in entropy and consequently increased orderliness in the system probably brought about by reduction in the number of molecules of the active constituents of the extracts in the bulk solution due to adsorption [32]. The decrease in orderliness was not concentration dependent and may have resulted from the loss of heat to the surroundings.

Kinetic considerations

The percentage inhibition effectiveness decreased with increase in temperature for all the concentrations of the extracts studied which signifies possible shift in adsorption-desorption equilibrium towards desorption process as temperature increases. This agrees with Le' Chatellier's principle which describes shifts in equilibrium position to annul the effects of changes in equilibrium conditions. However, the introduction of intensifier blend elicited enhanced effectiveness on the extract even when temperature increased to 90°C. Corrosion rate data obtained from this study were also fitted into Arrhenius kinetic model (equation 11) to elucidate the effect of temperature on the inhibition efficiency and adsorption behaviour the extracts.

$$K - \exp(-\frac{E_a}{RT}) \qquad (11)$$

Activation energy (E_a) was deduced from Arrhenius plot of log *CR* against the reciprocal of temperature. In accordance with the concept of activation, the acid molecules must acquire sufficient energy to overcome a minimum energy barrier (E_a) required to collide, attack and dissolve the steel in the aqueous medium. The E_a values of the inhibited solutions are larger than that of the free acid solution which implies that the inhibited acid molecules must pass over a higher energy barrier to corrode the metal. Acid molecules that are unable to acquire this higher energy become deactivated, hence inhibition (protection) of the metal corrosion.

Table 4. Kinetic and Thermodynamic parameters.

System	$A(x10^{-5})$	E_a(kJ/mol)	ΔH(kJ/mol)	ΔS($x10^{11}$kJ/mol)
Blank	1.05	1.65	-1.44	-3.83
1.0 mg/L	3.55	2.22	-0.88	-3.83
3.0 mg/L	3.23	2.37	-2.09	-3.83
5.0 mg/L	2.28	2.89	-2.24	-3.83

Health, Safety and Environmental Considerations

Since heavy metals are known to be toxic, the amount of copper ions present in the inhibitor was evaluated to assess its friendliness or otherwise. Copper does not break down in the environment. Its accumulation in water may have slight effects on biodiversity in case of exposure. The amount of copper obtained from AAS measurement was 1.02 ± 0.11 µg. This value falls within the Recommended Dietary Allowance and Tolerable Upper Intake Level provided by both EPA and WHO. Based on this result, it is believed that the corrosion inhibitor formulation will be safe to environment and personnel if applied in the industry.

Conclusion

Based on the results obtained from this study, it may be concluded that extract of annatto is an effective corrosion inhibitor for mild steel in 1.0 M HCl at 30-60°C. Addition of HI/CuI blend to the extract synergistically improves the effectiveness of the inhibitor even at temperatures up to 90°C. The performance of the corrosion inhibitor formulation is affected by the solvents used. The absorption maxima and absorbance of the formulations were shifts in the solvents from values in water. The formulation functions by spontaneous adsorption of its phyto-compounds on the steel surface with the evolution of heat. The formulation can serve as a cheap and non-toxic alternative for chemical dyes used as inhibitors.

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