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Bioprospecting of Neem and Hibiscus Rosasinensis

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Abstract:*The present investigation was carried out about the corrosion inhibition and adsorption behavior of Neem and Hibiscus, as a green inhibitor of Zinc corrosion in acidic mediated of corrosion causing soil microbes by using weight loss and thermodynamic studies. Even analyze the quantitatively and qualitatively biochemical substances present in Neem and Hibiscus leaves of aqueous and ethanol extract which act as anticorrosive agent of metallic and non-metallic substances in acidified soil. Ethanol and aqueous extract of Neem and Hibiscus leaves extract showed the strong antimicrobial activity against soil microbes such as S.aureus, Streptococcus, B. subitilis, Lactobacillus, Proteus, Cornybacterium, Pseudomonas, A.niger, Mucor and Desulphovibro sp. Langmuir and Freundlich, Temkin and Florry-Huggins models are employed to analysis adsorption occurred in the experimental data of adsorption isotherms. The Freundlich, Langmuir and Temkin models are employed to analysis adsorption occurred in the experiment.*

Keywords: *Neem, Hibiscus, S.aureus, Streptococcus, B. subitilis, Lactobacillus, Proteus, Cornybacterium, Pseudomonas, A.niger, Mucor and Desulphovibro sp. Langmuir and Freundlich, Temkin and Florry-Huggins models, Zinc, Adsorption, corrosion inhibition.*

I. INTRODUCTION

Soil is the region for the proliferation of microbes with many colonies which developing around soil particles. Many microbes in soil habitats normally are much higher than those in water. Soil as a corrosive environment is probably of greater complexity than any other environment. In facts, Pipes, concrete, tube wells etc., in soil can be perforated within one or few months, presenting very localized or uniform corrosion attack. The chemical constituents of soil is Silica, Alumina and dissolved substances such as H^+, Cl^-, SO_4^-, HCO_3^- ions. Soil with poorest drainage like clay, silt and loam are the most corrosive than gravel and sand which is least corrosive. Corrosion is the deterioration of a metal as a result of chemical reactions between it and the surrounding environment. Both the types of metal and environmental conditions, mainly gases that are in contact with the metal, determine the form and rate of deterioration and also influenced by some microbial performing different electrochemical reactions and secreting proteins and metabolites that can have secondary effects. Some microbes are able to cause and also inhibit corrosion. The metallic corrosion in soil is aqueous and its mechanism is electrochemical.

Several effects have been taken by using so many preventive measures particularly green or organic inhibitors are important which is non-toxic to living organisms and also cheapest and safest.

Plants are the richest sources of valuable ingredients which have very high efficiency of inhibition and named as Green inhibitor or Natural inhibitors which are biodegradable, renewable source of energy and used as a effective corrosive inhibitors of a broad range of metals causing microbes in acidic mediated soil has been one of the key areas in my research work.

Biological samples used in this work are

II. NEEM (AZADIRACHTA INDICA)

Neem is a natural medicine since ancient times in ayurveda even each and every parts of Neem plant acts as medicinal values. Meliaceae or the Mahogany family is a flowering woody family of plants Species in the genus *Azadirachta* are closely related to and sometimes confused with species of the genus *Melia* and widely distributed throughout the tropics and subtropics, with only slight penetration into temperate zones.

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Neem has effect on degenerative diseases such as diabetes, cancer, TB, bronchitis, conjunctivitis, allergies, stress, insomnia, etc. The phytochemical substances present in Neem are alkaloids, quinines, resins, tannins, biochemical substances etc. Nimbin is the bitter compound isolated from Neem leaves. Bitterness is due to presence of terepenes. The most important bioactive compound is Azadirachtin which is an insect repellent. The flavonoids and azadirachtin act as anti-corrosive agents and also anti-microbial agents which prevent the corrosion caused by soil microbes in acidified medium of soil on buried metal in soil and also adsorption behavior properties on metal to prevent the corrosion.

Several studies worked out on the different parts of Neem plant for the various activities such as anti-inflammatory, antipyretic, antifertility, analgesic, immune stimulant, anticancer activity, anti-diabetic, antimicrobial, anti malarial, etc. Neem extract has been only involved very occasionally in environmental studies and research with the analysis of adsorption of Pb (II) from aqueous extract of Neem leaves by Bhattacharya and Sharma, Studies of Cu corrosion by Neem leaves extract in H_2SO_4 by Oguzie 2006, adsorption activity by Sanjay Sharma and Corrosion inhibitive properties of Neem in acid solution by Valek, 2007 and more.

III. HIBISCUS ROSASINENSIS

Hibiscus is a genus of flowering plants in the mallow family, Malvaceae. The genus is quite large, containing several hundred species that are native to warm-temperate, subtropical and tropical regions throughout the world. *Hibiscus rosa-sinensis*, known colloquially as Chinese hibiscus, China rose, Hawaiian hibiscus, and shoeblack plant, is a species of tropical hibiscus, a flowering plant in the Hibisceae tribe of the family Malvaceae, native to East Asia.

Hibiscus is used as anti-inflammatory, demulant, aphrodisiac, refrigerant, menorrhagic, anti-diarrhetic, anticomplementary activity, antifertility, etc. The phytochemical substances present in Hibiscus are steroids, flavonoids, tannins, biochemical substances, alkaloids, resins,vitamin B complex, terepenes etc. Flavonoids are present which gives bitter taste to leaves and used as anti-corrosive and anti-microbial activities which is equal to Neem.

Several studies worked out on different species of Hibiscus plant for various activities such as anti-diabetic, anti-pyretic, anti-microbial and anti-inflammatory etc. Several workers worked on this plant to be effective in the treatment of arterial hypotension by Dwivedi, 1977; antifertility effect of Hibiscus by Sethi,1986; Singh, 1982; corrosion inhibition for metal in acid medium by Rajendra, 2009, Anuradha,2007.

IV. CORROSION INHIBITION STUDIES

Corrosion-resistant zinc plating of iron (hot-dip galvanizing) is the major application for zinc. Other applications are in batteries, small non-structural castings, and alloys, such as brass.

Brass, an alloy of Zn that contains between 55% and 95% Cu is among the best known alloy. Zn is alloyed with Lead and Tin to make solder, a metal with a relatively low melting point used to join electrical components, Pipes and metallic items. Other Zn alloys includes Nickel silver, typewriter metal and German silver. Metallic Zn is used in galvanizing today, a protective coating to an item is experiencing corrosion. Zn alloys are versatile engineering materials. No other alloys provide the combination of strength, toughness, rigidity, bearing performance and economic cast ability; Precision, quality and repeat performance are distinctive advantage of Zn alloys.

Zinc is an essential mineral perceived by the public today as being of "exceptional biologic and public health importance", especially increasingly regarding prenatal and postnatal development. (Hambidge, K. M. & Krebs, N. F. (2007)). Zinc undergoes oxidation on the surface, thus protecting the underlying metal from degradation. Galvanized products are widely used in construction materials, automobile parts, and household appliances. When incorporated with copper compounds or arsenic-lead wet table powders and applied by spraying, zinc can minimize the toxic effects of these metals on fruits such as plums, apples and peaches. As a result of its wide use and hence susceptibility to corrosion (oxidation potential +0.76eV), the study of the corrosion inhibition of zinc has become an important area of research in corrosion science. Many nitrogen containing compounds including quinoline, aniline, brucine, and strychnine have shown good corrosion inhibition for zinc in acidic medium. Quinine sulphate, piperazine, caffine, barbitone and pyridine derivatives have been used as corrosion inhibitors for aluminium and zinc in acidic medium. Inhibition of corrosion of zinc in hydrochloric acid by some carbazide derivatives has also been reported. Foad El-Sherbini et al. (2005) have investigated the inhibition effect of ethoxylated fatty acids as inhibitors for the corrosion of zinc metal in 1.0 M hydrochloric acid solutions at various temperatures ranging from 25˚C to 55˚C by weight loss measurement and electrochemical methods.
Zn is not used in contact with acid and alkaline medium, because Zn easily corrodes in such media in very rapidly. Therefore only if the H_2 evolution type of attack is predominant and no other factor influence the corrosion process. Corroded by strong acidic medium should be maximized.

Zn deposition plays a negligible role in Zn corrosion

1) Corrosion generally occurs at a potential anodic to the reversible potential of Zn where deposition is insignificant compared to the dissolution.
2) Corrosion is usually encountered in solution containing very little ionic Zn.

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V. MATERIALS AND METHODS

I.SOIL SAMPLE COLLECTIONS:

The soil samples used for this work were collected from 3 different locations near Krishnarajapura area in Bangalore. The samples were labeled according to the site of collection as Garden soil samples, Sewage soil samples and Household soil samples. The samples were transported in polyethylene bags in ice pack to the laboratory. When samples could not process immediately, they were stored at 4°C for no longer than 18 to 24 h.

II.DETERMINATION OF SOIL PH:

Soil pH was determined according to the procedure described by Akpor et al. (2006) using Horiba make D-51 pH meter - Measuring object & amp.

III.BIOLOGICAL SAMPLE COLLECTIONS:

Leaves of the *Azadirachta indica and Hibiscus rosasinensis* tree were selected and collected from the Krishnarajapura area, Bangalore, Karnataka. It was ensure that the plant was healthy and uninfected. The leaves were washed under running tap water to eliminate dust and other foreign particles and to clean them thoroughly and a particular amount of leaves dried under shadow and some fresh leaves kept.

IV.PREPARATION OF AQUEOUS EXTRACT OF PLANT SAMPLES:

10 grams of air dried powder N*eem and Hibiscus rosasinensis* leaves were placed in different distilled water bath and boiled for 6 h. At intervals of 2 h it was filtered through 8 layers of muslin cloth and centrifuged at 5000 x g for 15 min. The supernatant of different samples was collected. After 6 h, the supernatant of different samples was concentrated to make the final volume one-fourth of the original volume. Finally 10 g of each material was extracted in 25 ml of distilled water giving a concentration of 40 mg/0.1 ml. It was then autoclaved at 121 °C and 15 lbs pressure and stored at 4 °C.

V.PREPARATION OF ETHANOL EXTRACT OF PLANT SAMPLES

10 grams of air dried powder *Neem and Hibiscus rosasinensis* leaves were placed in 100 ml of organic solvent (ethanol) in a conical flask, plugged with cotton and then kept on a rotary shaker at 190-220 rpm for 24 h. After 24 h, it was filtered through 8 layers of muslin cloth and centrifuged at 5000 x g for 15 min. The supernatant of different samples was collected and the solvent was evaporated to make the final volume one-fourth of the original volume, giving a concentration of 40 mg/0.1 ml. It was stored at 4 °C in airtight bottles for further studies.

VI.TEST SOLUTION

The concentrated HCl acid used for this has a density of 1.18 g/cm3, a percentage purity of 37% and molar mass of 36.5 /mol. Equation was used to obtain the Molarity of the concentrated HCl acid.

$Molarity$=Concentration x molar mass

Concentration = Standard volume x density x percentage purity

For 1 liter (1000 cm3) of standard HCl acid, Concentration = 1000 × 1.18 × 37%

Hence, the Molarity is given by: $Molarity$=1000 × 1.18 × 3736.5=11.96 M

From the relation in equation

$C_1V_1=C_2V_2$

Where C = Concentration and V = Volume

Since 100 ml of 2 m HCl is required, hence, 11.96 x V_1 =2 x 100, therefore V_1 =16.72 ml. It therefore implies that 16.72 ml of HCl acid was dissolved in 100 ml of distilled water in a standard flask to obtain the desired concentration.

VI. ANTIMICROBIAL ACTIVITY OF HIBISCUS ROSASINENSIS AND NEEM LEAF EXTRACT

All the extracts of leaves have shown the activity. Investigations were carried out of plant materials as alternative sources of antibacterial and antifungal agents. It has become more common over the past few years, due to the increased rate of development of antibiotic resistance organism. The inhibition of microbial growth *in-vitro* by the extracts of leaves could be due to the presence of some active compounds in the extracts. These active compounds may act alone or in combination to inhibit microbial growth.

PHYTOCHEMICAL STUDIES

All the solvents were used based upon their increasing polarity index. The extracts were evaporated to dryness on a water-bath. The plant extracts were distilled off with distillation apparatus and yielded quantities of (leaf) extracts in different solvents were obtained and were further taken to evaluate the phytochemical studies. The percentage yield of plant extracts are shown in Table.

To find the percentage yield of extracts:

$$\text{Percentage of yield extracts} = \frac{\textbf{weight of the extract}}{\textbf{weight of raw material}}$$

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PHYTOCHEMICAL SCREENING METHODS

A portion of the aqueous extract of each plant samples and also of the powdered form of the plant samples extract are used for the screening tests, both qualitative analysis and quantitative analysis using standard methods.

ANTIOXIDANT STUDIES:

Antioxidants are molecules that can delay or prevent an oxidative reaction (*Velioglu et al., 1998*). Antioxidants may offer resistance against oxidative stress by scavenging free radicals, inhibiting lipid peroxidation and many other mechanisms and thus prevent disease *(Marx, 1987*).

Plant-derived antioxidants, especially, the phenolics have gained considerable importance due to their potential health benefits. Epidemiological studies have shown that consumption of plant foods containing antioxidants is beneficial to health because it regulates down many degenerative processes and can effectively lower the incidence of cancer and cardio-vascular diseases *Arabshahi-Delouee, S.*

WEIGHT LOSS METHOD (GRAVIMETRIC METHOD)

The weight loss method was employed for the two temperatures 30˚C and 60˚C. In this procedure, the mass loss of the metal in without *Azardirachta indica* and *Hibiscus rosasinensis* extract (uninhibited solution) and with *Azardirachta indica* and *Hibiscus rosasinensis* extract (inhibited solution) were measured and recorded.

From the data, the percentage of inhibition efficiency (% I) and degree of surface coverage (Θ) were calculated using the following equations,

Percentage of inhibition efficiency $\mathbf{IE = (1 - W_2 / W_{1)} \times 100}$

Where W_1 and W_2 are the weight of the metal in uninhibited and inhibited solutions

Degree of surface coverage $\mathbf{(\Theta) = (1 - W_2 / W_1)}$

Corrosion rate (CR) = mm /d = 87.6 x (W / DxAxT)

W = weight loss in milligrams, D = metal density in g /cm^3,

A = area of sample in cm^2, T = time of exposure of the metal sample in hours, 87.6 is a conversion factor.

MECHANISM OF CORROSION INHIBITION

Generally, zinc dissolve in hydrochloric acid solution due to somewhat hydrogen type of attack, the reaction taking place at the microelectrodes of the corrosion cell being represented as,

$Zn \text{ -------> } Zn^{2+} + 2e^-$ (anodic reaction)

Reduction reaction is indicated by decrease in valence or the consumption of electrodes, as shown by the following equation.

$2H+ + 2e^- \text{ -------> } 2H_{(ads.)}$ (Cathodic reaction)

Or

$H + H_3O^+ + e^- \text{ -------> } H_2\uparrow + H2O$

Thus, the total corrosion reaction of zinc in acidic chloride solution is as following: (A. Zhang and L.Xin)

$$2Zn + 4H^+ + 4Cl^- + O_2 \rightarrow 2Zn^{2+} + 4Cl^- + H_2O$$

VII. ADSORPTION BEHAVIOUR

Adsorption is usually described through isotherms, that is, the amount of adsorbate on the adsorbent as a function of its pressure (if gas) or concentration (if liquid) at constant temperature. The quantity adsorbed is nearly always normalized by the mass of the adsorbent to allow comparison of different materials. (*Foo, K.Y.; Hameed, B.H. (2010).*

Several mathematical models can be used to describe experimental data of adsorption isotherms. The Langmuir and Freundlich, Temkin and Florry-Huggins models are employed to analysis adsorption occurred in the experimental data of adsorption isotherms. The Freundlich, Langmuir and Temkin models are employed to analysis adsorption occurred in the experiment.

RESULT

The present study was carried out on the *Azardirachta indica and Hibiscus rosa-sinensis* revealed the presence of medicinal bio-active constituents, antioxidant, antimicrobial activity, corrosion inhibition and adsorption behaviour.

I.SOIL pH:

The pH values ranged from 6.3 – 7.3. The soil pH in Sewage soil was higher than household soil and garden soil. However, differences in the soil pH values of the different sampling locations were not observed to be statistically significant.

II.MICROBIAL ANALYSIS OF SOIL:

The occurrence of aerobic and anaerobic heterotrophic microbes presents in the different soil samples. In Garden soil, Lactobacillus, Bacillus subtilis,Proteus, Pseudomonas, Micrococcus, Staphylococcus, Corynebacterium, Desulphovibrio, D. Africans, Aspergillus niger, Penicillium, mucor, Trichophyton and Microsporium. But Streptococcus sp is absent in garden soil.

In Household soil, Except Lactobacillus and Proteus, remaining all microbes are present. In Sewage soil, Except Lactobacillus, Proteus and Micrococcus remaining all microbes are present.

In these, corrosion causing microbes are Desulphovibrio, Bacillus subtilis,Proteus, Pseudomonas, Corynebacterium and A.niger.

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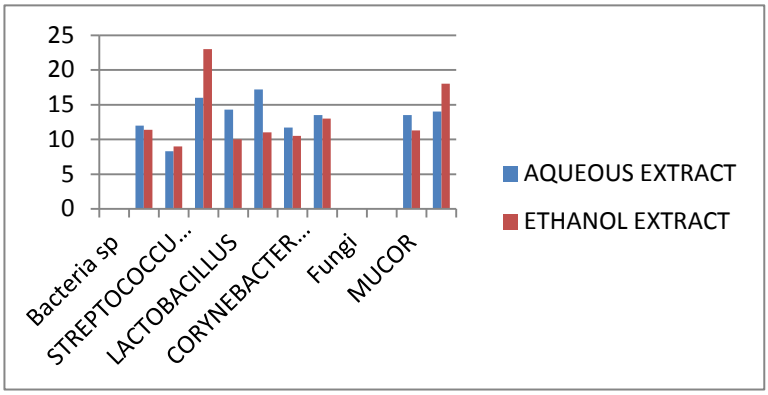
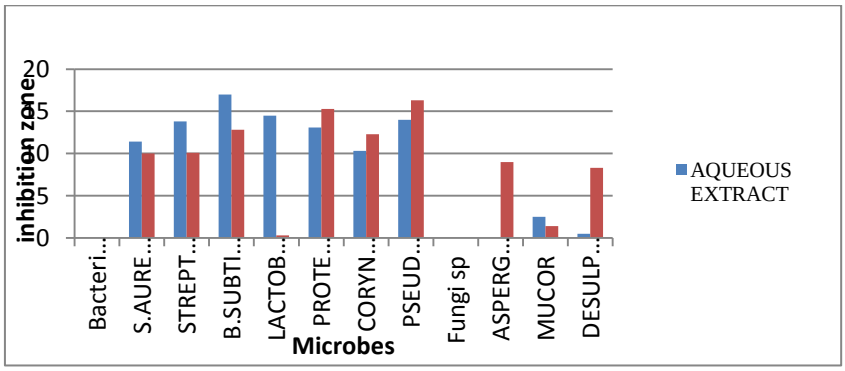
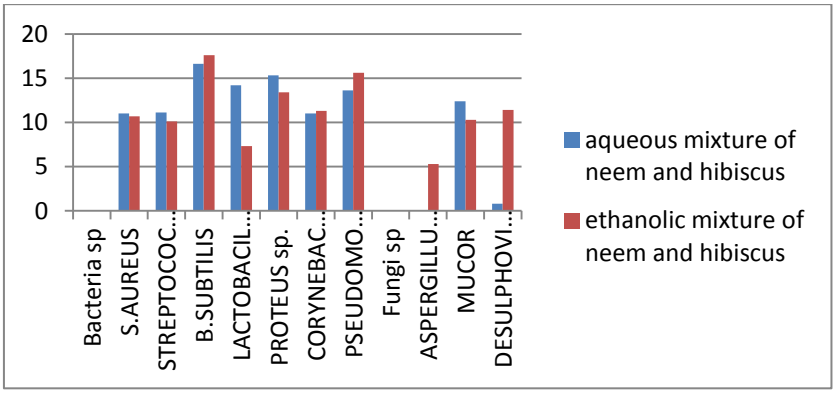
ANTIMICROBIAL ACTIVITY OF AQUEOUS AND ETHANOL EXTRACT OF *NEEM* IN AGAR WELL DIFFUSION METHOD (MM).



ANTIMICROBIAL ACTIVITY OF AQUEOUS AND ETHANOL EXTRACT OF HIBISCUS ROSASINENSIS IN AGAR WELL DIFFUSION METHOD (MM).



ANTIMICROBIAL ACTIVITY OF AQUEOUS AND ETHANOL EXTRACT OF MIXTURE OF NEEM AND HIBISCUS ROSASINENSIS IN AGAR WELL DIFFUSION METHOD (MM).



Disc and well diameter = 6 mm

Zone of inhibition (claustro et.al)

Interpretative ranges	range (mm)	Descriptive
zone of inhibition	< 10	Resistant
zone of inhibition	10 to 13	Intermediate
zone of inhibition	14 to 19	Sensitive
zone of inhibition	> 19	very sensitive
no zone	-----	------

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PHYTOCHEMICAL ANALYSIS

S.NO.	TESTS	AQUEOUS EXTRACT OF HR	ETHANOL EXTRACT OF HR	AQUEOUS EXTRACT OF NEEM	ETHANOL EXTRACT OF NEEM	AQUEOUS EXTRACT OF MIXTURE OF HR AND NEEM	ETHANOL EXTRACT OF MIXTURE OF HR AND NEEM
1	TEST FOR PHENOLS						
A.	FeCl3 TEST	++++	++++	++++	++++	++++	++++
B	GELATIN TEST	++++	++++	++++	++++	++++	++++
2	TEST FOR TANNINS	++++	++++	++++	++++	++++	++++
3	TEST FOR SAPONINS						
	FOAM TEST	++++	++++	++++	++++	++++	++++
4	TEST FOR PHLOBATANNINS	++++	++++	++++	++++	++++	++++
5	TEST FOR FLAVONOIDS	++++	++++	++++	++++	++++	++++
6	TEST FOR STEROIDS						
A.	SALKOWSKI TEST	++++	++++	++++	++++	++++	++++
B	LIBERMANN-BURCHARD TEST	++++	++++	++++	++++	++++	++++
7	TEST FOR ALKALOIDS						
A.	MAYERS TEST	----	----	++++	++++	++	++
B	HAYERS TEST	----	----	++++	++++	++	++
8	TEST FOR PROTEINS						
A.	NINHYDRINS TEST	++++	++++	++++	++++	++++	++++
B	BIURET TEST	++++	++++	++++	++++	++++	++++
9	TEST FOR CARBOHYDRATES						
A.	MOLISCH TEST	++++	++++	----	----	++	++
B	FEHLING TEST	++++	++++	----	----	++	++
C	BENEDICTS TEST	++++	++++	----	----	++	++
D	STARCH TEST	----	----	----	----	----	----
10	TEST FOR GLYCOSIDE	++++	++++	++++	++++	++++	++++
11	DETECTION OF GUM AND MUCILAGE	++++	++++	++++	++++	++++	++++

NOTE: "++++" = ABSOLUTELY PRESENT; "----"= ABSOLUTELY ABSENT; "++" = PARTIALLY PRESENT

QUANTITATIVE ANALYSIS

The results of quantitative analysis on five major groups of phytochemical constituents such as Phenols, Tannins, Saponins, Alkaloids and Flavonoids in the *Azardirachta indica and Hibiscus rosa-sinensis* plants are summarized.

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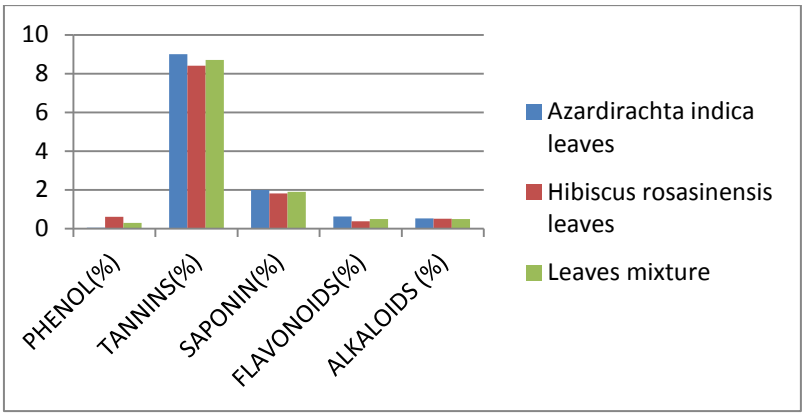
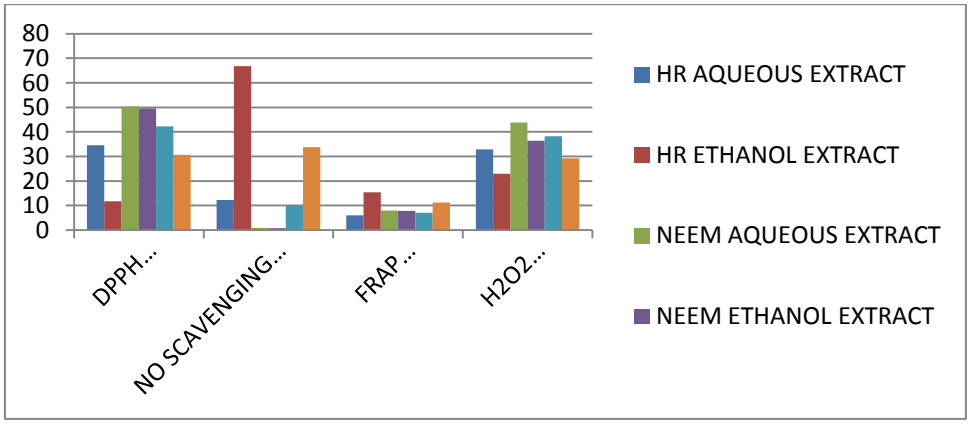


ANTIOXIDANT STUDIES

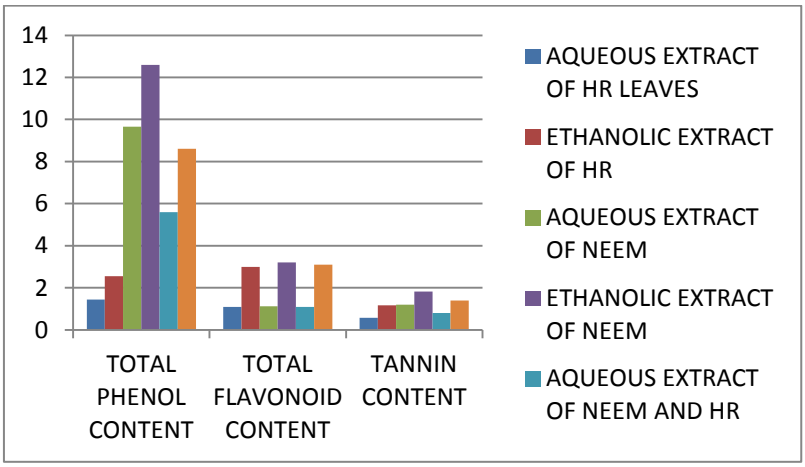
Plant-derived antioxidants, especially, the phenolics have gained considerable importance due to their potential health benefits. Epidemiological studies have shown that consumption of plant foods containing antioxidants is beneficial to health because it regulates down many degenerative processes and can effectively lower the incidence of cancer and cardio-vascular diseases. *Arabshahi-Delouee, S.*

ANTIOXIDANT ACTIVITY OF HIBISCUS ROSASINENSIS LEAF, NEEM & MIXTURE EXTRACT



The graph shows the class of antioxidant capacity of the different plant parts of Hibiscus rosasinensis, *A. indica* and both plant mixture. The order of antioxidant capacity for *A. indica* is as follows: Ethanolic extract > Aqueous extract . The order of antioxidant capacity for Hibiscus rosasinensis is as follows:Ethanolic extract > aqueous extract. The order of antioxidant capacity for both plant mixture extract is as follows:Ethanolic extract > aqueous extract. In this research, the modified method of scale of antioxidant capacity of Katalinic et al. (2006) was employed.

ESTIMATION OF TOTAL ANTIOXIDANT CAPACITIES:



The antioxidant capacity of ethanolic extract of Hibiscus rosasinensis leaves was slightly greater than that of the Aqueous extract of Hibiscus rosasinensis, and the difference was found to be significant ($p<0.05$). The antioxidant capacity of the ethanolic extract of *A. indica leaves was* higher than the antioxidant capacity of the aqueous extract of *A. indica leaves* and the difference was significant ($p< 0.05$). Also, the antioxidant capacity of ethanolic extract of *A. indica and mixed leaves* was slightly higher than the antioxidant capacity of the aqueous extract of *A. indica leaves* and the difference was not significant ($p> 0.05$).

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CORROSION INHIBITION ACTIVITY:

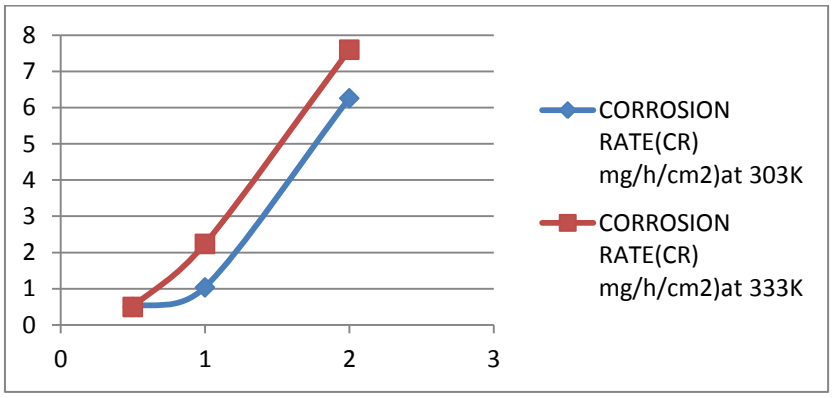
EFFECT OF CONCENTRATION OF HCL ON ZINC CORROSION:

Zinc corrodes in different concentrations of HCl solutions, since there was a decrease in the original weight of zinc. The corrosion is attributed to the presence of water, air and H+, which accelerate the corrosion process.

The corrosion of the zinc in HCl increases with the concentration of the HCl acid. Similar results were obtained at 303K and 333 K. The graph shows values of corrosion rate (CR) of zinc in all the concentrations of HCl studied and it shows that corrosion rate increases with an increase in HCl acid concentration. This observation is attributed to the fact that the rate of chemical reaction increases with increasing concentration. This observation has been reported by several authors (Ita and Edem, 2000; James et al., 2007).

CORROSION RATE OF ZINC IN ALL CONCENTRATIONS OF HCL

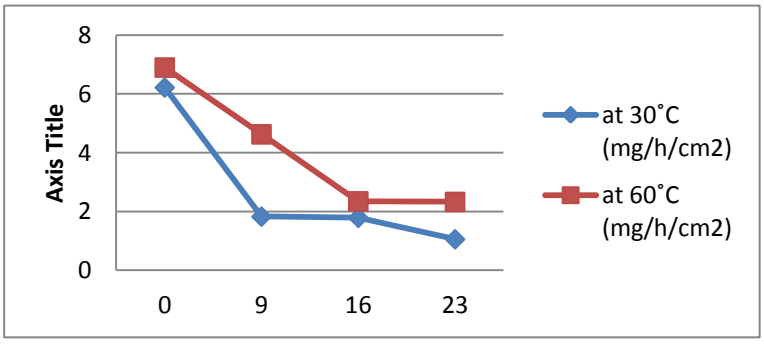
Values of corrosion rate (CR) of zinc in all the concentrations of HCl studied and it shows that corrosion rate increases with an increase in HCl acid concentration. This observation is attributed to the fact that the rate of chemical reaction increases with increasing concentration.



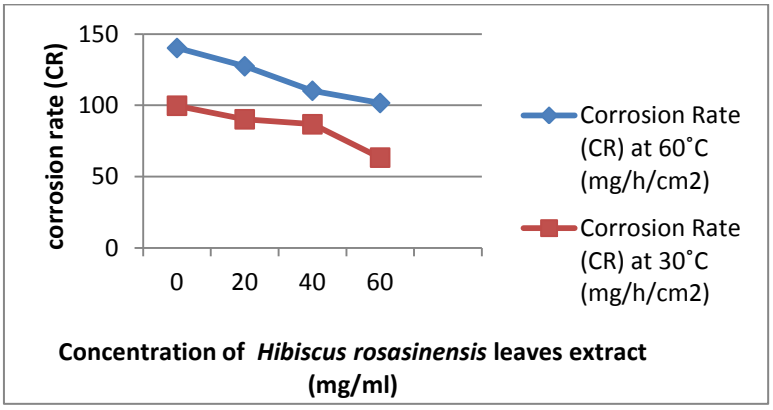
EFFECTS OF AQUEOUS EXTRACT OF *AZARDIRACHTA INDICA AND HIBISCUS ROSA-SINENSIS* ON THE CORROSION OF ZINC IN ACID MEDIA

This may be observed from the data in graphs that an addition of an increased concentration of the inhibitor generally retards the corrosion rate of zinc in acid (HCl) solution. This shows that aqueous extract of *Azardirachta indica and Hibiscus rosa-sinensis* inhibited the corrosion of Zinc in HCl.

Variation of weight loss change with increase in concentration of AZI leaves extract for HCl at the two temperatures investigated.



Variation of mass loss change with increase in concentration of HR leaves extract for HCl acid concentrations at the two temperatures investigated.



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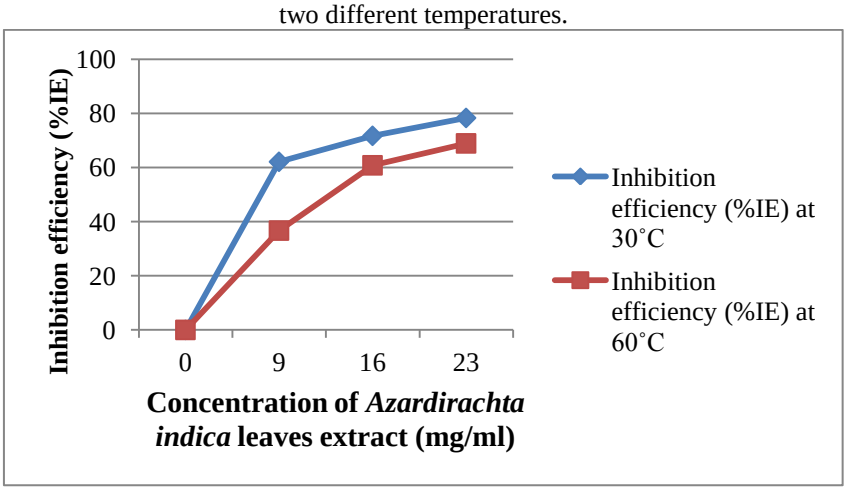
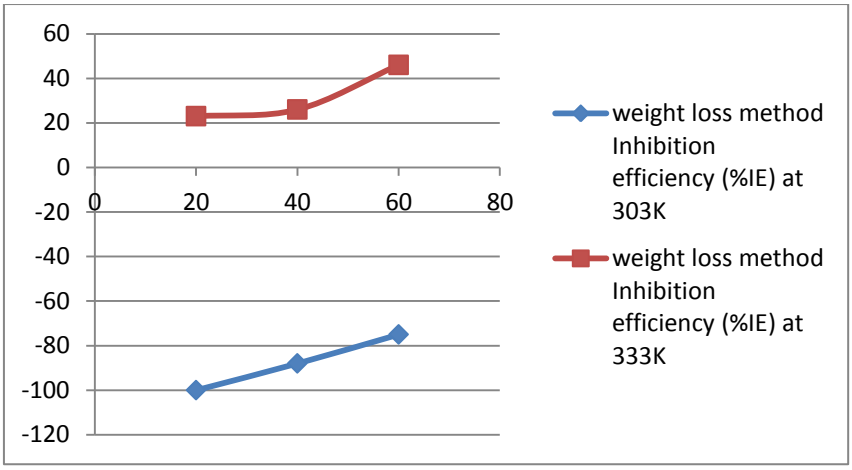
EFFECT OF INHIBITOR CONCENTRATION ON INHIBITION EFFICIENCY:

From the inhibition efficiencies obtained from the weight loss experiments for 2 N HCl, it is found that the Inhibition efficiency increases with increase in inhibitor concentration of both the extracts for acidic media.

Inhibition efficiency (%IE) for weight loss method of *Azardirachta indica* leaves extract for the corrosion of Zinc in 2N HCl at two different temperatures.



Inhibition efficiency of HR leaves extract for different concentrations and at different temperatures.



EFFECT OF TEMPERATURE ON THE INHIBITION EFFICIENCY OF BOTH NEEM AND HIBISCUS PLANT EXTRACTS

We can observe from the graph that, as the reaction temperature is increased (i.e. 30˚C and 60˚C), the inhibition efficiency increases. Thus it is appropriate to say that increase in temperature favours the inhibition efficiency of both Neem and Hibiscus plant extracts on zinc in Hydrochloric acid.

A value of activation energy for the corrosion reaction of zinc in the presence and absence of different concentration of *Azardirachta indica and Hibiscus rosasinensis leaves* extract has been calculated using Arrhenius Equation

Corrosion rate = Ae $^{E_a}/^{RT}$

Taking logarithm on both sides

LogCR = LogA - $\frac{Ea}{2.303R}$**T**

Where A is Arrhenius constant, [Ea] is the activation energy of the reaction, R is the gas constant (8.314J/mol.K.) and T is the temperature (K)

Considering a change in temperature from 303K (T_1) to 333K (T_2), the corresponding values of the corrosion rates at these temperatures are a_1 and a_2, respectively.

Substituting these values in above equation

Log $\frac{CR2}{CR1} = \frac{Ea}{2.303R}\left(\frac{1}{T1} - \frac{1}{T2}\right)$

Values of [Ea] for the inhibited corrosion reaction of zinc have been calculated using Equation.

The activation energy in the absence of the inhibitor is 2872.06 J/mol for *Azardirachta indica* (AZI) and 9449.11 J/mol and is lower than the values obtained for the inhibited systems. The values in the presence of the inhibitor support the mechanism of physical adsorption.

For a physical adsorption, it is expected that the value of [Ea] should be less than 80000 J/mol. (Foad El-Sherbini)

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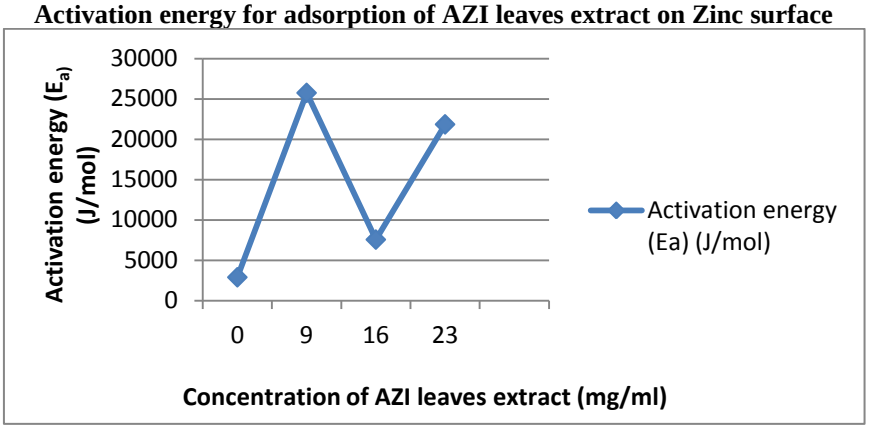
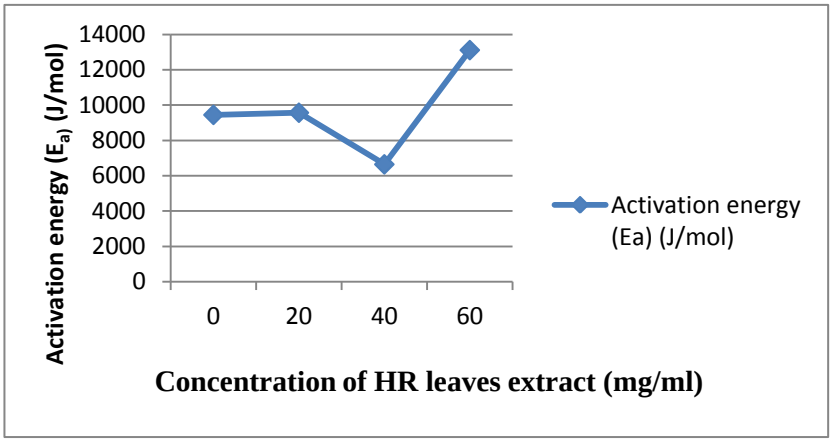
Activation energy for adsorption of AZI leaves extract on Zinc surface



Activation energy for adsorption of HR leaves extract on Zinc surface



ADSORPTION BEHAVIOUR:

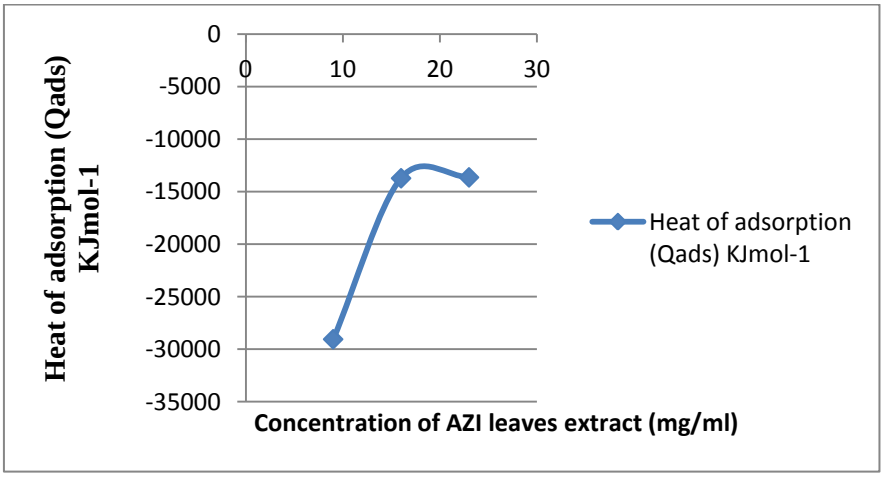
THERMODYNAMIC PARAMETERS FOR THE HEAT OF ADSORPTION Q_{ADS}:

The heat of adsorption *Q*ads on the surface of Zinc was calculated by using Equation

$$\mathbf{Q\ (ads) = 2.303R\ [\log\ (\frac{\theta 2}{1-\theta 2})\ -\ \log\ (\frac{\theta 1}{1-\theta 1})]\ x\ \frac{T1*T2}{T2-T1}\ \ KJmol^{-1}}$$

where *R* is the gas constant, $\theta 1$ and $\theta 2$ are the degree of surface coverage at temperatures, *T*1 and *T*2 respectively. Calculated values of activation energy and heat of adsorption are shown in Graph. The values ranged from –2.12 to –4.87 KJ·mol–1, indicating that the adsorption of aqueous extract of Neem and Hibiscus on Zinc surface is exothermic. (Bhattacharyya, K.G.; Sharma, A)

Heat of adsorption (Qads) of the AZI leaves extract on the surface of Zinc



Heat of adsorption (Qads) of the HR leaves extract on the surface of Zinc

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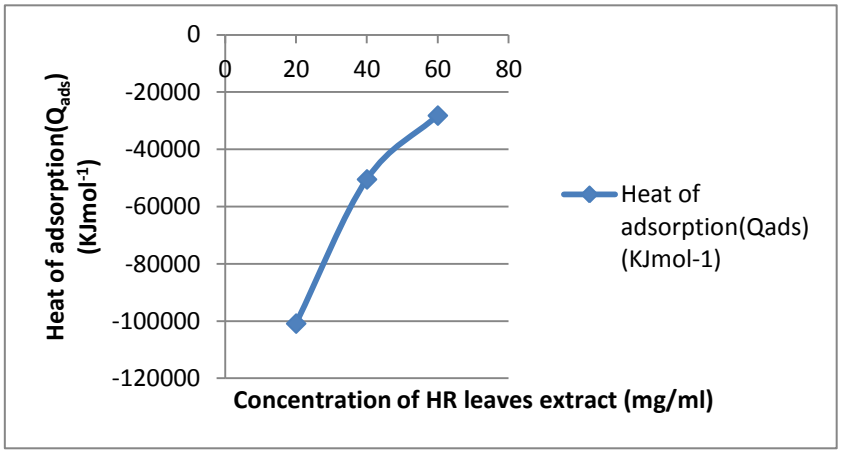


MECHANISM OF CORROSION INHIBITION

The mechanism of inhibitor of corrosion is believed to be due to the formation and maintenance of a protective film on the metal surface. Further, when log (θ /1-θ) is plotted against log C straight lines are obtained in the case of aqueous extract of *Azardirachta indica and Hibiscus rosa-sinensis* studied. This suggests that the inhibitor cover both the anodic as well as cathodic regions through general adsorption following Langmuir isotherm, Frumkin, Temkin and Flory-Huggins.

Data obtained for the degree of surface coverage were used for the evaluation of different adsorption isotherms (Langmuir, Frumkin, Temkin and Flory-Huggins).

LANGMUIR – FREUNDLICH ADSORPTION MODEL:

The Langmuir– **Freundlich** adsorption model is the most common model used to quantify the amount of adsorbate on an adsorbent as a function of partial pressure or concentration at a given temperature.

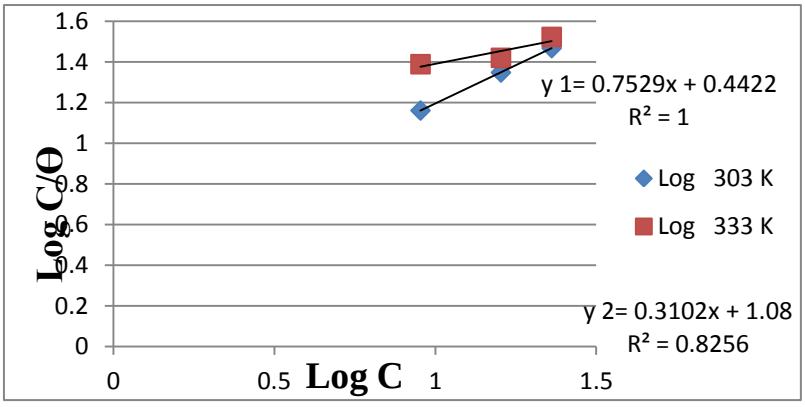
Langmuir adsorption isotherm is expressed according to Equation

$$\frac{C}{\theta} = \frac{1}{K} + \mathbf{C}$$

where *C* is the concentration of the inhibitor, *K* is the adsorption equilibrium constant and Θ is degree of surface coverage of the inhibitor. Taking logarithm of both sides of Equation (1) yields Equation (2).

$$\mathbf{Log}\ \frac{C}{\theta} = \mathbf{Log\ C - Log\ K}$$

Langmuir isotherm for the adsorption of *Azardirachta indica* leaves extract on Zinc surface



Langmuir isotherm for the adsorption of hibiscus rosasinensis leaves extract on Zinc surface

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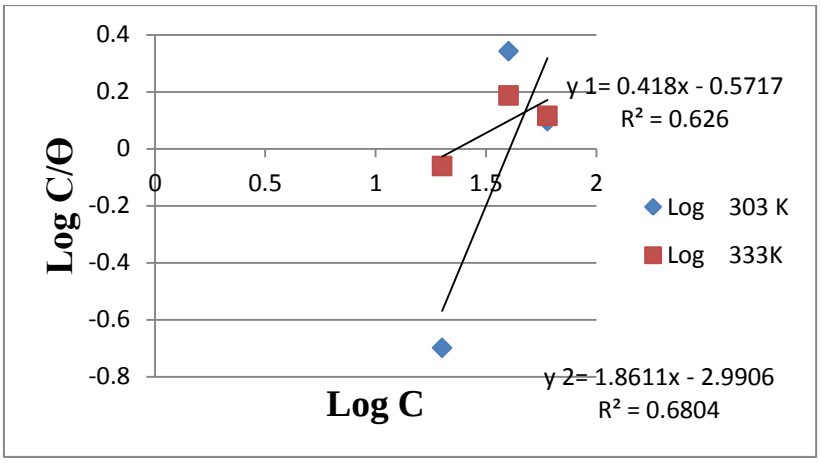


Plotting Log $\frac{C}{\theta}$ against logC gave a linear relationship as shown in Fig: 10 and 11 gave linear relationship, which shows that adsorption data fitted Langmuir adsorption isotherm. Adsorption parameters obtained from Langmuir adsorption isotherms are recorded in Table-20. The values of attractive parameter (1/n) are negative in all cases, indicating that repulsion exists in the adsorption layer.

TEMKIN ISOTHERM:

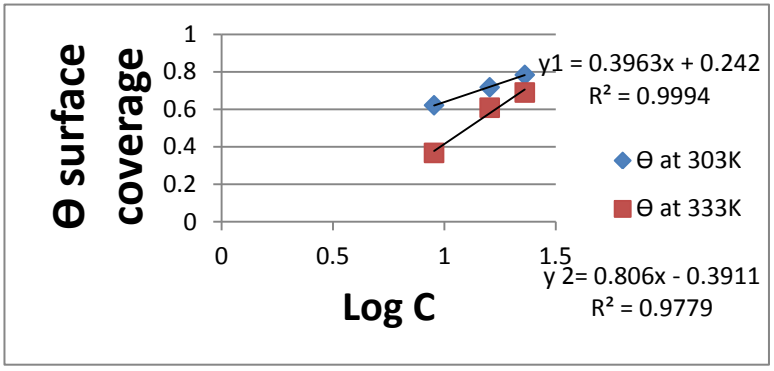
For Temkin adsorption isotherm, the degree of surface coverage (θ) is related to inhibitor concentration (C) according to Equation

Exp (-2*aΘ*) = *K* C

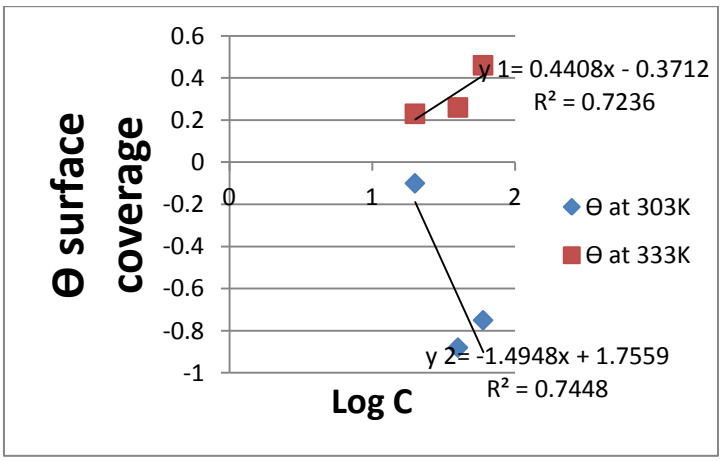
where K is the adsorption equilibrium constant and a, is the attractive parameter. Rearranging and taking loga-rithm of both sides of Equation 3

$$\Theta = \frac{-2.303 \log K}{2a} - \frac{2.303 \log C}{2a}$$

Temkin isotherm for the adsorption of *Azardirachta indica* leaves extract on Zinc surface



Temkin isotherm for the adsorption of Hibiscus rosasinensis leaves extract on Zinc surface



Plots of Θ against log$C$, as presented in graphs, gave linear relationship, which shows that adsorption data fitted Temkin adsorption isotherm. Adsorption parameters obtained from Temkin adsorption isotherms are recorded. The values of attractive parameter (a) are negative in all cases, indicating that repulsion exists in the adsorption layer.

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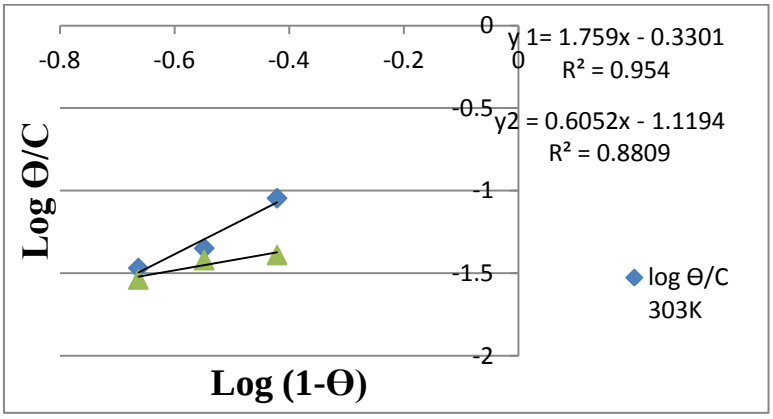
FLORY-HUGGINS ISOTHERM:

Flory-Huggins adsorption isotherm can be expressed according to Equation

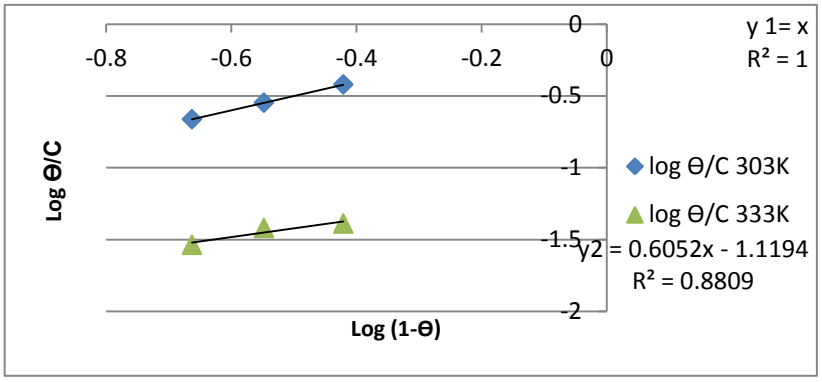
Log ($\frac{\theta}{C}$) = log K+ x log (1 – Θ)

where *x* is the size parameter and is a measure of the number of adsorbed water molecules substituted by a given inhibitor molecule.

Flory-Huggins isotherm for adsorption of aqueous extract of *Azardirachta indica* leaves on HCl media



Flory-Huggins isotherm for adsorption of aqueous extract of *Hibiscus rosasinensis* leaves extract on HCl media



The plots of Log ($\frac{\theta}{C}$) against log (1 - Θ) are shown in graph which the data con-formed to Flory-Huggins isotherm. The values of the size parameter 'a' are positive. This indicates that the adsorbed species of aqueous extract of *Azardirachta indica* leaves is bulky since it could displace more than one water molecule from the Zinc surface.

Free Energy of Adsorption

The equilibrium constant of adsorption of aqueous extract of *Azardirachta indica* and *Hibiscus rosasinensis* leaves on the surface of Zinc is related to the free energy of adsorption (Δ*G*ads) according to Equation.

ΔG = - 2.303 RT log(55.5K)

ΔG = - 2.303 RT [log 55.5 + log K]

where *R* is the gas constant and *T* is the temperature. The free energy of adsorption was calculated from values of *K* obtained from Langmuir and Freundlich , Temkin and Flory-Huggins according to Equation and is recorded.

Adsorption parameters for adsorption of aqueous extract *Azardirachta indica* and *Hibiscus rosasinensis* leaves on the surface of Zinc.

The parameters of Langmuir and Freundlich, Temkin and Florry – Huggins isotherm are presented in Table.

ISOTHERMS	TEMPERATURE	R2	LOG K	ΔGADS	PARAMETER
LANGMUIR METHOD AZI	303 K	1	1.16	- 16.8	1/n = 0.752
	333 K	0.8256	1.36	- 19.7	1/n = 0.310
	303 K	0.626	-0.56	- 6.86	1/n = 0.418

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HR					
	333 K	**0.6804**	**-0.04**	**- 10.86**	**1/n = 1.861**
TEMKIN METHOD	**303 K**	**0.9994**	**0.36**	**- 8.02**	**α = 0.396**
AZI	**333 K**	**0.9779**	**0.62**	**- 7.16**	**α = 0.806**
HR	**303 K**	**0.7236**	**0.2**	**- 8.95**	**α = 0.440**
	333 K	**0.7448**	**- 0.92**	**- 5.25**	**α = 0.494**
FLORRY-HUGGINS METHOD	**303K**	**0.954**	**-1.04**	**- 4.08**	**a = 1.759**
AZI	**333 K**	**0.8809**	**-1.4**	**- 2.19**	**a = 0.605**
HR	**303 K**	**1**	**-0.44**	**- 7.56**	**a = 1.0**
	333 K	**0.8809**	**-1.4**	**- 2.19**	**a = 0.605**

The R^2 (correlation coefficient) values of *Azardirachta indica* leaves extract at 303K and 333K which is nearby unity (1) indicate strong adherence to all adsorption isotherm and the R^2 (correlation coefficient) values of *Hibiscus rosasinensis* leaves extract at 303K and 333 K which is in between the value of unity indicates neutral adherence to all adsorption isotherm. The application of all adsorption isotherms to the adsorption of extract of *Azardirachta indica and* Hibiscus rosasinensis on surface of Zinc indicated that there is no interaction between the adsorbate and adsorbent.

In the HCl test medium, it seems the attachment/adsorption was more fairly adherent and not quickly susceptible to depassivation to create a fresh bare surface for active corrosion reactions/anodic dissolution to occur. The inhibition efficiency was observed to be indirectly proportional to temperature as the inhibition fell as the test temperature raised. as the temperature increased, the increasing atomic/molecular vibrations and agitation weakened the interfacial bond between the extract's active molecular constituents and the metal surface.
This can be attributed to the fact that higher values of activation energy(Ea) in the presence of inhibitor compared to its absence are generally consistent with a physisorption, while uncharged or lower values of Ea in inhibited solution suggested sharing or transfer of charges from the organic inhibitor to the metal surface to for co-ordinate covalent bond.

The increase in the Ea for the corrosion is attributed to a decrease in the adsorption of the inhibitor on the metal surface as the temperature increased and subsequently increase in corrosion rate will result due to the greater exposed area of metal surface to the acid. The values are negative, indicating that the adsorption of the extract on the copper surface was exothermic. The negative value of free energy of adsorption (ΔG o ads) indicated that the spontaneous adsorption inhibitor on the surface of metal.

The thermodynamic data obtained in the presence of Neem and Hibiscus leaves extract at various temperature were recorded in the graph . these values represent the algebraic account of the values of adsorption and desorption. A negative values of ΔG, Gibb's free energy indicates the spontaneous adsorption of inhibitor on the surface of Zn metal. The adsorption is mostly to be exothermic and associated with a decrease in entrophy ΔS of solute while opposite for solvent. The gain in ΔS which accompanies the substitutional adsorption process is attributed to the increase in solvent ΔS, that is the absolute free energy ΔG values increase with increase of IE as the adsorption of organic substances accompany by desorption of aqueous molecules off the surfaces. The high IE may be attributed to the presences of Tannins, terepenoids and other phenolics substances that have been extracted by soaking the leaves of Neem and Hibiscus in water and ethanol. This inhibition may be also due to synergistic interactions between the adsorbed compound.

These results suggested that IE of secondary metabolites depends upon the factors such as their charge distribution, no. of adsorption sites, heat of adsorption, mode of interaction with metal surface, mode of inhibition of microbial growth in moist condition and formation of metallic complex.

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CONCLUSION

Ethanol extracts of fresh Neem and HR were more efficient than aqueous extract. This study reveals that antimicrobial effect of Neem and HR will make it easier for dosage determination and chemotherapeutic index the extract. Each extract has its MIC which is the highest dilution plant extract that still retain an inhibitory effect against the microbial growth which causes corrosion. These extracts have to be proved that the Neem has higher antioxidant potential than HR. The antioxidant such as Phenols, Flavonoid, Tannins, Terpenoids, Alkaloids etc., have proved to be present in these extract which is more efficient for antimicrobial and anticorrosion activity.

The percentage of inhibition in the presence of these inhibitors was decreased with temperature which indicates the physical adsorption was the predominant inhibition mechanism because the quantity of adsorbed inhibitor decreased with increasing temperature.

The IE of the plant extracts increased with increasing in extract concentration and with temperature moisture and atmosphere. These results suggested that IE of secondary metabolites depends upon the factors such as their charge distribution, no. of adsorption sites, heat of adsorption, mode of interaction with metal surface, mode of inhibition of microbial growth in moist condition and formation of metallic complex.

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