EFFECTS OF ORGANIC RESINS AND PLANT EXTRACTS ON CORROSION RATE OF MEDIUM CARBON STEEL IN TETRAOXOSULPHATE VI ACID MEDIUM

BY

Auwal KASIM B. Eng. (ABU) 2000
M.Sc./ENG/38229/2002 – 2003

AN M.Sc THESIS SUBMITTED TO THE POSTGRADUATE SCHOOL , AHMADU BELLO UNIVERSITY, ZARIA, NIGERIA

IN PARTIAL FULFILMENT FOR THE AWARD OF MASTERS OF SCIENCE DEGREE IN METALLURGICAL ENGINEERING

DEPARTMENT OF METALLURGICAL ENGINEERING
AHMADU BELLO UNIVERSITY, ZARIA.
NIGERIA

AUGUST 2007

DECLARATION

I declare that the work in the thesis entitled " **Effects of organic resins and plant extracts on corrosion rate of medium carbon steel in tetraoxosulphate VI acid medium**" has been performed by me in the Department of Metallurgical Engineerimg under the supervision of Prof O. B. Oloche and Dr. S. A. Yaro.

The information derived from the literature has been duly acknowledged in the text and a list of references provided. No part of this thesis was previously presented for another degree or diploma at any University.

Auwal KASIM

| --- | --- | --- |
| ***Name of student*** | ***Signature*** | ***Date*** |

CERTIFICATION

This thesis entitled "**Effects of organic resins and plant extracts on corrosion rate of medium carbon Steel in tetraoxosulphate vi acid medium**" by ***Auwal KASIM*** (M.Sc./ENG/38229/2002 – 2003) meets the regulations governing the award of the degree of Master of Science in Metallurgical Engineering of the Ahmadu Bello University, Zaria and is approved for its contribution to knowledge and literary presentation.

---------- ----------

Prof. O.B. Oloche Date
(Chairman, Supervisory Committee)

---------- ----------

Dr. S.A. Yaro Date
(Member, Supervisory Committee)

---------- ----------

Dr. Ola Aponbiede Date
(Head of Department)

---------- ----------

Prof. S.A. Nkom Date
(Dean, Postgraduate School)

ACKNOWLEDGEMENT

First to Almighty Allah for making it possible for me to see the light of this moment.

Then to my amiable supervisor, Prof. Oyihi B. Oloche, not only for his untiring effort towards guiding me but also in making sure that the work was executed. May God bless him, his immediate family and the entire Oloche family. I am also profoundly grateful to my co-supervisor, Dr. S.A. Yaro, for supplying me with the material used in this work and making valuable contributions to the work.

I would also like to acknowledge the contributions of my friends and the entire Departmental staff for supporting me and rendering valuable assistance in cause of this work. May God reward them.

I am particularly indebted to my well-wishers most especially Prof. Charles Okuofu, Dr. I.A. Madugu, Dr. Junaid Kabir, Dr. A. Ismail, Dr. I.A. Muhammad, Engr. Y.D. Amartey and Muhammad Auwal Ibrahim for rendering constructive criticism and assisting in typing the work.

Finally, I would like to acknowledge the immense contributions of my parents and entire family for their own quota in making me what I am today. To my humble and dedicated wife, Sa'adatu, and little daughter, Fa'izah, my Almighty Allah continue to shower His blessing on them. I love you all.

DEDICATION

To the less-privileged and oppressed whom, despite their God-endowed talent, cannot afford formal education.

ABSTRACT

The effects of organic resins **(Methylene blue and Neutral red)** and plant extracts **(*piliostigma thonningii* and *Gmelina arborea)*** on corrosion rate of medium carbon steel in 0.2M H_2SO_4 acid pickling solution were studied with a view to comparing them with a known standard inhibitor **(Sodium Benzoate)**. Gravimetric and Gasometric measurements were carried out at different inhibitor concentration and Temperature ranges of 0.05 – 0.5% and 30 – 60^0C respectively. Results obtained revealed that all the four compounds tested acted as mixed-type inhibitors, reducing the dissolution of iron and retarding H_2 evolution, comparing favourably with the standard inhibitor at all inhibitor concentrations and temperatures studied. The maximum inhibition efficiencies of the compounds tested were obtained at 30^0C and increased progressively in order of: **Neutral red** (83.29%)**, Methylene blue** (90.96%)**, Sodium Benzoate** (91.50%)**, *Gmelina arborea*** (96.98%) and ***Piliostigma thonningii*** (97.94%)**.** The mechanism of inhibition was elucidated by Kinetic and thermodynamic models. It was concluded that the adsorption of the compounds onto the steel surface, which obeyed the Langmuir and Temkin adsorption isotherms, is the main mechanism of inhibition by these compounds.

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CHAPTER ONE

1.0 Introduction

The method of prevention of metal corrosion based on the use of corrosion inhibitors (henceforth referred to as inhibitors) i.e., chemical compounds or compositions 'which, when present in a system at sufficient concentrations, decrease the corrosion rate has been known for several centuries (ISO, 1989). However, it was only in the middle of the twentieth century that a scientific concept about the mechanism of inhibition was known and first achievements in the direct synthesis of inhibitors appeared after that (Kuznetsov, 2004).

Corrosion inhibitors are used in numerous systems, from water supply systems to the protection of microelectronics and contemporary military equipment. Considering that losses from metal corrosion exceed 5% of the gross national product in industrial countries, the application of inhibitors, which is one of the main methods of corrosion protection, should be considered as a scientific and engineering task of current interest (Kuznetsov, 2004).

Pickling of metals for the purpose of scale removal is widely practiced in the metallurgical industry in the manufacture of various semi-finished products (pipes, sheets, bands), in the machine-construction industry for removing scale formed during the heat treatment of alloys

and during other technological processes (punching, pressing, welding e.t.c.), as well as in power plant for the acid washing of steam boilers and other power installations, in order to clean them of the scale, corrosion products, and encrustations that accumulate during assembly and operation of the installations (Kuznetsov, 2004).

In view of the fact that scale is most commonly removed by chemical means in acids (HCl, H_2SO_4), conditions must be created so as to ensure that the acids dissolve the metal as little as possible after scale removal; this, as already mentioned, can be achieved solely with the use of acid-corrosion inhibitors, which are infact used in the above-mentioned branches of industry (Rozenfeld, 1981).

It is however emphasized that one of the most recent development in pickling techniques, ultrasonic pickling, does not eliminate the use of inhibitors, but rather proffers solutions to the problems of environmental pollution and improvement of pickling yield (Goode *et al.,* 1996).

1.1 Aims and Objectives

The aim of this research work is to investigate the inhibiting effect of organic resins and plant extracts on the corrosion of medium carbon steels in H_2SO_4 acid pickling medium by comparing the result obtained with those of a known standard organic inhibitor, example, sodium benzoate.

Other aims and objectives include to:

1. Investigate inhibitor efficiency of organic resins in H_2SO_4 acid pickling solution for medium carbon steels.
2. Determine whether the extracts of *Piliostigma thonningii* (Monkey bread or camel's foot) and *Gmelina arborea* (Gamhar), and organic resins could inhibit the corrosions for medium carbon steels in H_2SO_4 acid pickling solution.
3. Investigate the influence of Temperature on the performances of the inhibitors.
4. Determine the exact mechanisms of inhibition using thermodynamic and kinetic models.

1.2 Background Information/justification

In metallurgical industries, scale is most commonly removed by chemical means in acids (HCl, H_2SO_4). The aggressive nature of these acids is a source of concern to metallurgists, hence conditions must be created so as to ensure that the acids attack the metal as little as possible. This can be achieved solely with the use of acid-corrosion inhibitors.

It was reported that for batch descaling of medium carbon steels and continuous cleaning processes, H_2SO_4 acid is used. It also provides a better

environment for inhibitors to exhibit higher degree of coverage and inhibition (Selim & Ateya, 1977; Gouda & Shatter, 1970).

The choice of medium carbon steels was not unconnected to their wide use in engineering applications; comparative cheapness, availability and formability. Their subjection to acids (e.g. H_2SO_4) is a common feature during processing – chemical cleaning/pickling (Noor, 2005; Popova *et al.*, 2003;).

The plant extracts were chosen because recent investigators have found out that some plant extracts could be used as corrosion inhibitors in some environments (Abiola and Oforka, 2004; Ekpe *et al.*, 1995). This was corroborated by the fact that these plants extracts are in-expensive, ecologically friendly/acceptable and posses no threat to the environment (Ebenso *et al.*, 2004).

Methylene blue and Neutral red are organic resins used as indicators in Analytical Chemistry. However, recent investigators (Unaegbu, 2004; Tang *et al.*, 2003) have revealed that they could be used as corrosion inhibitors for mild steel in HCl and NaOH solutions respectively, but this has not been comprehensively exploited for medium carbon steel in sulphuric acid despite the fact that these resins are cheap, non-toxic and readily available.

Sodium Benzoate, on the other hand, is a well-known standard acid pickling inhibitor for carbon steels and was chosen for comparative purposes and verification of the results obtained.

Gravimetric method (weight loss) was used to compute the corrosion rates. The volumes of H_2 evolved by the steel samples in different pickling solutions with or without the inhibitors were measured using the arrangement in Fig. 3.1. To thoroughly understand the mechanism of the inhibition, the effects of inhibitor concentration and experimental temperatures on the inhibition efficiency were studied.

1.3 Scope of the study

The study involves corrosion rate determination of the medium carbon steel using weight loss measurements (Gravimetric method) and determination of the volume of H_2 (Gasometric measurement) from the steel samples. The pickling temperature was varied from 30 – 60^0C with an immersion time ranging from 1 – 5 hrs in 0.2M H_2SO_4 acid pickling solution.

1.4 Limitations of the study

There are different ways of evaluating corrosion attack. In this works, the cathodic attack would be evaluated by measuring the volumes

of H_2 evolved using the simple arrangement shown in Fig. 3.1, while the anodic attack is to be computed by weight loss measurement.

The acid concentration was fixed at 0.2M because it is the standard acid concentration for pickling medium carbon steels, while the experimental temperature range of 30 – 60^0C is assumed to be the pickling temperature within the time limits of 1 – 5hrs (Njoku, 1998).

1.5 Contribution to Knowledge

To the best of my knowledge, no previous work has been carried out on the corrosion inhibition properties of the extracts of *piliostigma thonningii* and *Gmelina arborea* trees despite their vast abundance in the Tropical Savannah region. Thus, investigation into their corrosion inhibition ability will provide pioneering knowledge on the list of inexpensive, non-toxic and ecologically friendly/acceptable inhibitors.

CHAPTER TWO

2.0 Literature review

2.1 Corrosion of steel in acid solutions

Corrosion of iron in acid solutions proceeds to the right with the discharge of two electrons. Correspondingly, the hydrogen evolution reaction proceeds to the left with the acceptance of the electrons. The corrosion rate for iron in acid solution is defined (in the absence of external currents) by the condition that the total oxidation current ($Fe = Fe^{2+} + 2e^-$) and the total reduction current ($2H^+ + 2e^- = H_2$) are equal and correspond to the overall reaction:

$$Fe + 2H^+ = Fe^{2+} + H_2 \quad \text{……..……. (2.1)}$$

The electrode potential corresponding to this condition of zero net current is called the **Corrosion Potential**. The corrosion of iron in pickling solution occurs by an electrochemical process in which the overall reaction may be divided into two partial and separate electrode reactions:

<u>At the Anode</u>: (Oxidation) $Fe = Fe^{2+} + 2e^-$ ……..…… (2.2)

<u>At the Cathode:</u> (Reduction) $2H^+ + 2e^- = H_2$.. ……..…….…. (2.3)

<u>Overall</u> : $Fe + 2H^+ = Fe^{2+} + H_2$ ……..…….……. (2.4)

According to Larrabee and Mathay (1960), acid solutions are mildly-to-strongly corrosive to ferrous metals because of the following:

(i) The high Hydrogen-ion concentration of acid solutions promotes Hydrogen evolution.

(ii) The invisible oxide layer normally present on iron is rapidly destroyed by acids.

Certain metallic phases are more favourably oriented for the occurrence of either the anodic (oxidation) or cathodic (reduction) reactions. Hence, Abdul and Sanad (1972) reported that the discharge of Hydrogen ions (H^+) takes place more readily on cementite than on ferrite phases because cementite enhances corrosion by acting as cathodic sites.

2.2 The role of solutions

Most forms of corrosion are the result of electrochemical processes; therefore, the effectiveness of corrosion inhibitors is largely determined by the electrochemical potential of the metal that is to be protected. This potential, together with the pH and the electrochemical reactivity of any component added to the corrosive environment, will determine whether oxidation/ reduction reactions will occur on the metal surface. The electrochemical potential is the driving force for the oxidation to occur while the pH characterizes the activity of the dissociation

products. Together, these two variables define the aggressiveness of the corrosive environment. Therefore, the factors involved in inhibiting corrosion are highly sensitive on the nature and variables involved in chemical solutions (Kuznetsov, 2004).

The materials, which build up the protective layer on the steel, are adsorbed organic inhibitors which come from solution surrounding the metal. For the case of pickling of steels, organic molecules are added in specific concentrations to the H_2SO_4 bath for the purposes of corrosion inhibition. Since the metal surface covered is proportional to the inhibitor concentrations, the concentration of the inhibitor in the medium is critical. There is an optimum concentration, which must be met, which is also highly dependant on concentrations of other solution additives as well as the pH. The inhibitor concentration must be monitored very precisely throughout a pickling operation as if the concentration were to fall below the critical concentration value, inhibition would cease. For corrosion inhibition in acidic solutions, as in the pickling process, a variety of organic compounds can be used. These include triple-bonded hydrocarbons, acetylenic alcohols, sulfoxides, sulfides, mercaptans, as well as many families of condensation products. Careful choice of inhibitors is essential to

correct corrosion inhibition. For example, some organic compounds inhibit corrosion in hydrochloric solutions, but stimulate corrosion in sulfuric solutions. In a pickling situation where one or both of these acids may be used in a given process, the correct choice of inhibitors is crucial to the successful inhibition of oxide formation (Schweitzer, 1989).

2.3 Acid pickling

Chemical cleaning and acid pickling processes are widely used in industrial processes to remove scales on metallic surface exposed to high concentration acidic media at some elevated temperatures (Noor, 2005; Popova *et al.*, 2003). Inhibitors are thus required to protect the metals against such an acid attack (Trabanelli, 1987; Schmitt, 1984). Many natural and synthetic inhibitors (gelatin, glue etc) were applied in earlier times to suppress this attack.

Rozenfeld (1981) reported that the most commonly used acid solutions in pickling are H_2SO_4 and HCl and concluded that the optimal concentration of H_2SO_4 acid for pickling steels in the metallurgical industry is 20 to 22%, while that of HCl acid is 18 to 20%.

It was also reported that H_2SO_4 acid is the cheapest, most commonly employed and very efficient for batch descaling of medium carbon steels

and continuous cleaning processes, while HCl acid is a specific purpose oxide remover (employed prior to galvanizing or tinning stainless steel) and is the preferential acid used in batch pickling of hot-rolled or heat-treated high carbon steel (**www.corrosionsource.com**).

2.4 Mechanism of pickling

According to Evans (1960), the oxide films appearing on carbon steels and low-alloy steels comprise several layers which differ in composition, fig 2-1, and that the bottom layer of "high-temperature" scale has a composition similar to wustite (FeO); the next layer consists of magnetite (Fe_3O_4), and the outermost layer is hematite, ($Fe_2O_{3)}$. The "low temperature" scale consists of magnetite and hematite. Wustite oxide is unstable at temperatures below 575°C, and therefore it is absent in "low-temperature" scale.

Bogoyavlenskaya (1967) established that the "low-temperature scale has a more complex composition; apart from hematite and magnetite, it contains a third layer, directly adjacent to the metal, which consists of wustite (a solid solution of magnetite and wustite), inclusions of highly disperse metallic iron, and wustite. "High-temperature" scale consists of only two layers: hematite and magnetite, because wustite is more soluble and dissolves more easily/readily in acids compared to hematite and

magnetite, it is attacked first by the acids. The removal of wustite, hematite and magnetite from a surface is largely governed by the action of local corrosive elements appearing during the voluntary breakup of the film:

Iron (anode)/acid/Fe^{3+} oxide (cathode).

At the cathode, Fe^{3+} is reduced before Fe^{2+}, which passes into solution. This phenomenon is called REDUCTION DISSOLUTION.

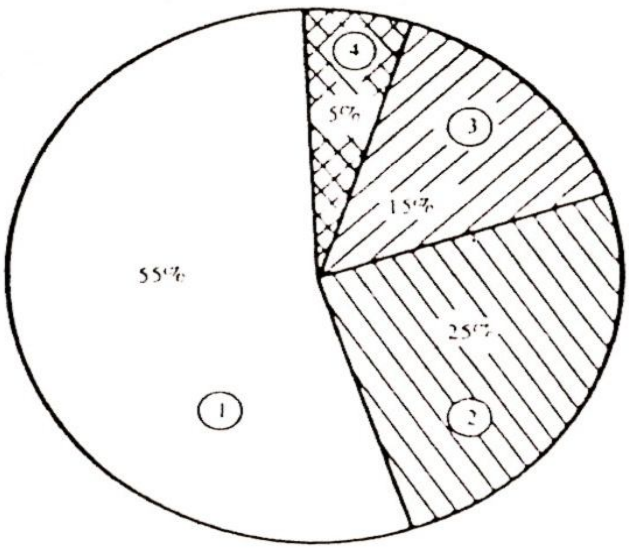
The interaction of H_2SO_4 with the iron oxides in the carbon steels and low-alloy steels is elucidated by the following equations (Rozenfeld, 1981):

$$FeO + H_2SO_4 = FeSO_4 + H_2O \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \ldots(2.5)$$

$$Fe_2O_3 + 3H_2SO_4 = Fe_2(SO_4)_3 + 3H_2O \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2.6)$$

$$Fe_3O_4 + 4H_2SO_4 = FeSO_4 + Fe_2(SO_4)_3 + 4H_2O \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2.7)$$

$$Fe + H_2SO_4 = FeSO_4 + H_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2.8)$$



Key:
1.Dissolution of steel
2. carry over with parts sent for washing
3. overflow with solutions used
4. Dissolution of scale

Fig. 2.1: Composition of Scale on Steels and its removal by pickling
***Source*: *Rozenfeld, 1981*.**

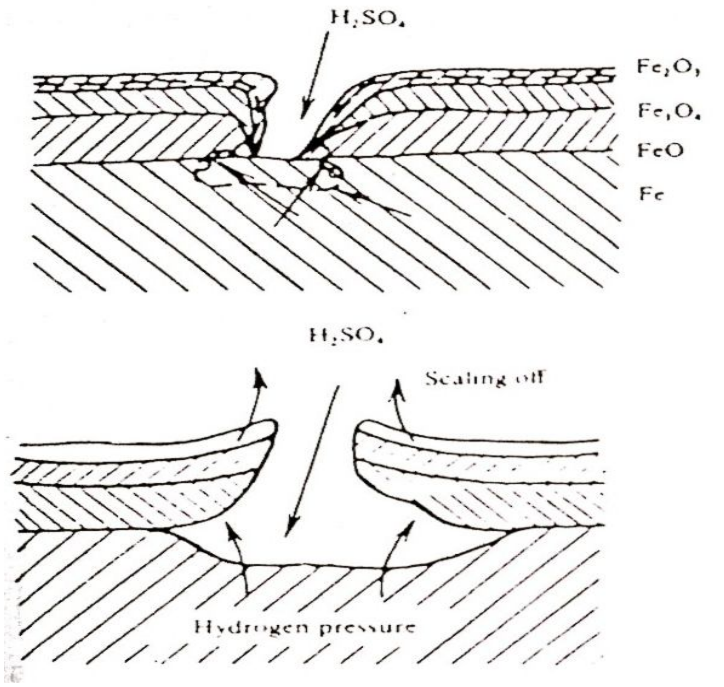


Fig. 2.2: Expenditure of acid during pickling of steels
Source*: *Rozenfeld, 1981.

2.5 Synthetic organic inhibitors

Makhlouf *et al.* (1996) reported that the essential features of inhibition theory indicated that organic inhibitors are capable of forming onium ions and accordingly exist in acid solutions as cations. These ions are cathodically adsorbed and thus blanket the cathodic area, preventing Hydrogen ions from attaching to the surface and Hydrogen gas evolution.

Babagi *et al.* (1989); Ekpe *et al.* (1995); Onuchukwu (1990); Hackerman and Makrides (1954), reported the effect of organic

compounds with functional groups containing hetero-atoms of oxygen (O), Sulphur (S) and Nitrogen (N), on the corrosion behaviour of steel mainly in the acid environment and concluded that these atoms adsorb onto the steel surface, thereby forming a thin film which protects the steel from acid attack.

Protection efficiency of organic inhibitors is attributed mainly to the presence of a polar group acting as an active center for adsorption on the metallic surface (Gomma and Wahdan, 1994).

Kuznetsov (1996) reported that the majority of adsorption inhibitors are organic compounds and that many researchers used the linear free energy (LFE) relationship to reveal the role of the inhibitor structure.

Szauer and Klenowicz (1975); Mayanna and Setty (1975) revealed that Nitrogen-containing organic compounds are known to act as corrosion inhibitors.

Martinez and Stern (2003) established that most of the well-known acid inhibitors are organic compounds that contain Nitrogen, Sulphur, Oxygen and multiple bonds in the molecules through which they adsorb onto the metal.

Tang *et al.* (2003) justified that efficient inhibitors should possess plentiful π-electrons and unshared electron pairs on either Nitrogen atoms or sulphur atoms of the inhibitor to the d-orbitals of Iron, and by means of transference of electrons chemical adsorption may occur on the steel surface. Thus, corrosion may be suppressed by the protective film on the steel surface.

Bouklah *et al.* (2005) investigating the inhibitive ability of some organic compounds found that those containing electronegative functional groups and π-electrons in triple or conjugated double bonds are usually good inhibitors; heteroatoms such as Sulphur, Phosphorus, Nitrogen and Oxygen as well as aromatic ring in their structures are the major adsorption centers. It was concluded that the inhibitive effect was enhanced by several Nitrogen-containing organic compounds.

Sing (1993); Abd-El-Nabey *et al.* (1986); Raman and Labine (1986), established that organic compounds containing both N and S atoms are of particular interest as they give better inhibition efficiency than those containing N or S alone. Among these are thiourea derivatives, which are found to be toxic and induce

permeation of Hydrogen into the metal causing Hydrogen embrittlement (Schmit, 1984).

Unaegbu (2004) investigating the inhibitive action of Methylene blue dye on Al corrosion in KOH solution, reported that Methylene blue (MB) inhibits Al corrosion in KOH solutions, the Inhibition Efficiency (IE%) increasing with increase in MB concentration and decreasing with rise in temperature. The inhibitor adsorption, the author concluded, approximated to Freundlish and Langmuir Isotherms.

Tang *et al.* (2003) in the research work on the effect of Neutral red on the corrosion inhibition of cold rolled steel in 1.0M HCl acid solution established that Neutral red is an effective inhibitor for corrosion of cold rolled steel in 1.0M HCl acid, and the IE% increased with decrease in temperature. It was concluded by asserting that Neutral red is a mixed-type inhibitor for steel in 1.0M HCl and that it acts by process of adsorption, which obeyed the Langmuir adsorption Isotherm.

Njoku (1998) while studying the effects of inhibitors on corrosion of low carbon steel in HCl acid pickling solution concluded that formaldehyde, Acetaldehyde and Benzaldehyde

inhibit both the corrosion and Hydrogen evolution reactions of low carbon steels in HCl solution to a varying degree, implying that they are both Anodic and Cathodic inhibitors.

Selim and Ateya (1977) investigated the corrosion Kinetics of mild steel in the presence of cyanoguanidine formaldehyde resins and concluded that the presence of the resins decreased both the rate of Hydrogen evolution and corrosion rate to the same degree. The activation energy of Hydrogen evolution and of the overall corrosion reaction were found to be equal and characteristic of diffusion controlled processes.

2.6 Natural plant extracts as inhibitors

Naturally occurring materials, mostly known to be non-toxic, have found an increasing number of applications in many fields due to the diversity of the chemical structures of such materials. Investigation of natural inhibitors is particularly interesting because they are in-expensive, ecologically friendly and posses no threat to the environment (Ebenso *et al.,* 2004).

Stern and Geary (1957) using embrittlement detector tests have shown that **tannins** are effective inhibitors for controlling stress corrosion cracking in steam boilers. *Quebracho* extract from the bark of a South

American tree by the same name is one such tannin, which is sometimes added to boiler waters for preventing scaling.

Tannins are natural products, characterized by their ability to precipitate proteins. Tannins are high-molecular-weight (>500) compounds with many phenolic groups, distinguished by three principal groups; the condensed, the hydrolysable (gallotannins and ellagi-tannins) and the phlorotannins (Ramesh *et al.*, 2003; Hagerman, 1988). The diverse biological effects of tannins and their common occurrence in plants have created a widespread interest in their use and applications as corrosion inhibitors in various fields of interest.

Martinez (2002); Martinez and Stern (2001); Booth and Mercer (1964) established that the inhibitive effect of some plants' solution extracts has been attributed to the presence of tannin in their chemical constituents.

Ekpe *et al.* (1994); Hosary and Selim (1984) reported that natural products of plant origin contain different organic compounds (E.g alkaloids, tannins, pigments, organic and amino acids) and are mostly known to have inhibitive action.

Other reports have also shown that some naturally occurring substances, such as honey (El-Etre and Abdallah, 2000; El-Etre, 1998); henna (Al-Sehaibani, 2000) and extracts of fruits (Saleh *et al.*, 1980; El-Hosary *et al.*, 1972, 1980) have inhibitive properties/abilities.

Ekpe *et al.* (1994) and Saleh, *et al.* (1980) used the aqueous extracts of some natural products (fruits, fruit shells, leaves, seeds) as corrosion inhibitors of some metals.

Hammouti *et al.* (1995) reported that the application of extracts of an antibiotic and *pyrroldine* alkaloids *bgugaine* and *irniine* had shown that *bgugaine* was a highly efficient corrosion inhibitor for Iron corrosion in 1M HCl.

Abiola and Oforka (2002) found that the *Cocosnucifera* juice inhibits the corrosion of mild steel in Hydrochloric acid.

Ebenso *et al.* (2004) investigated the mode of inhibiting action of leaf extracts of *Carica papaya* (Pawpaw) and *Azadirachta indica* (Neem) by calculating some kinetic and thermodynamic parameters for aluminuim corrosion and inhibitor adsorption processes in HCl medium using weight loss, thermometric and hydrogen evolution techniques. It was found that the extracts showed significant

inhibitive action in HCl induced corrosion of Aluminium and that the inhibition was probably due to the adsorption of the extracts onto the surface of Aluminium. It was concluded that the adsorption obeyed Freundlish, Temkin and Flory-Huggins adsorption isotherm at all concentration studied at 40°C.

2.7 Classification of inhibitors

Fontana and Green (1987) classified inhibitors into the following: adsorption-type, oxidizers, hydrogen evolution poison and scanvengers.

Uhlig (1963) established that there are several classes of inhibitors conveniently designated as follows: (i) Passivators (ii) Organic inhibitors (iii) Vapor phase inhibitors.

Uhlig's position was corroborated by Kirk (1989) who reported that inhibitors may be classified into inorganic, organic or vapor-phase. He then noted that inorganic inhibitors may function by a mechanism different from organic or vapor-phase.

Bockris & Drazk (1972); Evans (1960) simply classified corrosion inhibitors depending on whether their actions cause a decrease of the anodic reaction (oxidation – generally termed the

corrosion reaction) or the cathodic reaction (reduction – hydrogen evolution or oxygen reduction reaction).

Fisher (1971) advanced a more complex classification of inhibitors based on the specific mechanism by which they achieve inhibition: Interface-inhibition and electrolyte-layer inhibition. It was further suggested that interface inhibition results from substances which are adsorbed at the metal surface and decrease the rates of physical, chemical or electrochemical processes in the corrosion mechanism while electrolyte-layer-inhibition arises if an inhibitor interferes with processes which are not on the metal surface but in its vicinity such as the electrolyte layer closest to the metal surface.

Antropov (1972) asserted that the most commonly used inhibitors for neutral solutions are inorganic compounds of the anionic type and that corrosion inhibitors for acid solutions are almost exclusively organic substances in the form of amino, imino, carboxyle, carbonyl and thio groups.

2.8 Adsorption mechanism

Riggs (1973) revealed that in formulating organic inhibitor system, it is necessary to know the inhibition mechanism and the

application field of the molecules concerned. It is generally accepted that organic molecules inhibit corrosion by adsorption at the metal/solution interface, with the degree of adsorption depending on the chemical structure of molecules, the chemical composition of solutions, the nature of the metal surface, the temperature and the electrochemical potential at the metal/solution interface.

According to Kirk (1989), the main types of adsorption are Electrostatic, chemisorption, and π-bond (delocalised electron).

Kuznetsov (2004) in his review of physiochemical aspect of metal corrosion inhibition in aqueous solutions cited that as a rule, cation-active inhibitors slow down cathodic reactions and active metal dissolution. It was further reaffirmed that local corrosion is more efficiently prevented by anion-active inhibitors, however, the electrostatic interaction of an inhibitor with a metal surface is not the only motive force of adsorption.

Afanas'ev *et al.* (1989); Damaskin and Stenina (1986) found that contributions to electrostatic force can be made by "Squeezing-out" of inhibitor species from the interionic space and by hydrophobic interaction of non-polar inhibitor fragments with water. Donor-acceptor interactions between a metal and an inhibitor

can result in a stronger chemisorption binding of the latter to the surface.

Antropov (1972) proposed a simplified approach which is found to be useful for formulating inhibitor action. He proposed that if a metal is dissolved from the active state, which is usually the case in acids, then, for moderate metal surface coverage (θ), it is possible to single out two main contributions to the corrosion inhibition efficiency, viz., related to changes in the ψ_1 – potential and to the surface blocking:

$$\log \psi = \text{const.} \times \Delta\psi_1 - \log (1 - \theta) \quad \ldots\ldots (2.9)$$

where: γ is the inhibition coefficient defined by:

$$\gamma = K_o / K_{inh} \quad \ldots\ldots (2.10)$$

(K_o and K_{inh} are the corrosion rates in a reference solution and in a solution containing the additive inhibitor under study).

Grigoriev and Ekilik (1978) studied this problem in most detail in relation to acid corrosion, which usually occurs in the active dissolution region of potentials. They showed that if the inhibitor species are small and their adsorption increases the activation energy ($\Delta G^{\neq}$) due to the charge redistribution in the double electric layer, the following equation is valid:

$$\text{Log } \gamma_R = \log \gamma_H + \rho\delta \quad \text{.....(2.11)}$$

Where: ρ is the reaction parameter, which is assumed to be equal to unity for a standard reaction series and which depends on the nature of the reaction being studies and on the conditions under which it occurs, $^{*}\delta$ is a constant of a substituent R, which accounts for its electron-donor (δ<O) or electron acceptor (δ>0) effect on the reaction center in comparison with Hydrogen.

In general case of inhibitors capable of partial blocking of the active sites, the above equation assumes the form:

$$\log\left(\frac{\gamma_R}{\gamma_H}\right) = \rho\delta - \log\left(\frac{\theta_R}{\theta_H}\right) \quad \text{---------- (2.12)}$$

where: θ_H and θ_R are the degrees of coverage of the metal surface by the non-substituted and substituted inhibitor of the given reaction series, respectively.

Damaskin *et al* (1971) assumed that at the potential of maximum adsorption, the degree of surface coverage is given as a first approximation by the equation:

$$\theta = (C_o - C)/(C_o - C') \quad \text{.....(2.13)}$$

where: C_o is the capacitance of the double layer in the supporting electrolyte alone.

C is the capacitance in the solution with the organic substance added.

C′ is the capacitance of the double layer at the limit of coverage of the electrode surface with the organic substance.

The degree of coverage of the surface with the inhibiting substance can also be calculated using kinetic data. Here, Rozenfeld (1981), opined that the adsorbed organic substances, like the inorganic substances, put completely beyond the sphere of the anodic reaction that part of the surface which is coated with inhibitor (assuming that the rate of the anodic reaction on it drops to practically zero). Hence the following relation can be used to find θ:

$$\theta = 1 - i/i_o \quad \text{.....(2.14)}$$

where: i and i_o are the current densities at the given potential in electrolytes with and without inhibitors, respectively.

These relations are often used to calculate the degree of coverage for self-dissolution (corrosion). Then data on the dissolution rates in electrolytes with (K_{inh}) and without (K_o) inhibitors are employed.

$$\theta = 1 - \frac{K_{inh}}{K_o} \quad \text{.....(2.15)}$$

Sekine and Hirakawa (1986) evaluated the degree of surface coverage from weight loss measurement, thus:

$$\theta = (w_o - w)/(w_o - w_m) \quad \text{.....2.16)}$$

where: w_m is the smallest weight loss.

Bagotskii (1965) observed that in some cases the differences in the degrees of surface coverage by organic substances, calculated according to the kinetic characteristics and from direct measurements of the amount of substance adsorbed (for instance, with radioactive tracers), are found to be identical. This was observed while investigating the adsorption of higher aliphatic alcohols and Isostructural alcohols on a smooth platinum electrode.

The adsorption of inhibitors may also vary with the activation energy of the electrochemical reaction. This was established by Weber *et al* .(1959) who proved that the dependance of the rate constants of the cathodic and anodic reactions on the degree of surface coverage by the inhibitor is given by:-

$$K = K_{\theta = o}(1 - \theta) + K_{\theta = 1} \cdot \theta \quad \text{.....(2.17)}$$

where: K is the effective value of the rate constants of the electrode reactions, relative to the entire electrode surface, and $K_{\theta = o}$ and $K_{\theta = 1}$ are the rate constants of the electrode reactions for $\theta = o$ and $\theta = 1$

Bockris *et al.* (1964) revealed that for an organic compound to be adsorbed onto the metal surface from an aqueous solution, each organic molecule has to displace n molecules of water. They derived an equation for the standard free energy of the thermodynamic cycle for adsorption and desorption of water and organic compounds as follows:

$$\Delta G_a = \Delta G_v\left(org\right) - n\ \Delta G^o_{(w)} - RT\ln\frac{p_{(org)}}{p^n_{(w)}} + RT\ln\frac{C_s}{55.5} \quad \text{---------- (2.18)}$$

where: n is the number of water molecules.

$\Delta G^o_{(w)}$ is the standard free energy of water adsorption from the Solution.

$\Delta G_v\left(org\right)$ is the standard free energy of adsorption of organic compound from the solution.

$P^n{}_{(w)}$ is the vapour pressure of water at Temperature T.

$P_{(org)}$ is the vapour pressure of pure organic compound at Temperature T.

C_s is the saturation concentration of organic compound.

R is the universal gas constant.

The first two terms depend on the interaction energy of the organic compound and water with the metal surface; the third and fourth terms characterize the properties of the substance under consideration.

Szkarska and Wieczorek (1971) reported that the degree of coverage of the steel surface by the adsorbed molecules was found to be influenced by the following factors:

(i) Solubility of the given compound

(ii) Presence of functional group

(iii) Interaction between adsorbed molecules

They further revealed that within a given homologous series, the contribution of the interaction between adsorbed molecules increases with their length.

Hence, the process of adsorption and formation of protective layers on a metal substantially depend on the charges of the surface and inhibitor species (Kuznetsov, 2004).

2.9 Adsorption isotherms

Damaskin *et al.* (1971) and Damaskin and Stenina (1986) revealed that if data on the degree of surface coverage by the inhibitor is available, then the adsorption Isotherm can be determined, and the nature of this Isotherm yields valuable information about the properties of the adsorbed substance as well as their interaction with electrode surface.

Many equations have been proposed to describe the adsorption Isotherm. The experimental data are most often, according to Damaskin, described best by the Isotherms of Langmuir, Frumkin and Temkin:

$K_c = \theta/(1 - \theta)$ …… ……..(2.19)

$K_c = \frac{\theta}{1-\theta} \exp(-2a\theta)$ ……..(2.20)

$K_c = \frac{\exp(a\theta) - 1}{1 - \exp[-a(1-\theta)]}$ ……..(2.21)

where: K is the adsorptional – equilibrium constant,

C is the concentration of the substance in the solution, in moles/litre

a is the attraction constant.

The constant of adsorptional equilibrium K is found from the free energy of adsorption:

$K = \exp(--\Delta\sigma/RT)$ ……..(2.22)

σ is the interfacial tension and R the gas constant which can be calculated from the degree of coverage of the surface, if this coverage takes place according to the Lagmuir Isotherm:

$$\frac{C}{55.5} \exp\left[\frac{-\Delta G_{inh}}{RT}\right] = \frac{\theta}{1-\theta}$$ .... 60^0 C

Szkarska and Wieczorek (1971) also investigated the adsorption Isotherm on mild steel in H_2SO_4 acid solutions for primary aliphatic

amines, alcohols and acids containing 6 to 12 carbon atoms and observed that these compounds were adsorbed on the steel according to the Frumklin's adsorption Isotherm:

$$\frac{\theta}{1-\theta} \quad \exp(f\theta) = K_c \quad \text{.....(2.24)}$$

Where: K is equilibrium constant of the adsorption reaction

f is a parameter connected with the variation of absorption with coverage.

Bouklah *et al.* (2005) investigating the inhibiting properties of new bipyrazole derivatives in Hcl acid solution found, also, an S-shaped adsorption Isotherm on the steel surface electrode according to the Frumkin Isotherm:

$$\left(\frac{\theta}{1-\theta}\right) \exp\left(-f\theta\right) = \frac{1}{55.5} \exp\left(\frac{-\Delta G_{ads}}{RT}\right) \text{.....(2.25)}$$

where: f is a function of adsorptional energy and

ΔG_{ads} is the standard free energy of adsorption.

Bockris and Khan, (1993); Temkin (1941) and Frumkin, (1926) while studying the adsorption Isotherm of various organic inhibitors showed that the adsorption obeyed the following equation:

$$\theta = \frac{1}{F} \ln(Io\ C) \text{.....(2.26)}$$

***where*:** C is the additive concentration

Io is the value of Langmuir constant

F is a constant depending on intermolecular interactions in the adsorption layer and on the heterogeneity of the surface.

Khamis (1990) in trying to evaluate the standard adsorption free energy (ΔG^O), employed the following equation:

$$K = \left(\frac{1}{55.5}\right) \exp \left(\frac{-\Delta G^o}{RT}\right) \text{.....(2.27)}$$

The standard absorption entropy ΔS^O can be calculated according to the basic thermodynamic equation:

$$\Delta G^O = \Delta H^O - T\Delta S^O \text{ ....(2.28)}$$

Zhao and Mu (1999) reported that according to the Van't Hoff equation:

$$1n\ K = (--\Delta H/RT) + \text{constant} \text{ ....(2.29)}$$

Vashi and Champaneri (1997) calculated the values of activation energy (E_a) using the Arrhenius equation:

$$1n \left(\frac{r_2}{r_1}\right) = \left(\frac{E_a \Delta T}{RT_1T_2}\right) \text{ .... (2.30)}$$

where: r_1 and r_2 are corrosion rates at temperatures T_1 and T_2, respectively, and $\Delta T = T_2 - T_1$.

The heats of adsorption, Q_{ads}, could be calculated for the various inhibited systems using the following equation (Bhajiwala and Vashi, 2001; Ekpe *et al*.,1995):

$$Q_{ads} = 2.303R\left\{\log\left(\frac{\theta_2}{1-\theta_2}\right) - \log\left(\frac{\theta_1}{1-\theta_1}\right)\right\} \frac{T_1 \ T_2}{T_2 - T_1} \quad KJ\ MOL^{-1} \quad \ldots\ldots\ldots\ldots\ldots \ (2.31)$$

where: θ_1 and θ_2 are the surface coverages at temperatures T_1 and T_2 respectively.

The free energy of adsorption (ΔG_{ads}) at different temperatures were calculated, according to Rodosovic *et al.* (1995), using the equation:

ΔG_{ads} = - RT 1n (55.5K)……………………………………..(2.32)

where: K = θ/c(1 – θ)

θ is the degree of coverage on the metal surface,

C is the concentration of inhibitor *(in mol $^{-1}$)*

K is the equilibrium constant.

Tang *et al*. (2003) reaffirmed that the logarithm of the corrosion rate (υ) could be represented as a straight line functon of 1/T of steel in acid medium:

1n υ = -- E_a/RT + 1n A ………………………….. …………(2.33)

where**:** Ea represents the apparent activation energy

R is the universal gas constant

T is the absolute temperature

A is the pre-exponential factor.

2.10 Measurement of the degree of inhibition

The efficiency of inhibition, recorded as percent inhibition EI% percent is calculated as follows:

$$EI\% = \left(1 - \frac{W_{corr}}{W_{corr}^{O}}\right) 100 \quad \text{.....(2.34)}$$

Where: W_{corr} is the weight loss of the iron sheet in the presence of an inhibitor and W_{corr}^{O} is the weight loss of the iron sheet in the absence of an inhibitor.

In the case of the polarization method, the relation determining the inhibition efficiency (EI%) is given as follows:

$$EI\% = \left(1 - \frac{I_{corr}}{I_{corr}^{o}}\right) 100 \quad \text{.....(2.35)}$$

where: I_{corr}^{o} and I_{corr} are the uninhibited and inhibited corrosion densities, respectively, determined by the extrapolation of the Cathodic Tafel Curves to relevant corrosion potential.

Quraishi and Jamal (2002) established that the percentage inhibition efficiency (IE%) and surface coverages (θ) of each concentration could be calculated using the following equations:

$$EI\% = \frac{r_o - r}{r_o} \times 100 \quad \text{.....(2.36)}$$

$$\theta = \frac{r_o - r}{r_o} \quad \text{……..……. ……(2.37)}$$

where: r_o and r are the corrosion rates in the absence and presence of inhibitors respectively.

2.11 Factors affecting corrosion inhibition of carbon steels in acid solutions

2.11.1 Steel Composition

Abdul and Sanad (1972) investigated the corrosion and corrosion inhibition of carbon steel and cast iron in acid solutions and established that inhibitor efficiency increases as the carbon content of steel increased. In particular, it was observed that the inhibition efficiency of Quinoline ethiodide was highest at carbon content ≥0.97%. Discussing the observed phenomena, it was suggested that the attachment of the discharged inhibitor molecule on ferrite or pearlite phase was less tenacious than on a separate phase of cementite or graphite.

2.11.2 Concentration and Inhibitor Type

Vosta and Eliasek (1971) studied corrosion inhibition from aspect of quantum chemistry and noted that the physicochemical properties of corrosion inhibitors such as molecular weight, basicity, solubility, electron density, dipole moment, electronic structure, ion

size and charge play important roles in determining the selection of inhibitors. Discussing the results, it was stated that inhibitor efficiency depends mostly upon the energy of highest occupied molecular orbital (HOMO): K_i, which is a theoretical analogue to the ionization potential of the substance; and the energy of the lowest free molecular orbital (LFMO); K (-1), which illustrates the electron affinity of the molecule. They showed that inhibition efficiency increases with the energy of HOMO orbital and that inhibitor molecules act as electron donors when blocking corrosion reactions. This view of corrosion inhibitors acting as electron donors was upheld by Issa *et al.* (1973) and Desai *et al.* (1971).

Gouda *et al.* (1972) and Ammar and Riad (1969) showed that oxidizers play a bifunctional role in the corrosion of metals in aqueous solutions – intensifying the attack on metals at very low concentrations and inducing passivation at higher ones.

Talati and Modi (1979); Maitra and Barua (1974); Sampat and Vora (1974) reported that at constant acid concentration, inhibition efficiency of organic inhibitors increases with increased concentration of inhibitor but reaches a maximum at a certain

inhibitor concentration beyond which it remains practically constant.

2.11.3 Concentration and Acid Type

Gouda *et al.* (1967) arranged some inorganic acids according to increasing order of aggressiveness: $HClO_4$ < H_2SO_4 < HCl < HNO_3. H_2SO_4 acid is the cheapest and most commonly employed. It is very efficient for batch descaling of medium carbon steels and continuous cleaning processes. While HCl acid is a special purpose oxide remover (employed prior to galvanizing or tinning stainless steel); It is the preferential acid used in batch pickling of hot-rolled or heat-treated high carbon steel (**www.corrosionsource.com**).

2.11.4 Temperature

For organic compounds which show inhibitive properties, the effect of temperature varies according to inhibitors. Hoar and Holliday (1953) noticed that while some organic compounds are better inhibitors at elevated temperatures presumably due to increase in adsorption at higher temperatures, others are more efficient at room temperature.

2.11.5 Interaction between inhibitor and metal in acid solution

Several organic compounds that show inhibitive properties undergo one or a combination of these processes at the metal-solution interface: hydrogenation or reduction, protonation and polymerization (Antropov, 1967). The overall inhibition efficiency of these compounds depends on the electro-physical properties of the products of these reactions and the rate at which they are formed (Todd and Butzke, 1964).

2.12 Expressions of corrosion rate

Fontana and Greene (1987) suggested that to make meaningful comparison between metals and non-metals on the basis of their corrosion resistance, the rate of attack for each material must be expressed quantitatively. Corrosion rates have been expressed in a variety of ways in the literature, as listed in table 2.1 .

Table 2.1: Comparison of Corrosion-rate expressions for Engineering applications.

Expression	Comments
Weight loss, g or mg	Poor-sample shape and exposure time influence results
Percent weight change	
Milligrams per square decimeter per day (mdd)	Good but expressions do not give penetration rates
Grams per square decimeter per day	
Grams per square centimeter per day	
Grams per square centimeter per hour	
Grams per square meter per hour	
Grams per square inch per hour	
Moles per square centimeter per hour	
Inches per year	Better – expressions give penetration rates
Inches per month	
Millimeters per year	
Mils per year (mpy)	Best-expresses penetration without decimals or large numbers

Source: Corrosion Engineering, Fontana and Greene (1987).

In summary, the most desirable way of expressing corrosion rates is the mils per year (mpy) and it is readily calculated, according to Fontana and Greene (1987), from weight loss of the metal specimen during the corrosion test by using the formular:

$$mpy = \frac{534\ W}{DAT} \quad \text{.....(2.38)}$$

where: W is the weight loss, g

D is the Density of specimen, g/cm^3

A is the Area of Specimen, cm^2

T is the exposure time, hr.

From standpoint of convenience, mpy is preferred, since the corrosion rate of practically useful materials varies between approximately 1 and 200mpy. Thus, using this equation, it is possible to present corrosion data using small whole numbers and avoiding decimals.

On a more simplistic note, corrosion rate could also be calculated, (Njoku, 1998), using the following equation:

$$corrosion\ rate = \frac{Weight\ loss}{Surface\ Area\ x\ Time}\ g/cm^2/\min s \quad \text{----------(2.39)}$$

And the Hydrogen evolution rate using:

$$H_2\ evolution\ rate = \frac{V_{300}}{Surface\ Area\ x\ Time}\ cm^3/\min s \quad \text{----------(2.40)}$$

2.13 Experimental inhibitors

2.13.1. Sodium benzoate (C_7H_5OONa)

This a white amorphous, granular or crystalline, powder. It is odourless, or with a faint odour of Benzoin, tastes unpleasant, sweetish and saline. Its melting point is about 100^{o}C and it is soluble at 15.5 in about 2 parts of water, slightly soluble in alcohol (90%). Its formular weight is 144.1g (The British Pharmacopoeia, 1988).

2.13.2. Methylene blue ($C_{16}H_{18}N_3ClS, 3H_2O$)

Tetramethylthionine chloride is a dark greenish, crystalline powder with a metallic luster, or a dull, dark green or brown powder. It is almost odourless and is soluble in water, in alcohol (90%) and in chloroform. Mainly used as an indicator in analytical chemistry (The British pharmacopoeia, 1988).

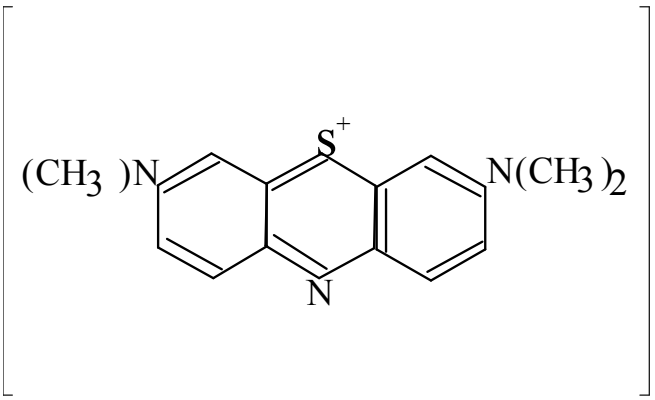


Fig. 2.3: Structure of Methylene blue
Source: The British pharmacopoeia 1988

2.13.3. NEUTRAL RED

Dimethylaminobenzene – O – carboxylic acid is also a common indicator in analytical chemistry. (The British pharmacopoeia 1988).

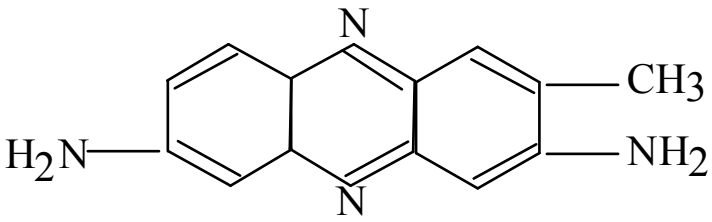


Fig. 2.4: Structure of Neutral Red

Source: The British pharmacopoeia 1988.

2.13.4. *Gmelina arborea* Roxb.

Kingdom: Plate

Division: Magnoliophyta

Class: Magnoliopsida

Order: Lamiales

Family: Verbenaceae

Genus: *Gemelina*

Species: *G. arborea*

Gmelina arborea, locally known as **Gamhar**, is a fast growing deciduous tree, occurring naturally throughout greater part of India at altitudes up to 1500 meters. It also occurs naturally in Myanmar, Thailand, Laos, Cambodia, Vietnam, and in southern provinces of China, and has

been planted extensively in Sierra Leone, Nigeria, Malaysia, and on experimental basis in other countries as well. It is also planted in gardens and avenues.

Gmelina arborea is a fast growing tree, which though grows on different localities and prefers moist fertile valleys with 750-4500 mm rainfall. It does not thrive on ill-drained soils and remains stunted on dry, sandy or poor soils; drought also reduces it to a shrubby form.

The *Gmelina arborea* tree attains moderate to large height up to 30 m with girth of 1.2 to 4.5 m with a clear bole of 9-15 m. It has a smooth whitish grey (ashy) corky bark, warty with lenticular tubercles exfoliating in regular patches when old.

It is a treat to see the *Gmelina arborea* tree standing straight with clear bole having branches on top and thick foliage forming a conical crown on the top of the tall stem. The bark is light grey coloured, exfoliating in light coloured patches when old, blaze thick, a chlorophyll layer just under the outer bark, pale yellow white inside.

Gmelina arborea wood is pale yellow to cream coloured or plukish-buff when fresh, turning yellowish brown on exposure and is soft to moderately hard, light to moderately heavy, lustrous when fresh, usually straight to irregular or rarely wavy grained and medium course textured.

Flowering takes place during February to April when the tree is more or less leafless whereas fruiting starts from May onwards up to June.

This tree is commonly planted as a garden and an avenue tree and also in villages along agricultural land, on village community lands and on wastelands. It is light demander, tolerant of excessive drought, but moderately frost hardy, has good capacity to recover in case of frost-injury. Gamhar tree coppices very well with vigorous growth. Saplings and young plants need protection from deer and cattle.

b. Utilization of the species

Gmelina arborea timber is reasonably strong for its weight. It is used in constructions, furniture, carriages, sports, musical instruments and artificial limbs. Once seasoned, it is a very steady timber and moderately resistant to decay and ranges from very resistant to moderately resistant to termites.

Its timber is highly esteemed for door and window panels, joinery and furniture especially for drawers, wardrobes, cupboards, kitchen and camp furniture, and musical instruments because of its lightweight, stability and durability. It is also used for bentwood articles. In boat

building it is used for decking and for oars. *Gmelina arborea* is a popular timber for picture and slate frames, turnery articles and various types of brush backs, brush handles and toys also for handles of chisels, files, saws, screw drivers, sickles etc. The wood is also used for manufacturing tea chests and general purpose plywood, blackboards, frame core and cross bands of flushdoor shutters. In instrument industry gambhar timber is widely employed for the manufacture of drawing boards, plane tables, instrument boxes, thermometer scales and cheaper grade metric scales. It is also used in artificial limbs, carriages and bobbins. It is an approved timber for handles of tennis rackets, frames and reinforcements of carom boards and packing cases and crates. Gamhar is used in papermaking and matchwood industry too. *Gmelina arborea* leaves are considered good for cattle (crude protein – 11.9%) and are also used as a feed to eri-silkworm.

c. Medicinal uses

The root and bark of *Gmelina arborea* are stomachic, galactagogue laxative and anthelmintic; improve appetite, useful in hallucination, piles, abdominal pains, burning sensations, fevers, 'tridosha' and urinary discharge. Leaf paste is applied to relieve headache and juice is used as

wash for ulcers. Flowers are sweet, cooling, bitter, acrid and astringent. They are useful in leprosy and blood diseases.

In Ayurveda, it has been observed that Gamhar fruit is acrid, sour, bitter, sweet, cooling, diuretic tonic, aphrodisiac, alternative astringent to the bowels, promote growth of hairs, useful in 'vata', thirst, anaemia, leprosy, ulcers and vaginal discharge.

The plant is recommended in combination with other drugs for the treatment of snakebite and scorpion sting. In snakebite a decoction of the root and bark is given internally.

Gmelina arborea is locally called by different names in different languages:

- Assamese- gomari
- Bengali- gamari, gambar, gumbar
- Gujarati- Shewan, Sivan
- Hindi- gamhar, khamara, khumbhari, sewan
- Kannada- kulimavu, kumbuda, kumulu
- Kasmiri- mara, shivani
- Latvian - gmelīne

- Malayalam- kumbil, kumbulu, kumilu, kumiska, pokki
- Maltese - sigra
- Marathi- shivan, siwan
- Oriya- bhodropornni, gambari, kumar
- Punjabi- gumhar, kumhar
- Sanskrit- bhadraparni, gambhari, gandhari, kasmari, krishnavrintaka, sarvatobhadra, shriparni
- Tamil- kumla, kumalamaram, kumil, ummithekku
- Telugu- gumartek, gummadi, summadi

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2.13.5. ***Piliostigma thonnigii*** **Schum.**

a. Species identity

Taxonomy

Current name: Piliostigma thonningii

Authority: (Schum.) Milne-Redh.

Family: Fabaceae - Caesalpinioideae

b. Synonym(s)

Bauhinia thonningii Schum.

c. Common names

(Hausa): Kalgo

(Arabic) : kharub, khuf aj jamal

(English) : camel's foot, monkey bread, Rhodesian bauhinia, wild bauhinia
(Luganda) : kigali
(Ndebele) : ihabahaba
(Shona) : mutukutu
(Swahili) : mchekeche, mchikichi

d. Botanic description

Piliostigma thonningii is a tree 4-15 m in height with a rounded crown and a short but often crooked bole. Twigs rusty-hairy. The bark is rough and longitudinally fissured, being creamy-brown when fresh and grey-brown later. Leathery green leaves up to 15 x 17 cm, bi-lobed one eighth to one third the way down with a small bristle in the notch, glossy above and heavily veined and somewhat rusty-hairy below. Flowers with 5 white to pink petals, pendulous, unisexual with male and female usually on separate trees; ovary topped by a thick flattened-globose stigma. Pods indehiscent, up to 26 x 7 cm, with rusty-brown hairs, which wear off as the pods mature, becoming somewhat contorted as they age. The pods persist on the tree but finally fall and decay on the ground to pea-sized seeds. An edible pulp surrounds these seeds. This species roots deeply. The generic epithet *Piliostigma,* means cap-like stigma. The specific epithet commemorates Peter Thonning, the Danish plant collector who collected the type in that portion of Danish Guinea that is now part of Ghana. *Piliostigma* was distinguished from Bauhinia by its unisexual flowers and indehiscent pods.

e. Ecology and distribution

Natural Habitat

P. thonningii is common in open woodland and wooded grasslands of sub-humid Africa at medium to low altitudes. It is found throughout tropical Africa except in Somalia. It is usually associated with *Annona senegalensis, Grewia mollis and Combretum spp.*

Geographic distribution

Native : Botswana, Kenya, Namibia, Senegal, South Africa, Sudan, Tanzania, Uganda, Zambia

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CHAPTER THREE

3.0 Materials and methods

3.1 Apparatus/equipment

Grinding Desk

Emery papers (220-800 grades)

Dessicator

Beaker

Funnel

Burette

Retort Stand

Water Bath

3.2 Materials

3.2.1 Steel sample

For the purpose of this research work, as – received steel rod was sourced from Gurara water project, Kaduna state. The compositional analysis of steel, as shown in the Table 4.1, was carried out at Ajaokuta Steel Complex by spectral method.

3.2.2 Organic Resins And Plant Extracts

The five inhibitors used for the purpose of this research work were - Neutral red and methylene blue, standard inhibitor (Sodium Benzoate) and two natural plants extracts of *P. thoningii* and *G. arborea.* The three synthetic organic compounds (Sodium Benzoate, Methylene blue and Neutral red) were obtained from the Department of Chemistry, Ahmadu Bello University, Zaria.The extracts of the *P. thoningii* and *G. arborea* were obtained using a

Soxhlet extractor according to the conventional methods (Walkers, 1972; Vashi and Champaneri, 1997). This involves refluxing about 5kg of dried powdered leaves of *P. thoningii* and *G. arborea* with 4%HCl and 4% H_2SO_4 at 100^0C for 5 hours respectively. Solutions of different concentrations of the natural inhibitors were then prepared.

3.2.3 Acid solution

The acid solution used composed of 20% H_2SO_4, concentrations of the inhibitors (0.05 to 0.5v/v% of the three synthetic organic compounds and two natural plant extracts) and the balance was distilled water. 20% H_2SO_4 was chosen because it is the standard limit of pickling carbon steels (Rozenfeld, 1981). This was corroborated by the facts that the small surface areas of the test coupons and the amount of reacted materials were very little, thus accurate measurements of weight losses and volumes of Hydrogen evolved would be difficult if the concentration were to be lower than 0.2M H_2SO_4 acid.

3.3 Phytochemical screening of *Piliostigma thonningii* and *Gmelina arborea*

The phytochemical screening of *P. thonningii* and *G.arborea* were carried out according to the conventional methods used elsewhere :

Alkaloids (Evans, 1996)

Anthraquinones and their derivatives (Sofowora, 1993)

Saponins (Silva *et al.,* 1998)

Tannins (Evans, 1996)

Steroids and Terpenoids (Cuilei, 1990)

Flavonoids (Mahran *et al.,* 1980)

The results obtained are tabulated in Table 4.2.

3.4 Sample preparation

Prior to the experiment, the as-received cold rolled steel rods were sectioned into specimen sizes of 15mm x 15mm (average Geometrical area 1.06 x $10^{-3}m^2$) and abraded with a series of emery papers from 220 to 800 grades. The specimens were then washed with distilled water followed by acetone and dried using a stream of air. After weighing accurately in a mettler AE166 (Delta range) analytical balance (NACE, 1984), they were then stored in a desiccator to prevent environmental interactions.

3.5 Experimental procedure

The experimental set up consisted of a beaker containing the H_2SO_4 acid pickling solution, and inhibitor(s) in which the steel samples, tied with thread, was (were) suspended and immersed in the solution. A funnel was placed over the sample so as to channel the evolved H_2 gas into the burette, figure 3.1.

A retort stand was used for holding the burette firmly in the upright position. The whole arrangement was placed in a thermostated water bath for the purpose of varying the experimental temperature from 30 to 60^0C.

A pickling solution was prepared by diluting concentrated H_2SO_4 acid with doubly distilled water to 20% concentration (by

volume) in a beaker and 400cm^3 acid was used. An initially weighed steel sample specimen was immersed (Suspended with a thread) in the solution together with a funnel to form an enclosure over the specimen. A burette lubricated with petroleum jelly was pushed over the funnel and firmly held in an upright position by means of a retort stand as reported by Njoku (1998). The solution was sucked up to the 50cm^3 mark on the burette (50cm^3 was used as a datum mark for all the experiments) and the burette was locked to prevent the interference of the atmospheric pressure on the volume of Hydrogen evolved as indicated on the burette. The arrangement was placed on a thermostated water bath for the purpose of varying the temperature to 30, 40, 50 and 60^oC.

The experiment was first conducted without any inhibitor addition to the pickling solution. A weighed steel sample was suspended into the pickling solution as explained above. The experimental temperature was first maintained at 30^oC (room temperature) for 5 hours after which the steel sample was removed from the solution, washed with water, dried and re-weighed. The volumes of Hydrogen evolved at an interval of 1hr were noted and recorded. The same procedure was repeated at 40, 50, and 60^oC (Without an inhibitor addition).

The procedure was run again with addition of varying concentration (0.05, 0.10, 0.15, 0.20, 0.25. 0.3, 0.4 and 0.5v/v%) of Sodium Benzoate (a known standard organic inhibitor) to the pickling solution at varying temperatures 30, 40, 50 and 60^oC. After this, the experiment was also repeated for the two synthetic organic

dyes (Neutral Red and Methylene Blue) and the two natural plant extracts (*P. thonnigii* and *G. arborea*) each separately.

In each case, the corrosion rate was computed by using equation 2.39, and the results obtained are shown in Figure 4.1- 4.10.

The Hydrogen evolution rate was computed using equation 2.40 and the results obtained are represented in figures 4.22 – 4.26.

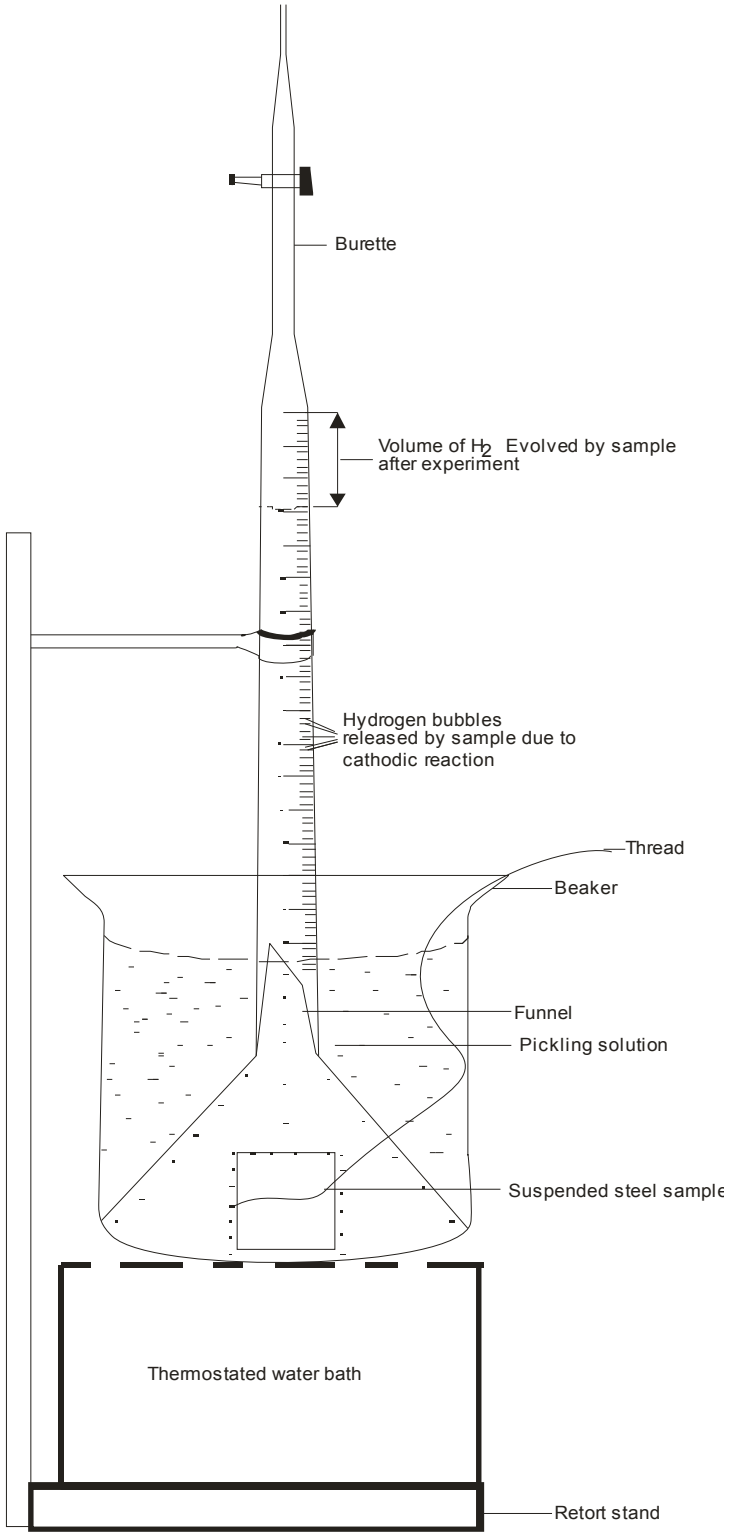


Fig. 3.1: Experimental set-up

CHAPTER FOUR

4.0 Results and discussion

4.1 Results

Table 4.1: chemical composition of the steel used in the test

%C	%Si	%Mn	%P	%S	%Cr	%Mo
0.360	0.178	0.685	0.026	0.041	0.071	0.0050

%Ni	%A1	%Co	%Cu	%Nb	% Ti	% V
0.131	0.0010	0.010	0.053	< 0.0050	<0.0010	< 0.0050

%W	%Pb	%Sn	%Zn	%Fe
<0.010	0.0050	0.010	0.0066	98.13

Table 4.2: Results of the phytochemical screening of *P. thonningii and G. arborea*

Chemical constituent	***Piliostigma***	***Gmelina***
Alkaloids	+	+
Anthraquinones	+	+
Saponins	_	_
Tannins	+	+
Steroids and Terpenoids	+	+
Nitrogen	+	+
Sulphur	+	+

Note: + indicates presence, - absence

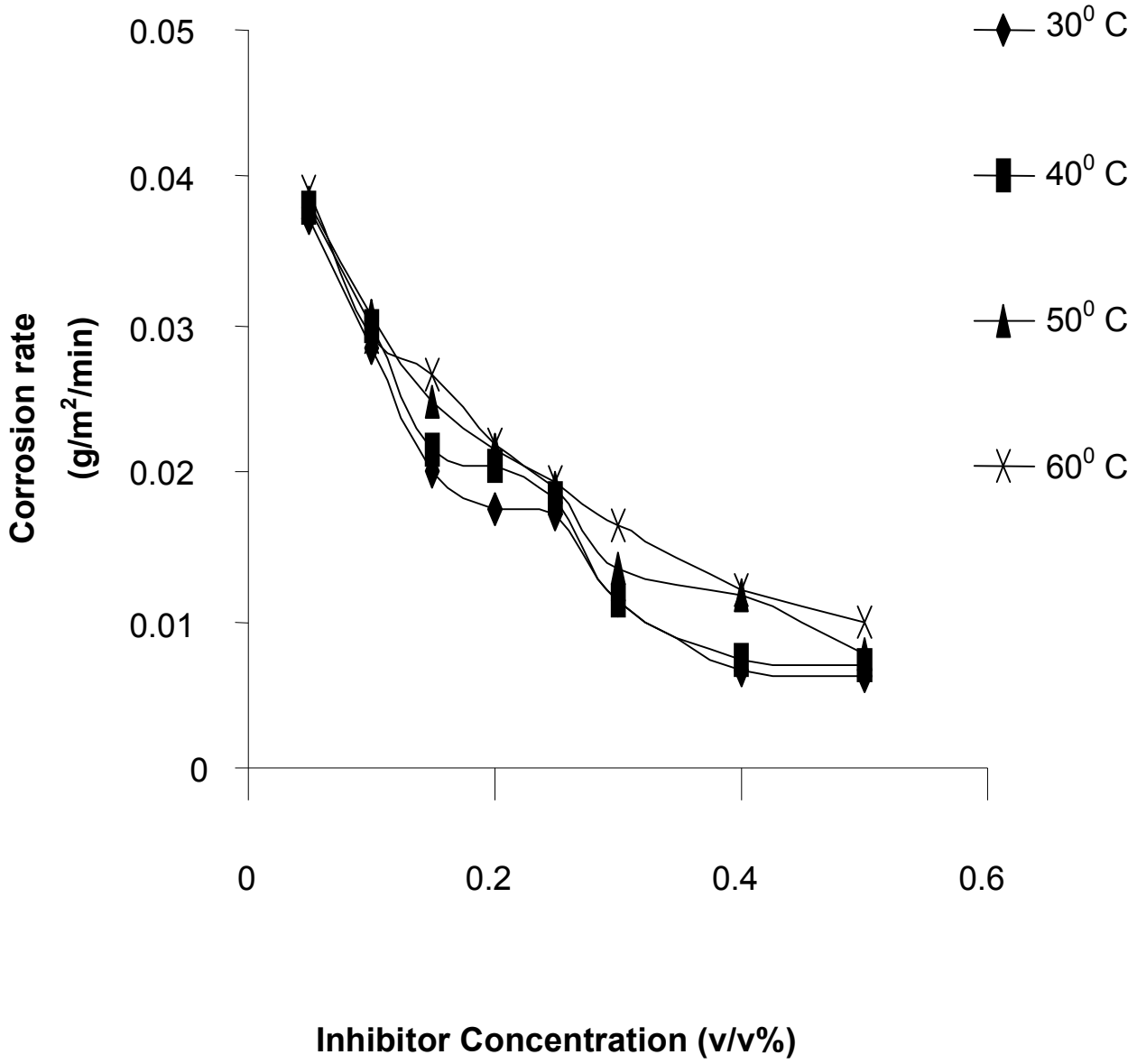


Fig. 4.1: Corrosion behaviour of medium carbon steel in 0.2M H_2SO_4 with the addition of varying concentrations of sodium benzoate

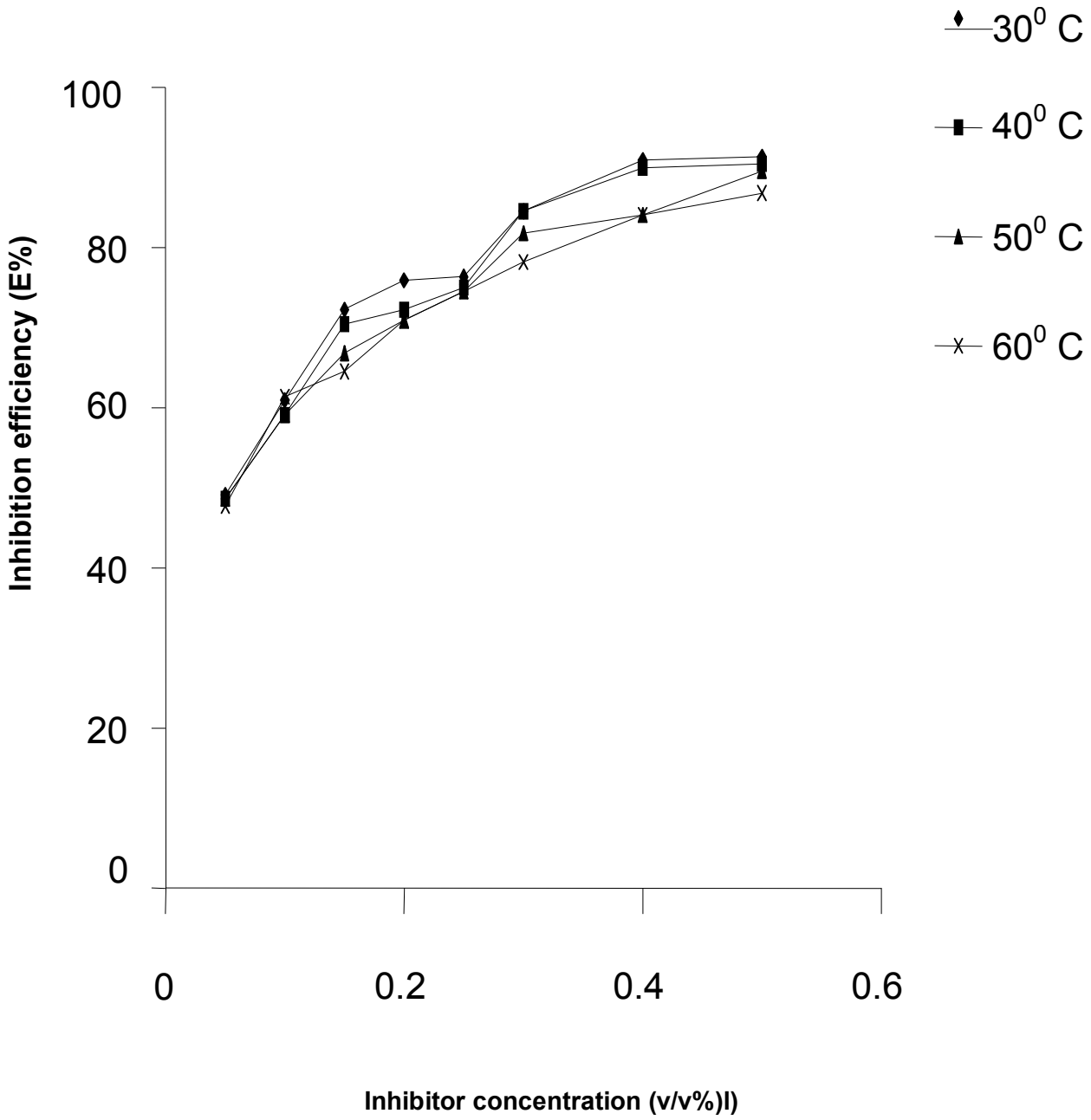


Fig. 4.2: Variation of Inhibition efficiencies with concentrations of sodium benzoate in 0.2M H_2S0_4 at different temperatures

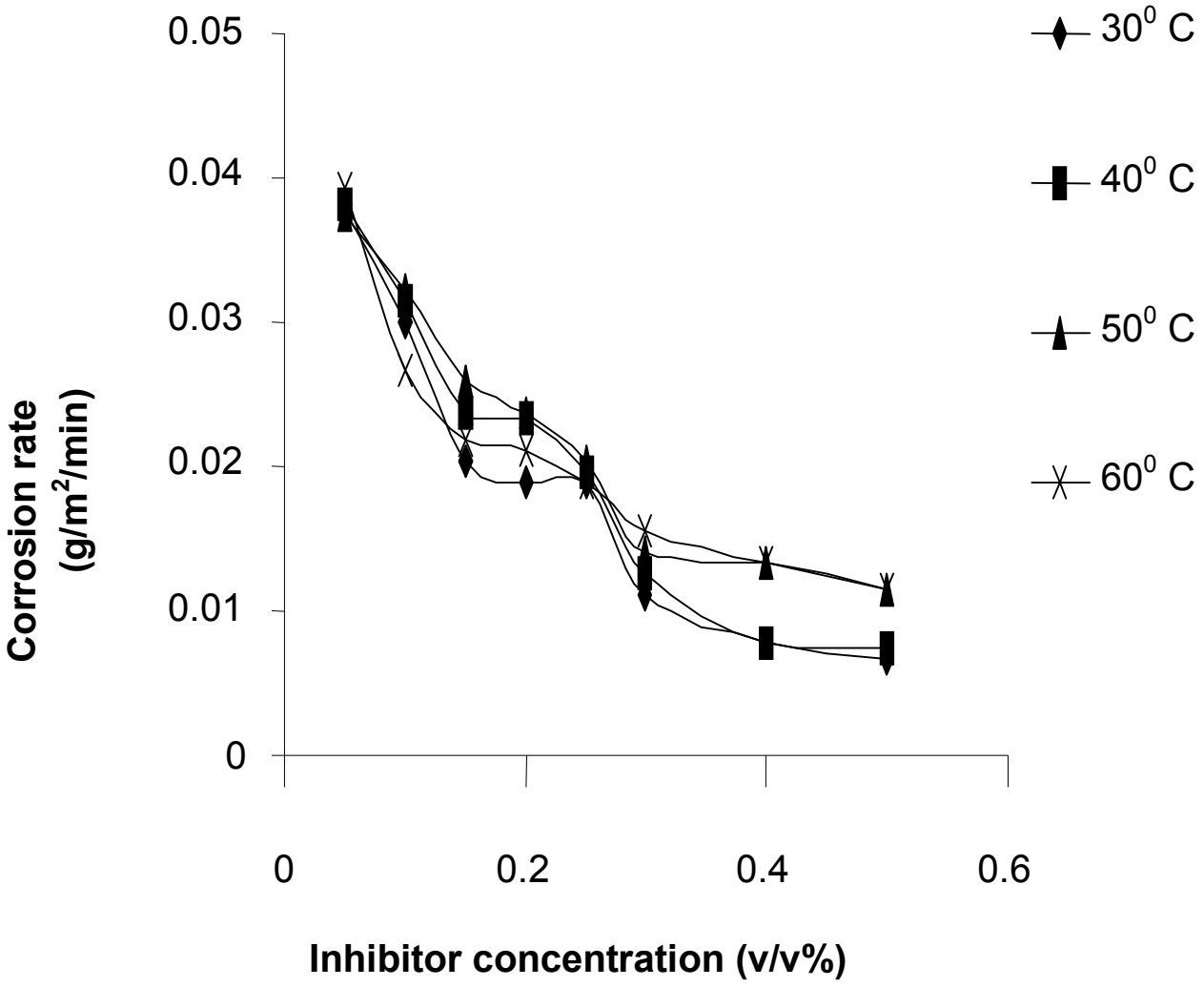


Fig. 4.3: Corrosion behaviour of medium carbon steel in 0.2M H_2SO_4 with the addition of varying concentrations of methylene blue at different temperatures

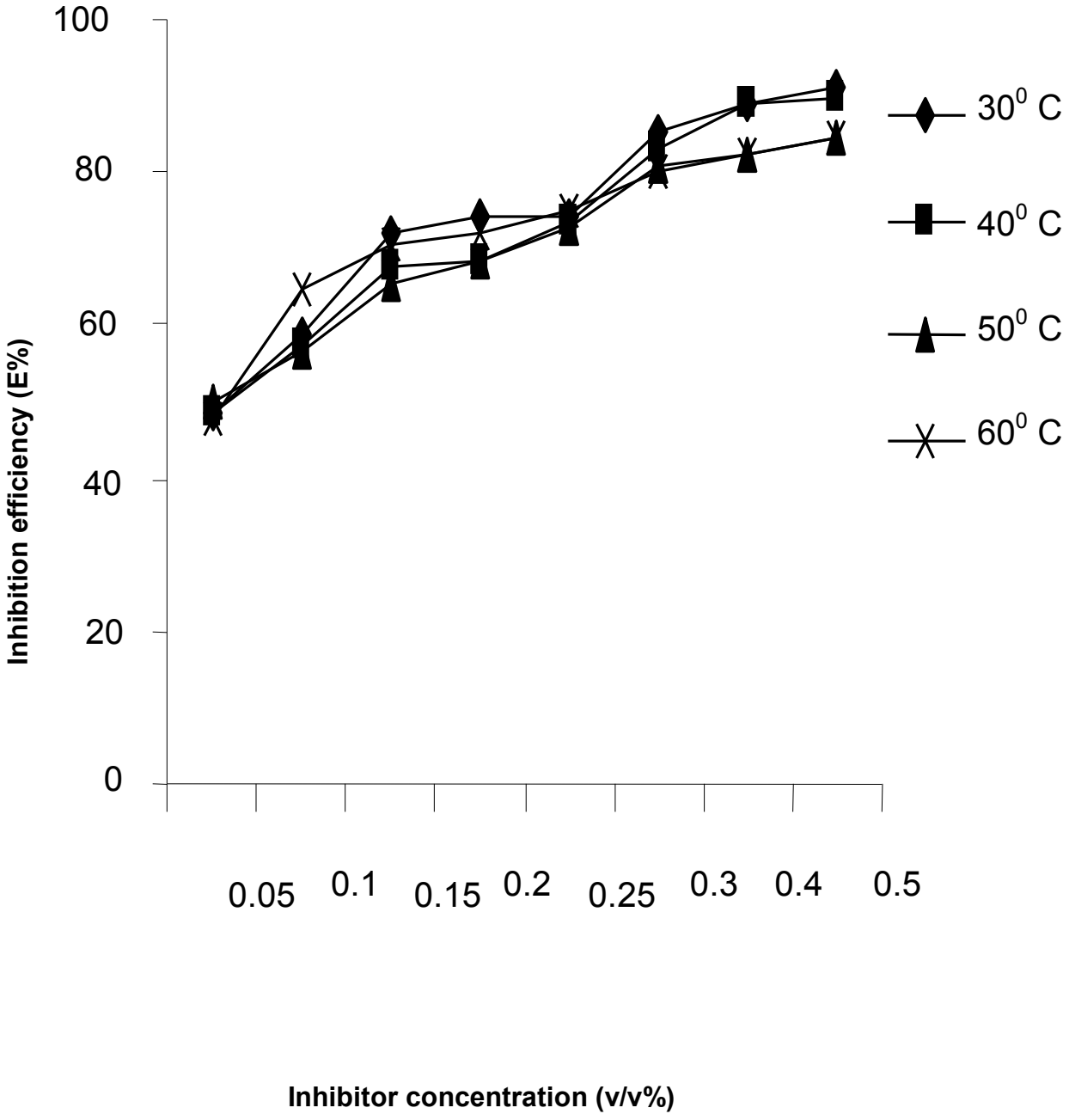


Fig. 4.4: Variation of Inhibition efficiencies with concentrations of methylene blue at 0.2M H_2SO_4 at different temperature

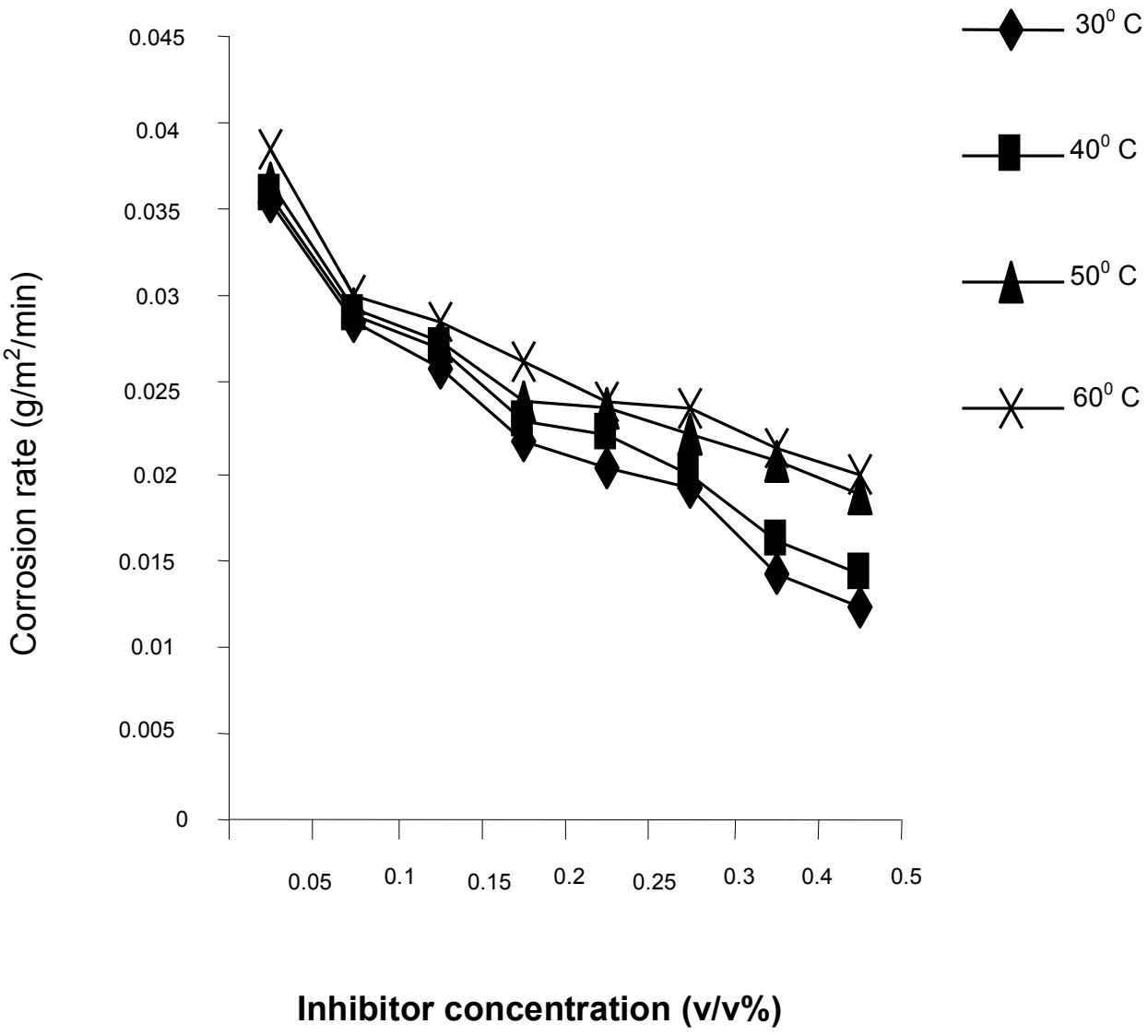


Fig. 4.5: Corrosion behaviour of medium carbon steel in 0.2M H_2SO_4 with the addition of varying concentrations of neutral red at different temperatures

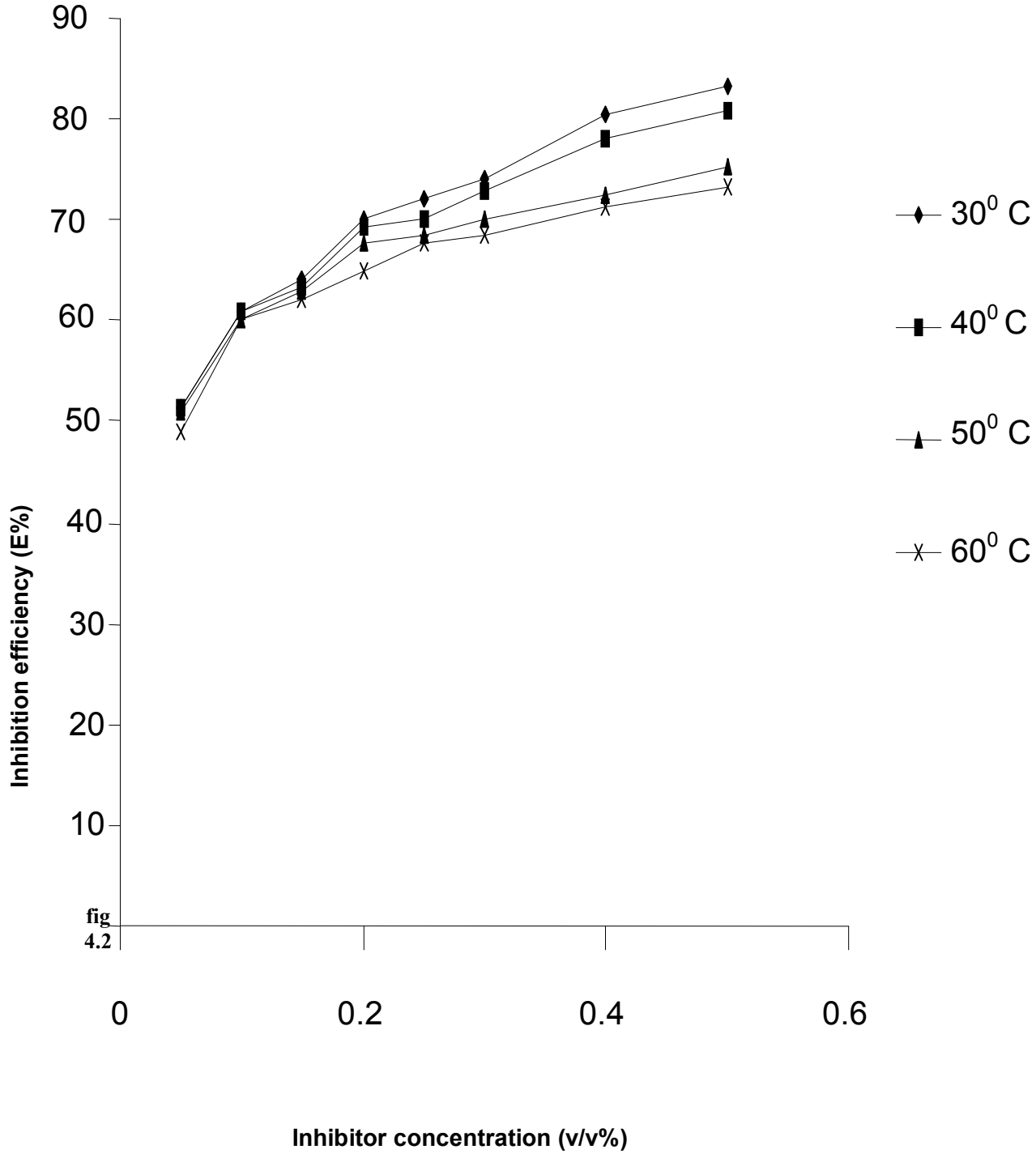


Fig. 4.6: Variation of Inhibition efficiencies with concentrations of neutral red at different temperatures in 0.2M H_2S0_4

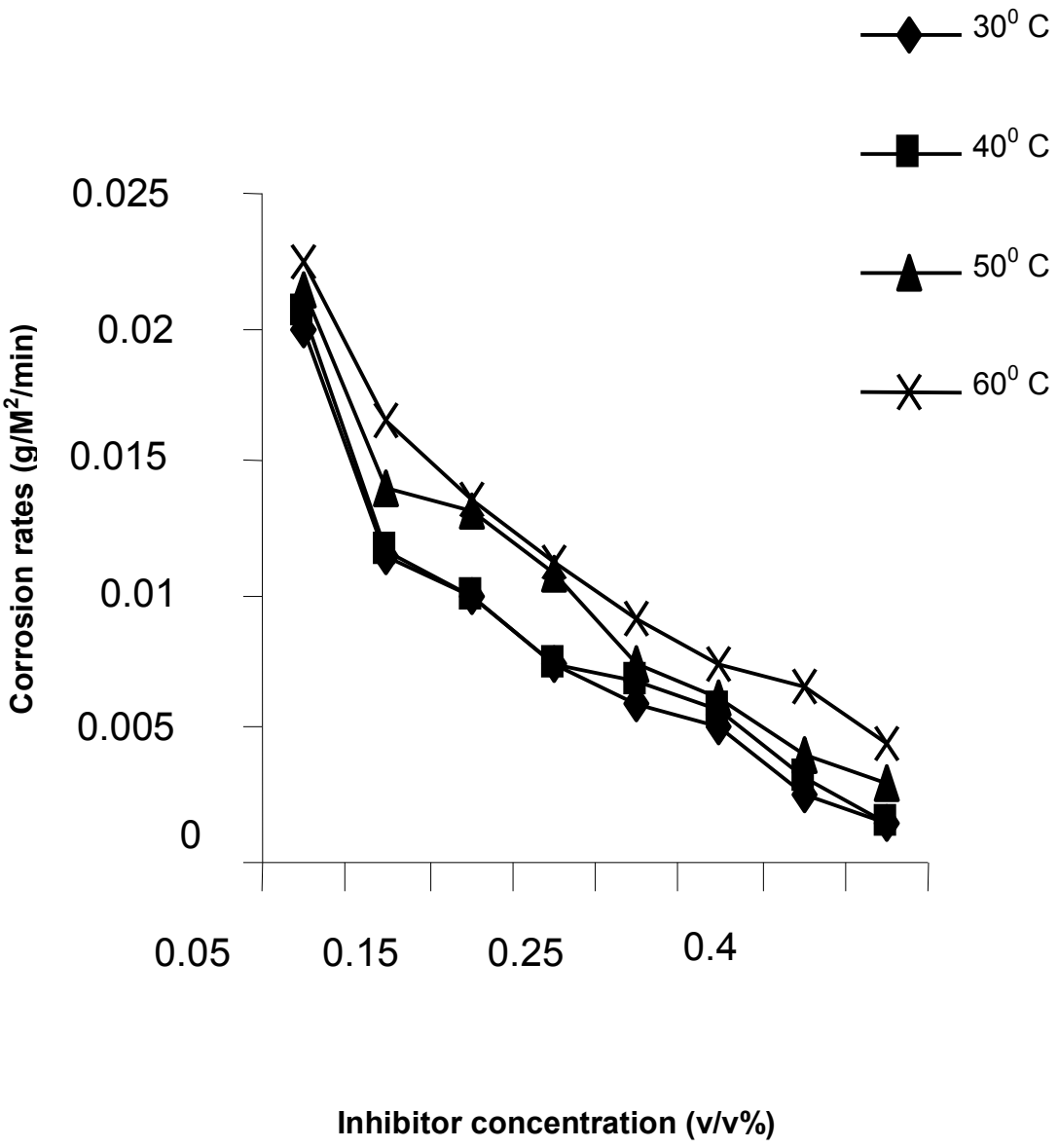


Fig. 4.7: Corrosion behaviour of medium carbon steel in 0.2M H_2SO_4 with the addition of varying concentrations of *Piliostigma thonningii* at different temperatures

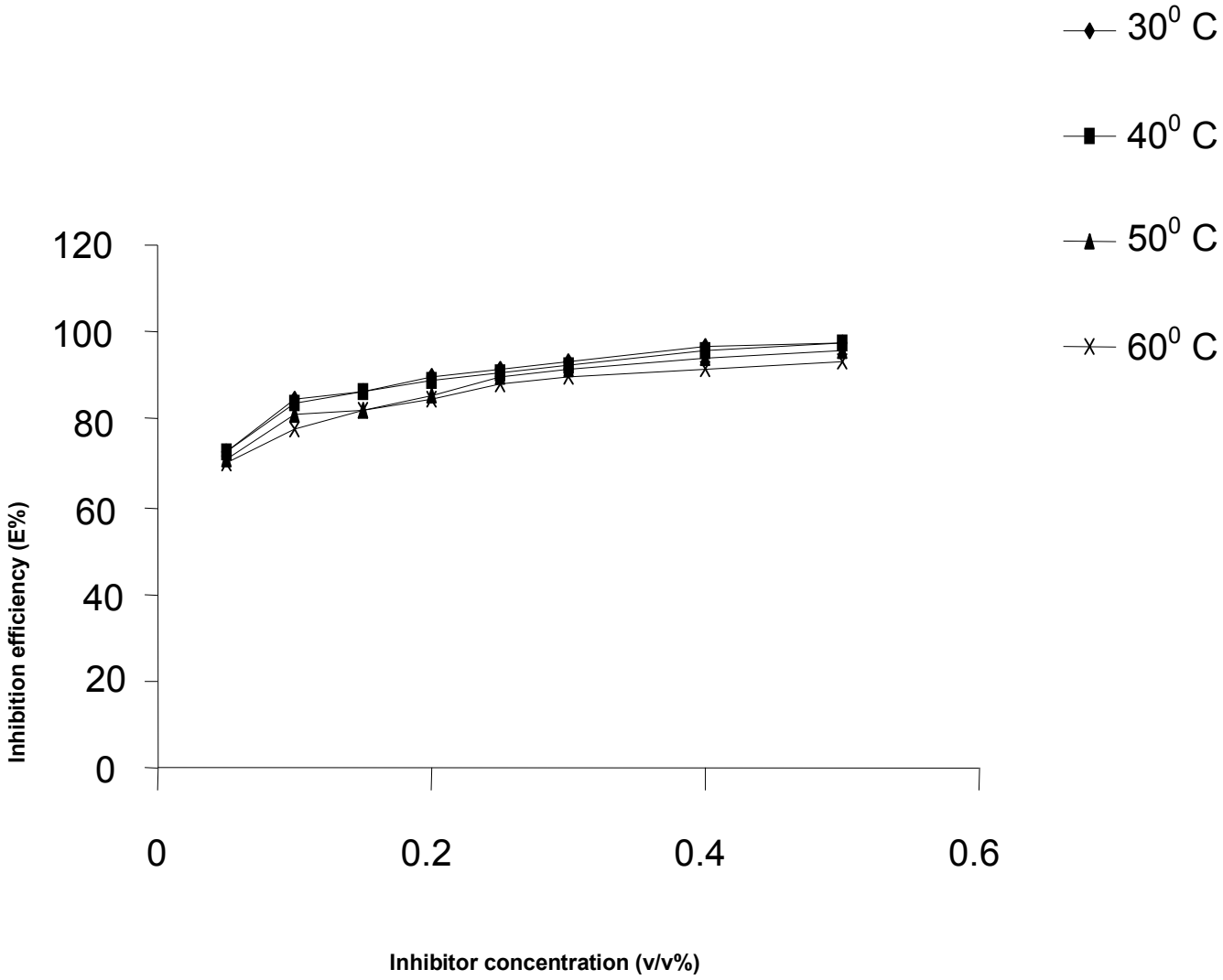


Fig 4.8: Variation of inhibition efficiencies with concentrations of *Piliostigma thonningii* at diffrent temperatures in 0.2M H_2S0_4

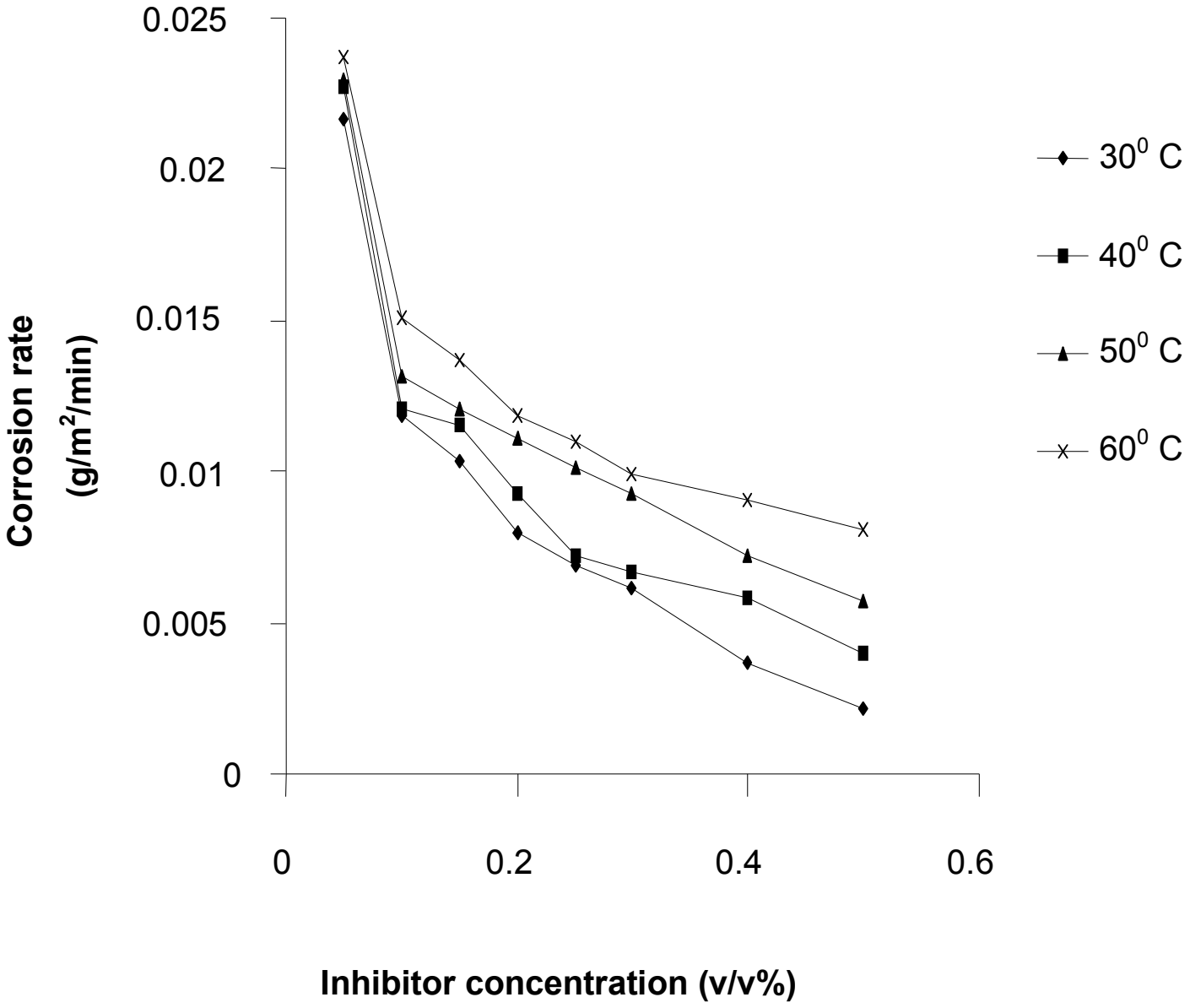


Fig. 4.9: Corrosion behaviour of medium carbon steel samples in 0.2M H_2SO_4 with the addition of varying concentrations of *Gmelina arborea* at different temperatures

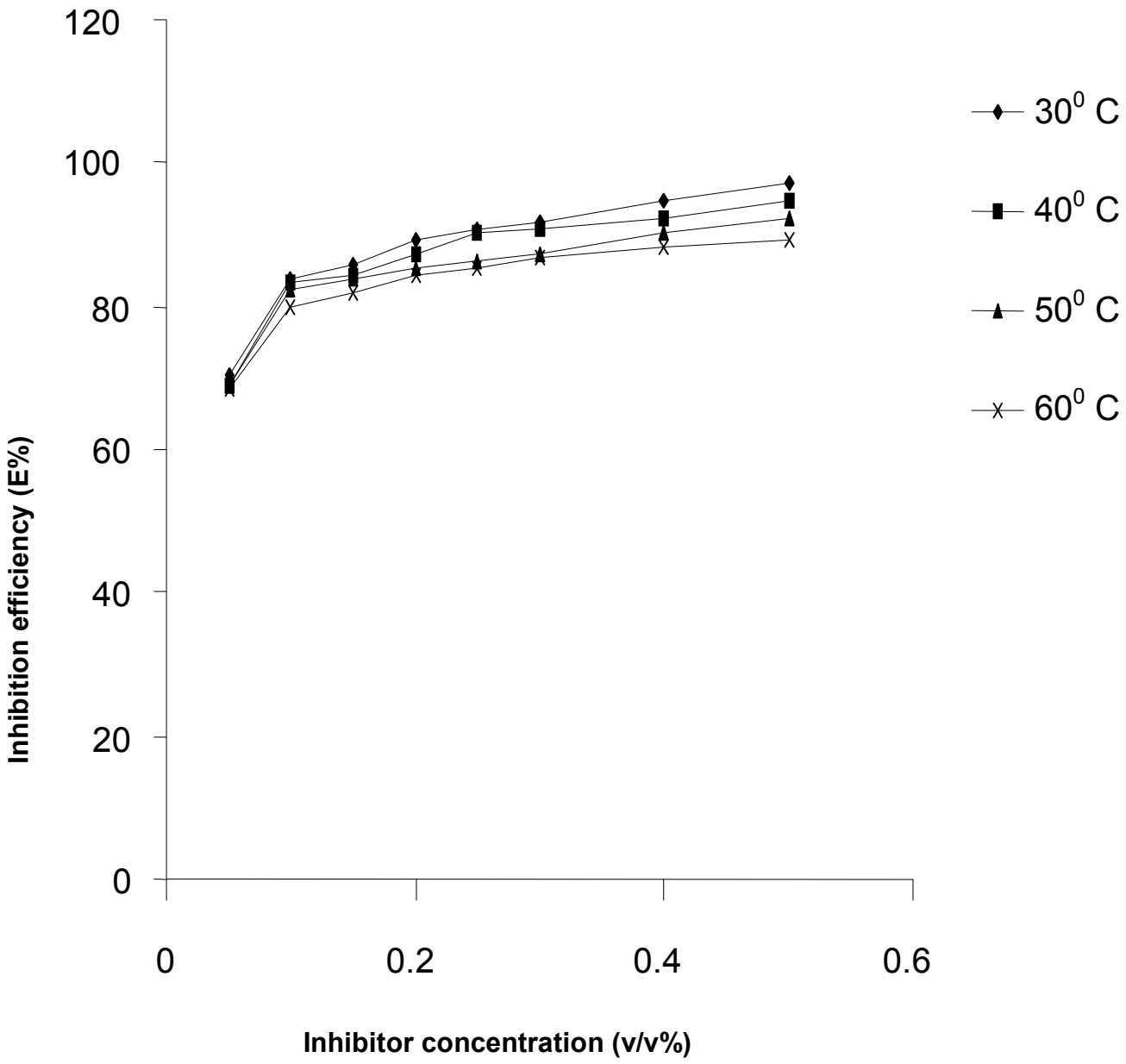


Fig. **4.10: Variation of inhibition efficiencies with concentrations of *Gmelina arborea* in 0.2M H_2S0_4 at different temperatures**

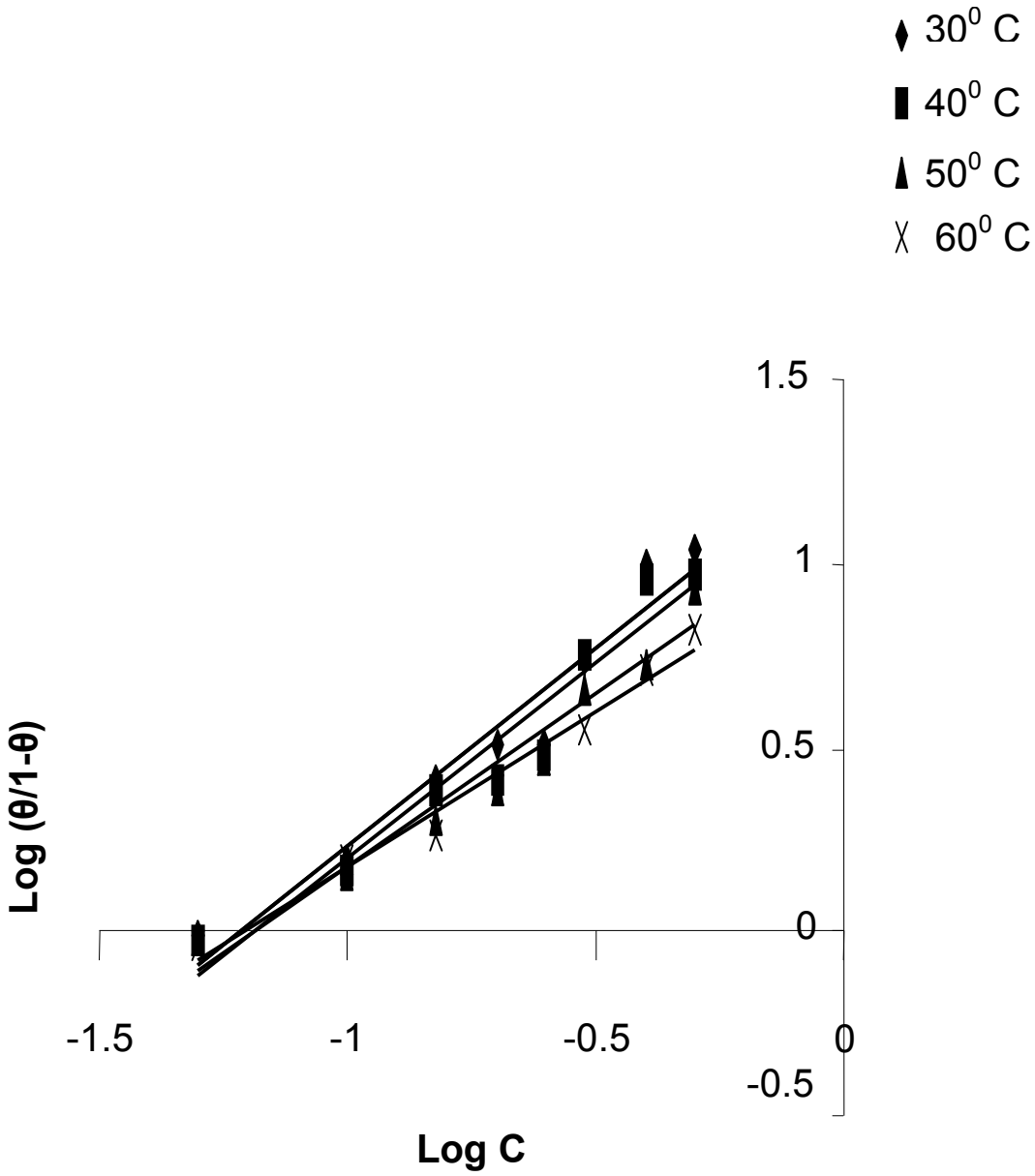


Fig. 4.11: Langmuir adsorption isotherms for the adsorption of sodium benzoate onto the steel surface

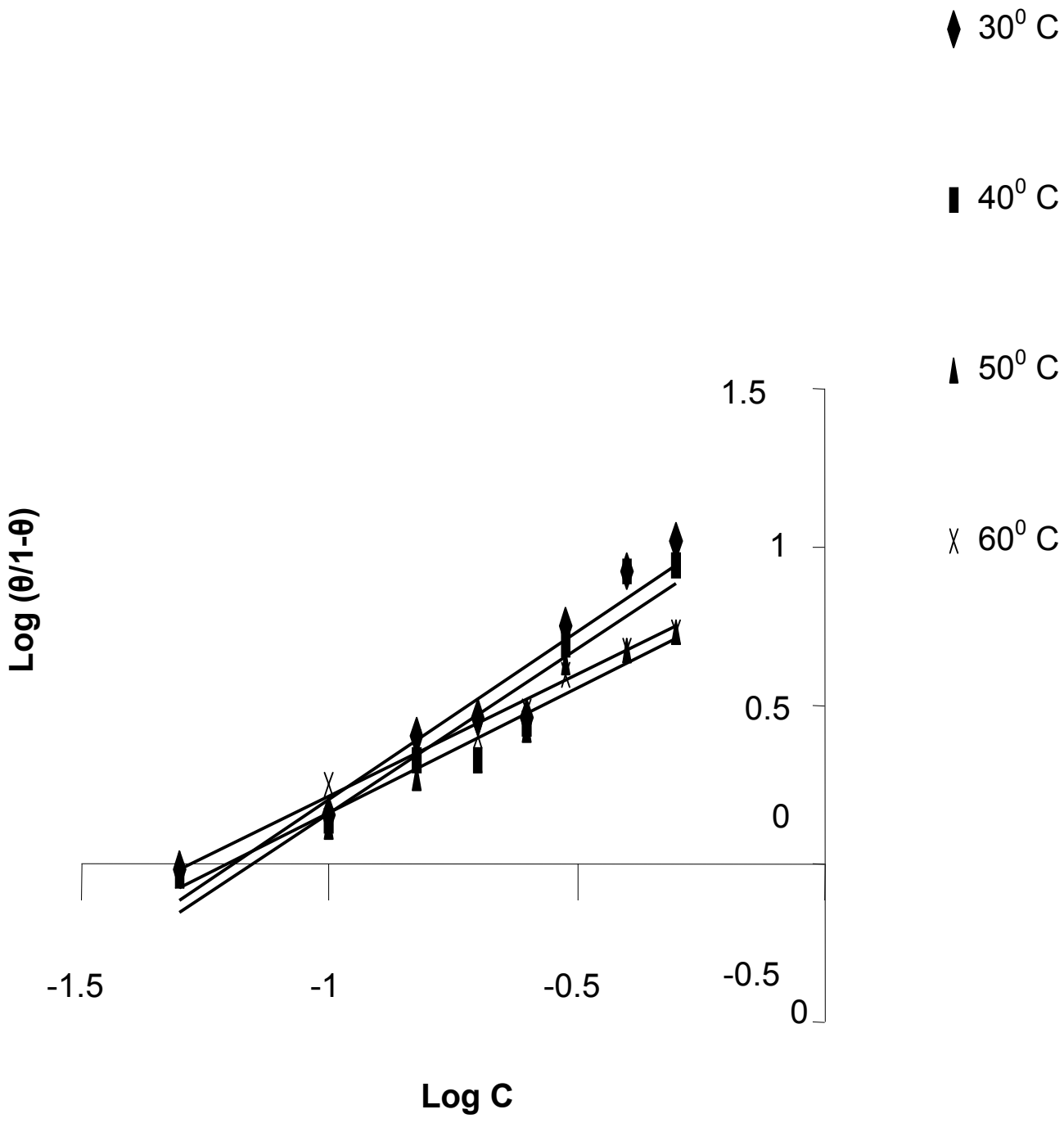


Fig.4.12: Langmuir adsorption isotherms for the adsorption of methylene blue onto the medium carbon steel surface

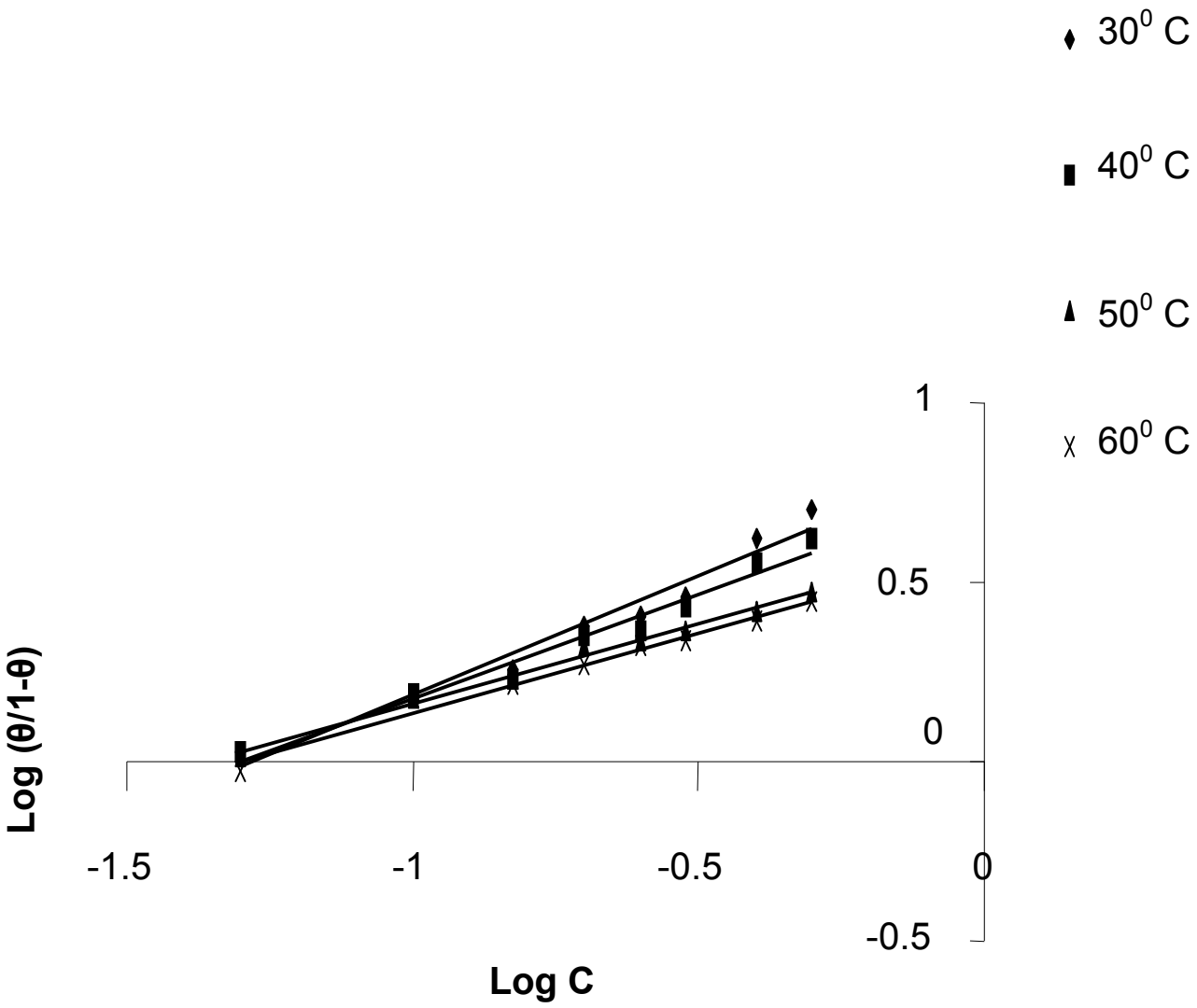


Fig 4.13: Langmuir adsortion isotherms for the adsorption of neutral red onto the steel surface

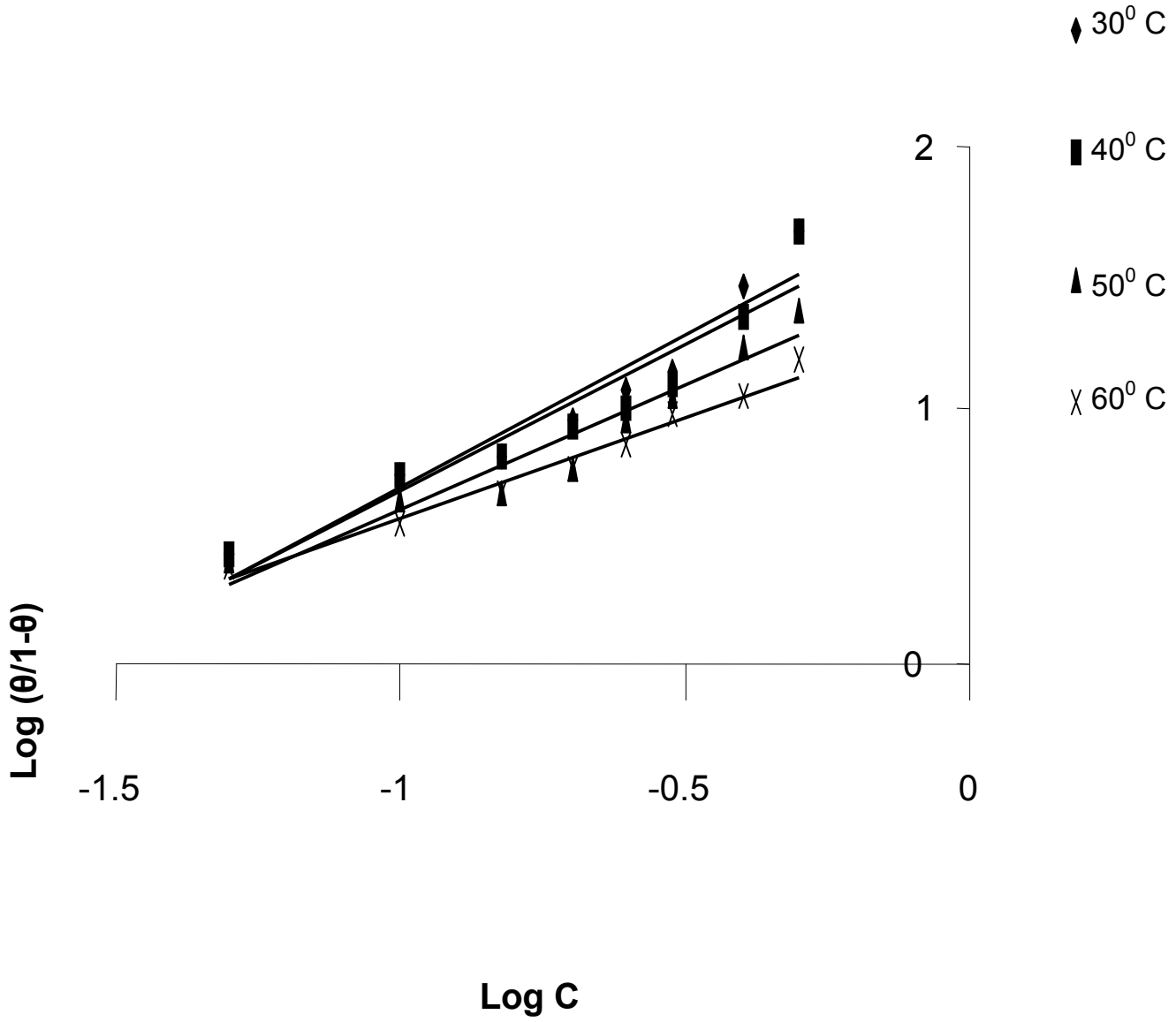


Fig 4.14: Langmuir adsorption isotherms for the adsorption of *Piliostigma thonningii* onto the steel sample

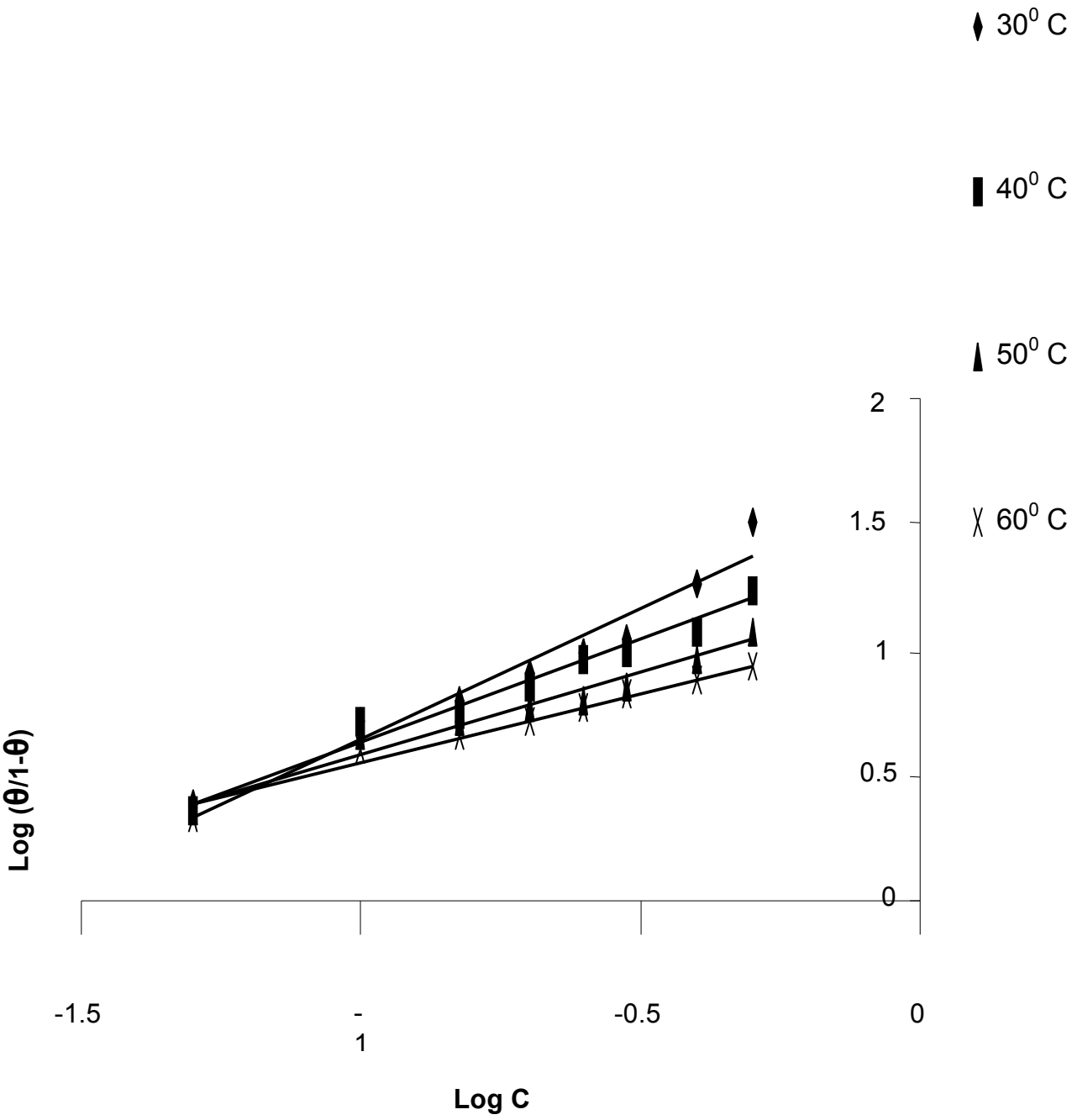


Fig 4.15: Langmuir adsortion isotherms for the adsorption of *Gmelina arborea* onto the steel sample

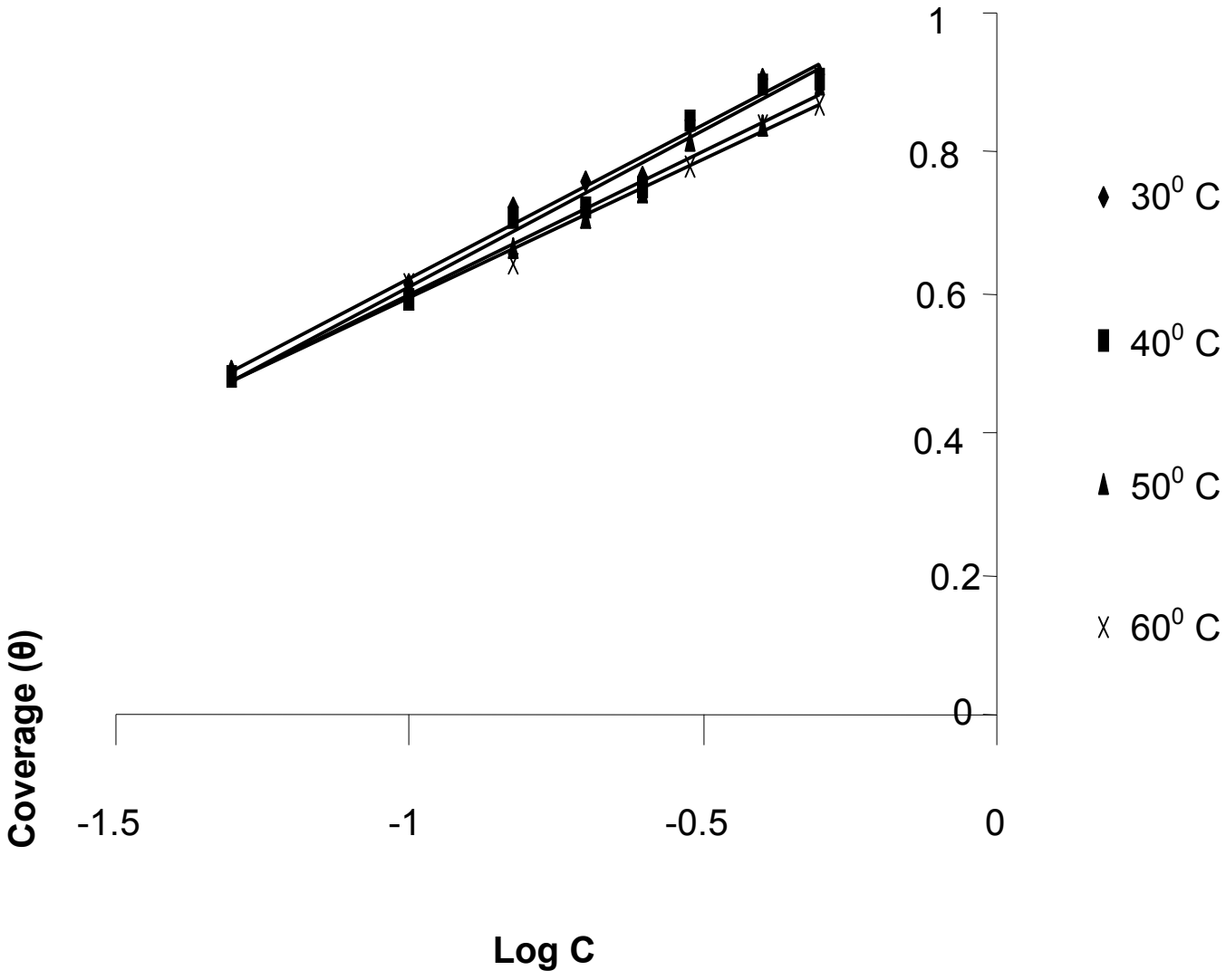


Fig. 4.16:Temkin adsorption isotherms for the adsorption of sodium benzoate onto the steel surfaces at different temperatures

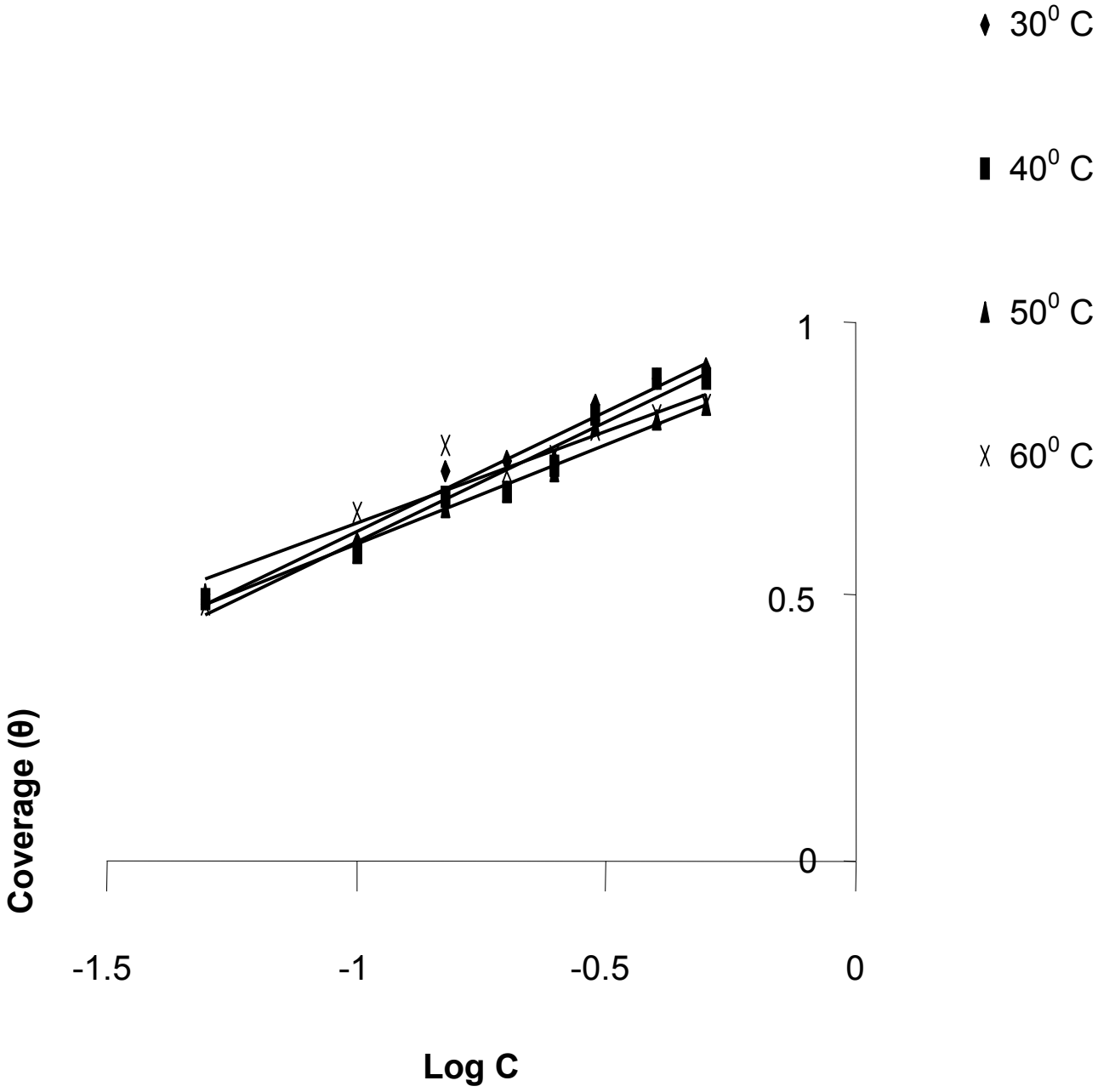


Fig. 4.17: Temkin adsorption isotherms for the adsorption of methylene blue onto the steel surfaces at different temperatures

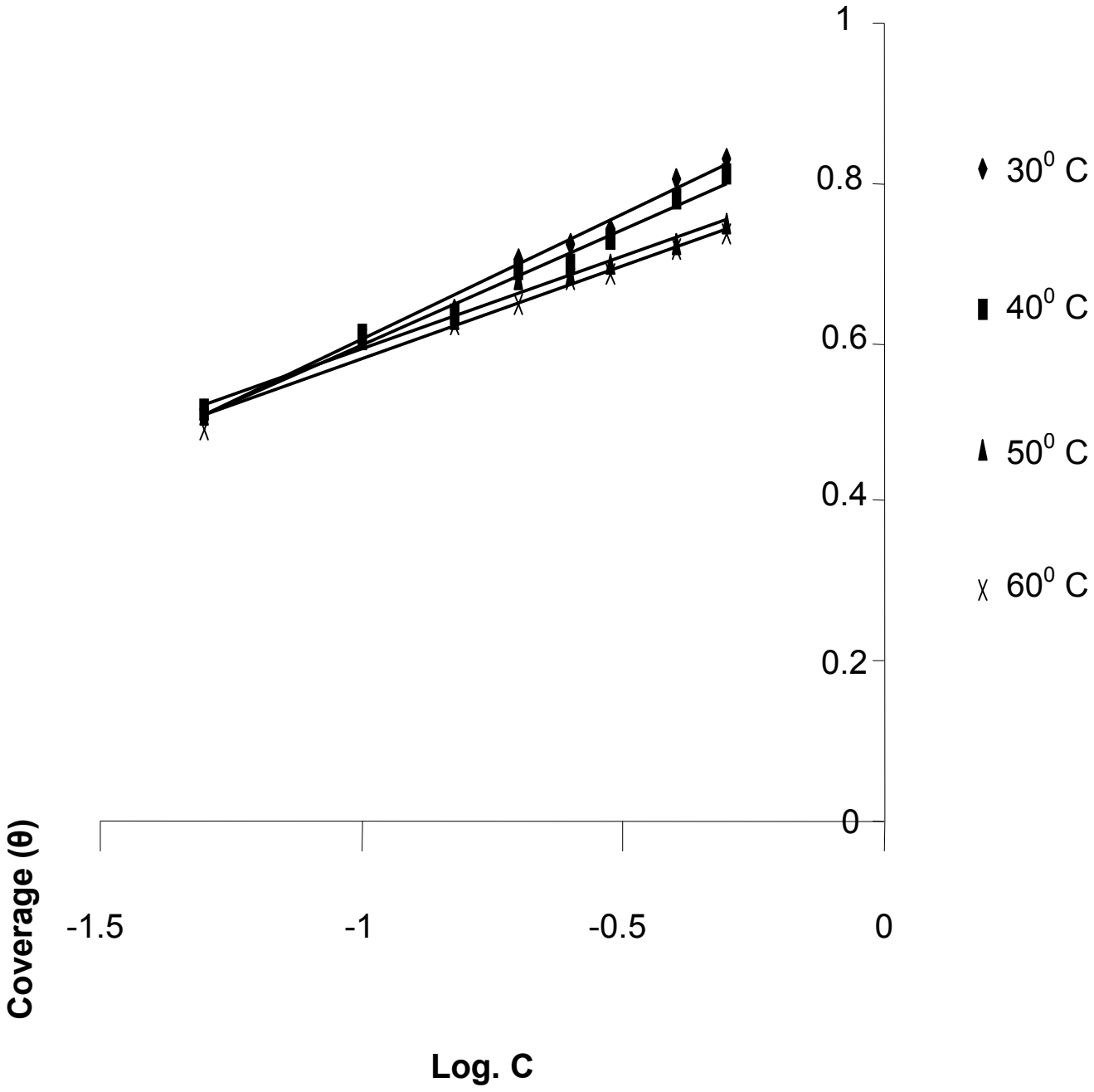


Fig. 4.18: **Temkin adsorption isotherms for the adsorption of neutral red onto the steel surfaces at different temperatures**

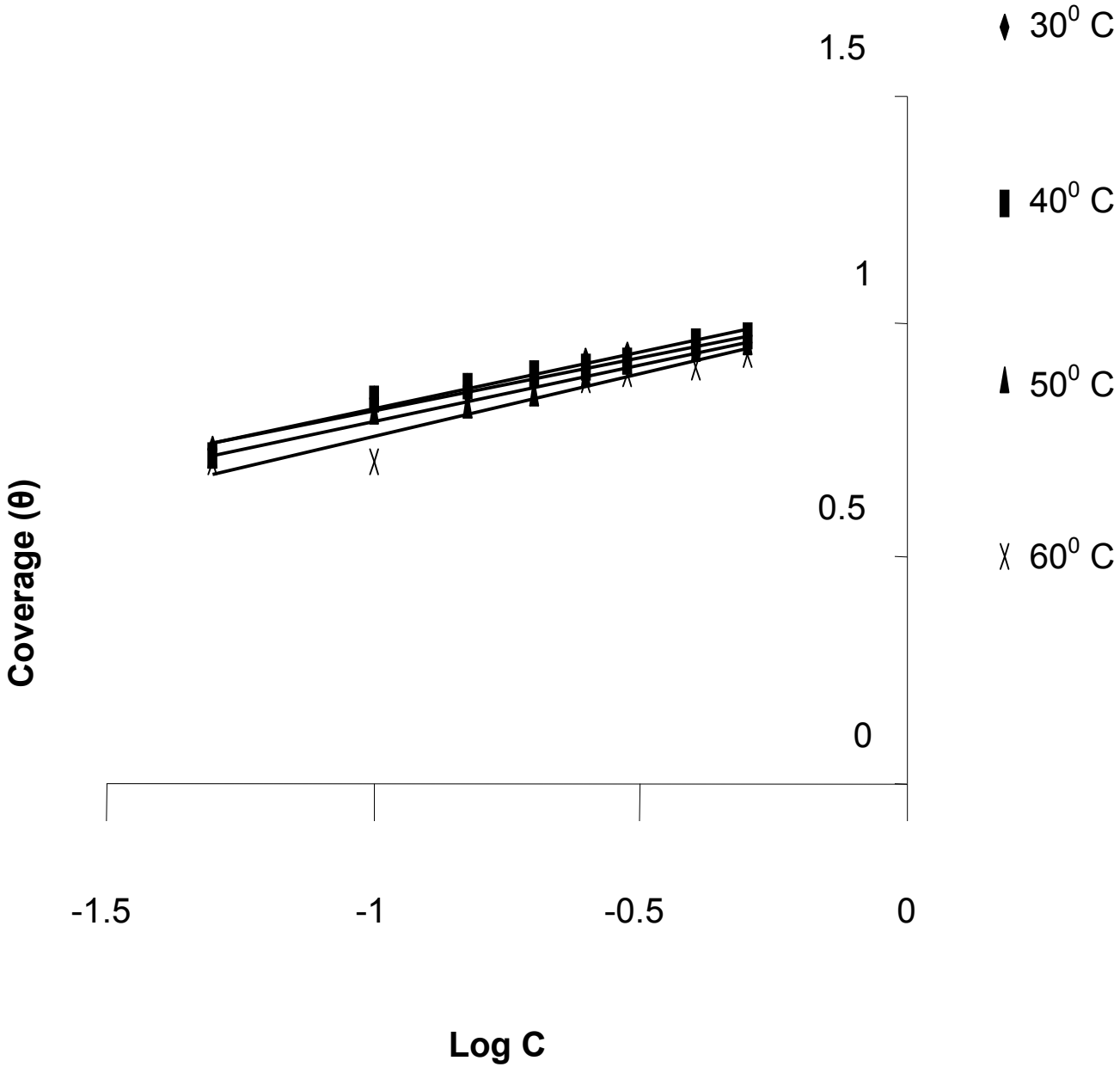


Fig. 4.19: Temkin adsorption isotherms for the adsorption of *Piliostigma thonningii* onto the steel surfaces at different temperatures

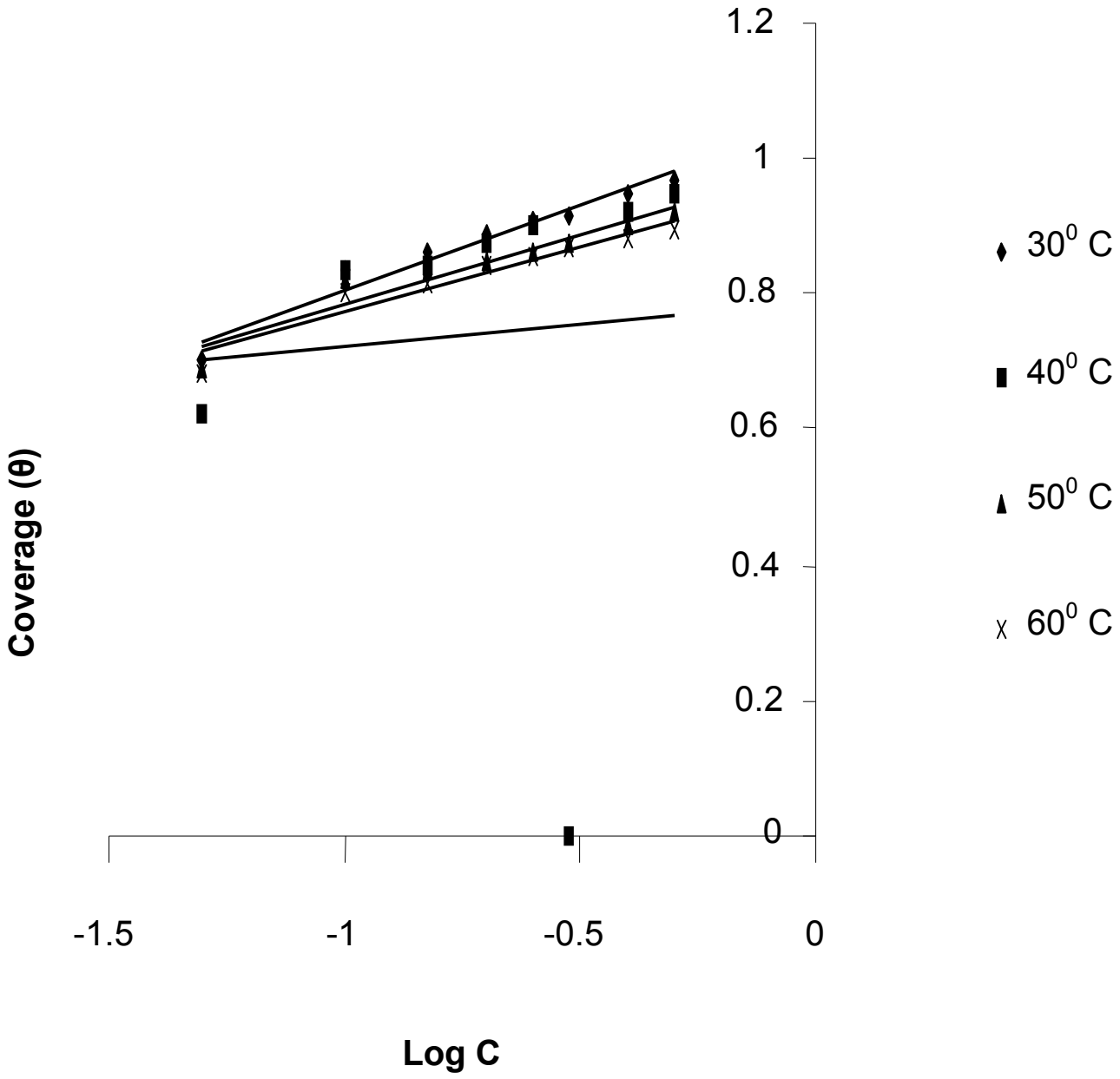


Fig 4.20:Temkin adsorption isotherms for the adsorption of *Gmelina arborea* onto the steel surfaces at different temperatures

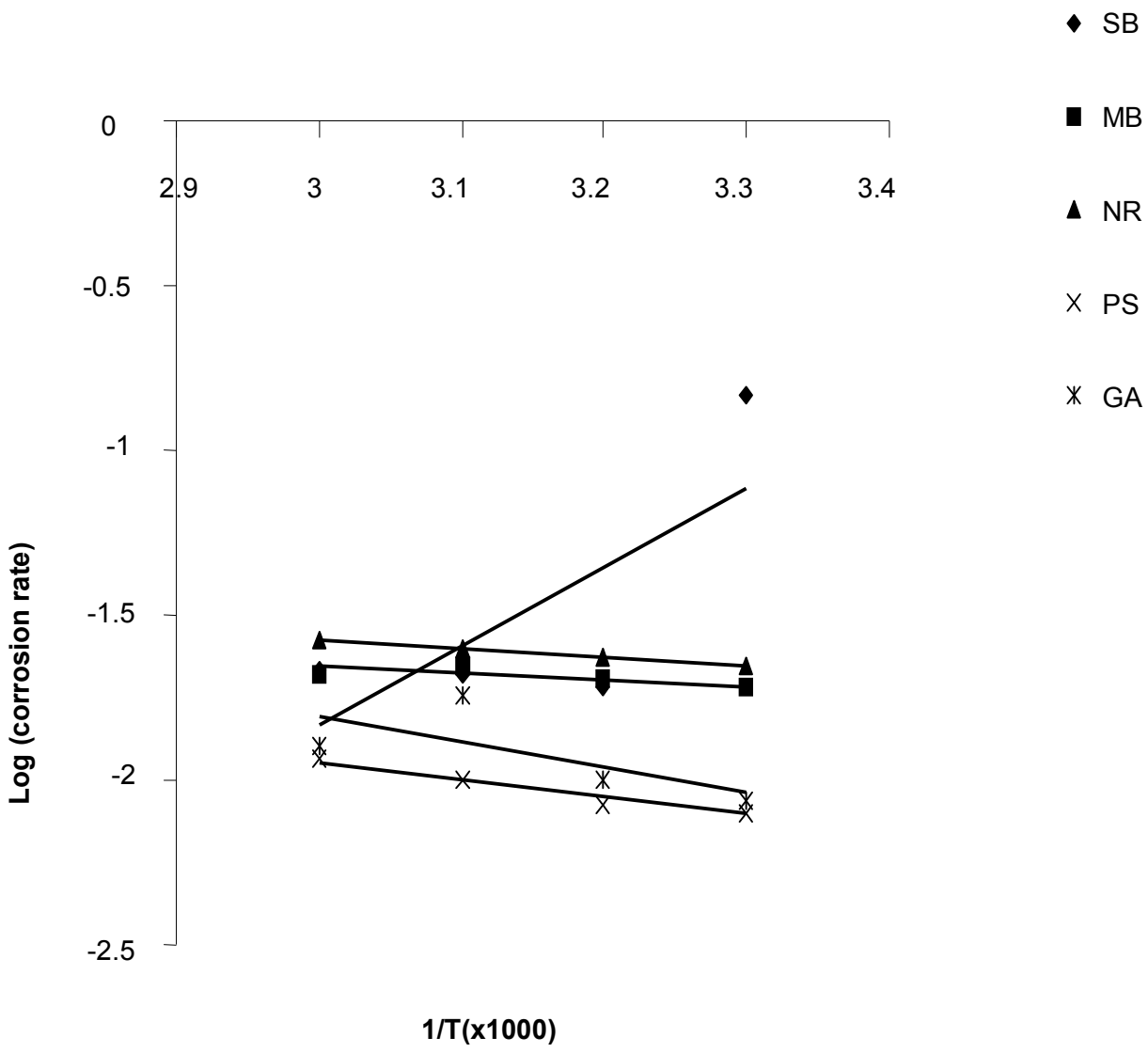
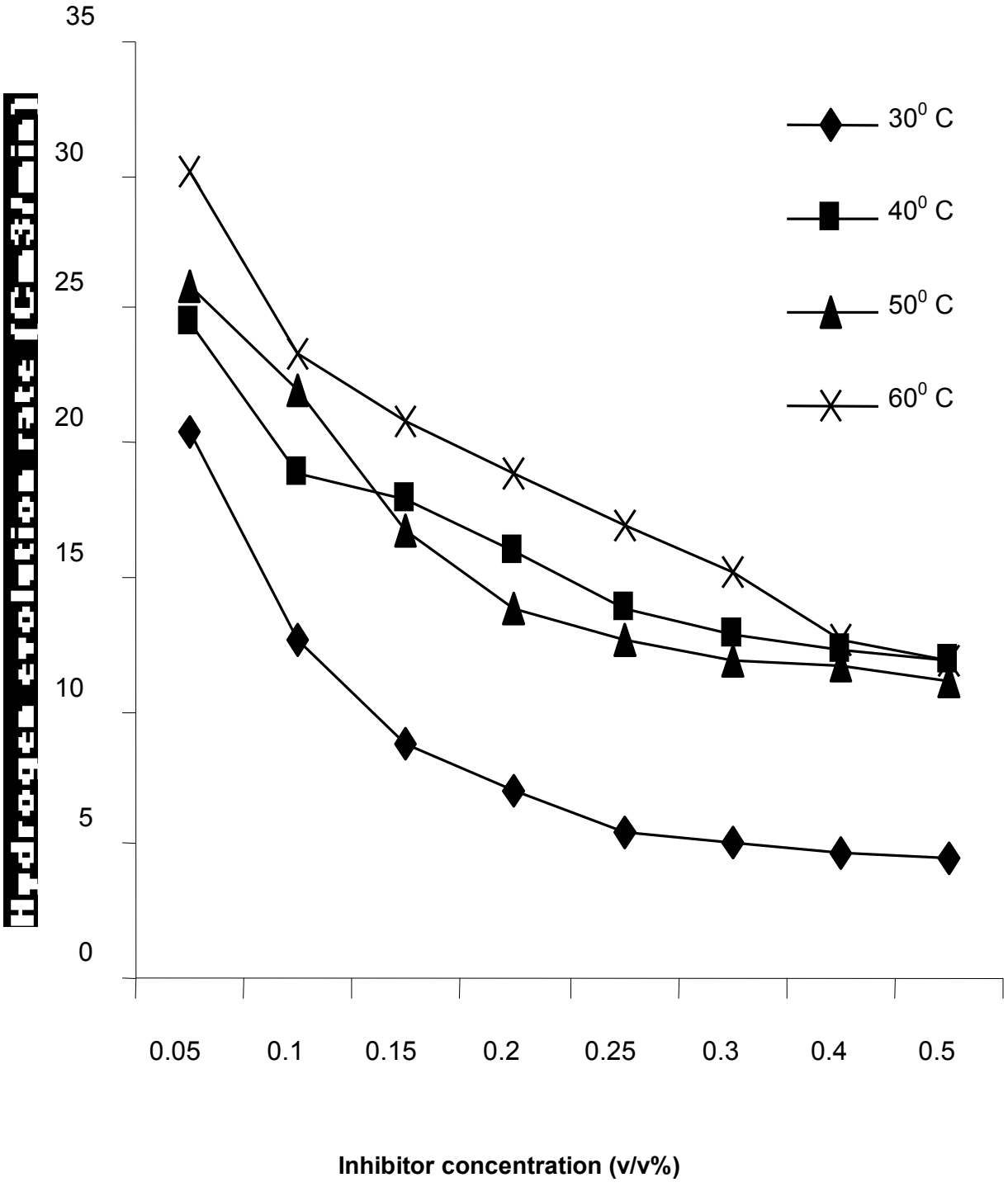


Fig. 4.21: Inhibition efficiencies obtained from the corrosion rates of different concentrations of methylene blue at 0.2M H_2SO_4 at different temperature



Fig, 4.22: **Hydrogen evolution characteristics of the steel samples in 0.2M H_2SO_4 with the addition of varying concentrations of sodium benzoate at different temperatures**

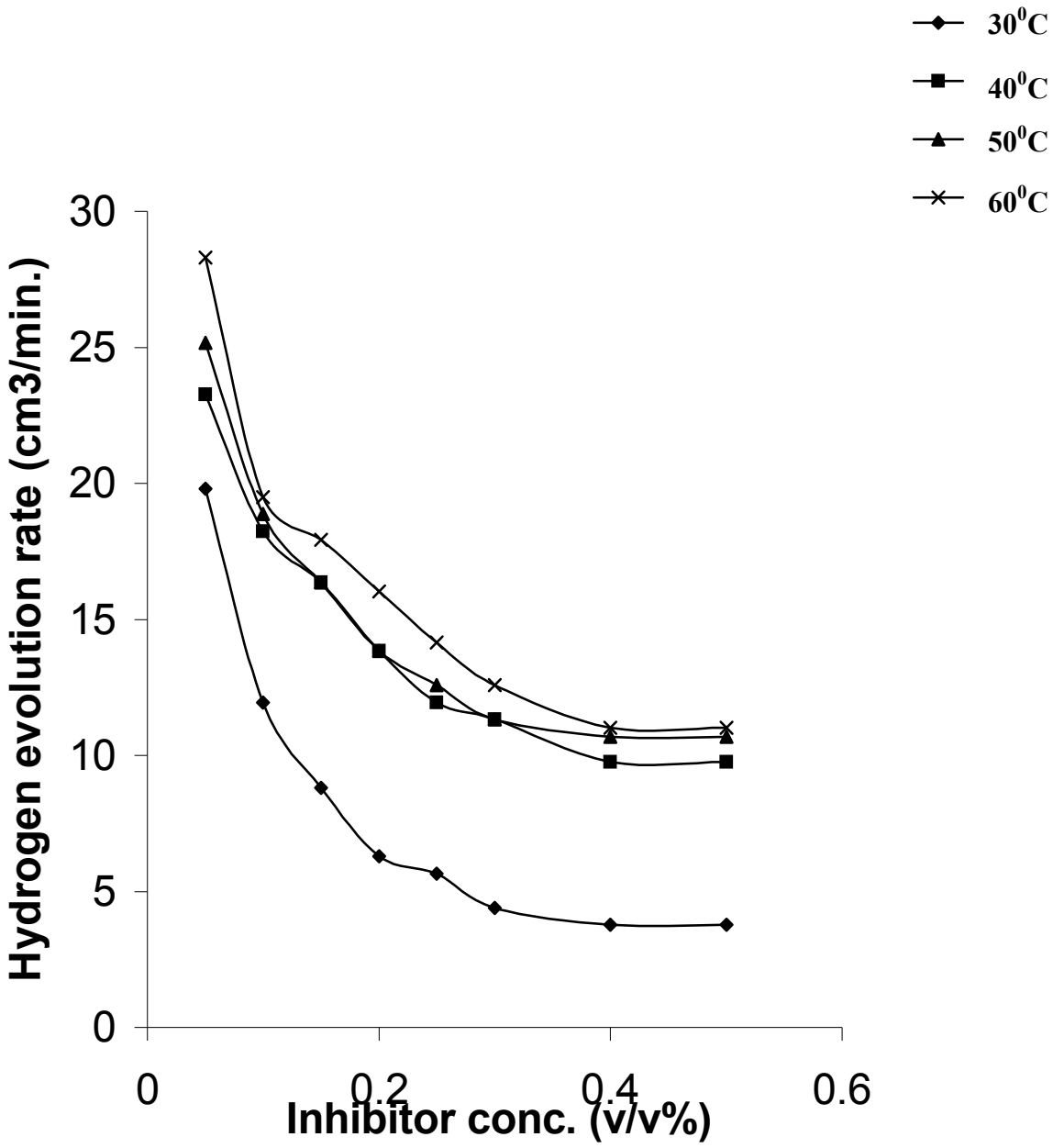


Fig. 4.23: Hydrogen evolution characteristics of medium carbon steel samples in different concentrations of methylene blue at different temperatures.

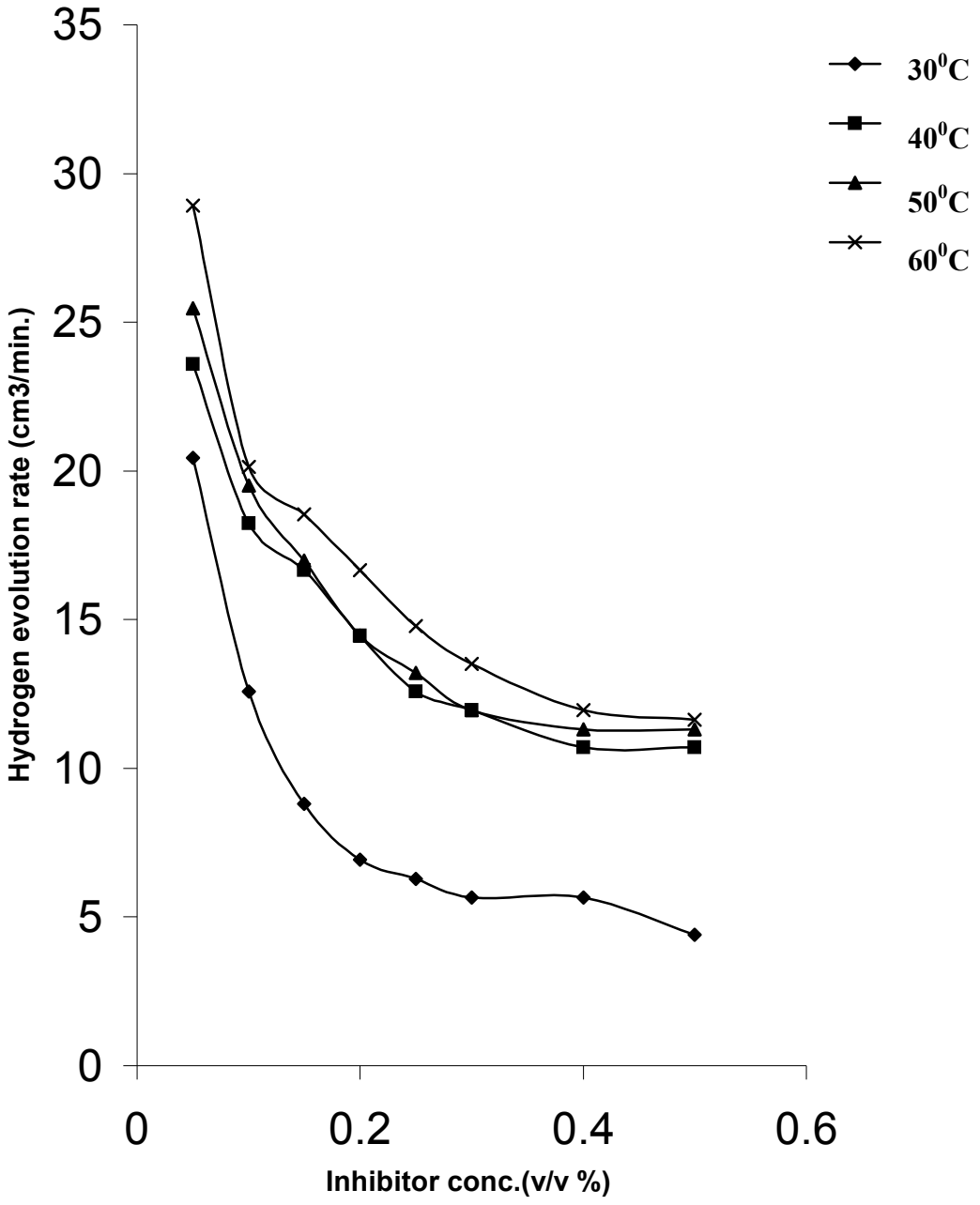


FIG.4.24: Hydrogen evolution characteristics of medium carbon steel samples in different concentrations of neutral red at different temperatures.

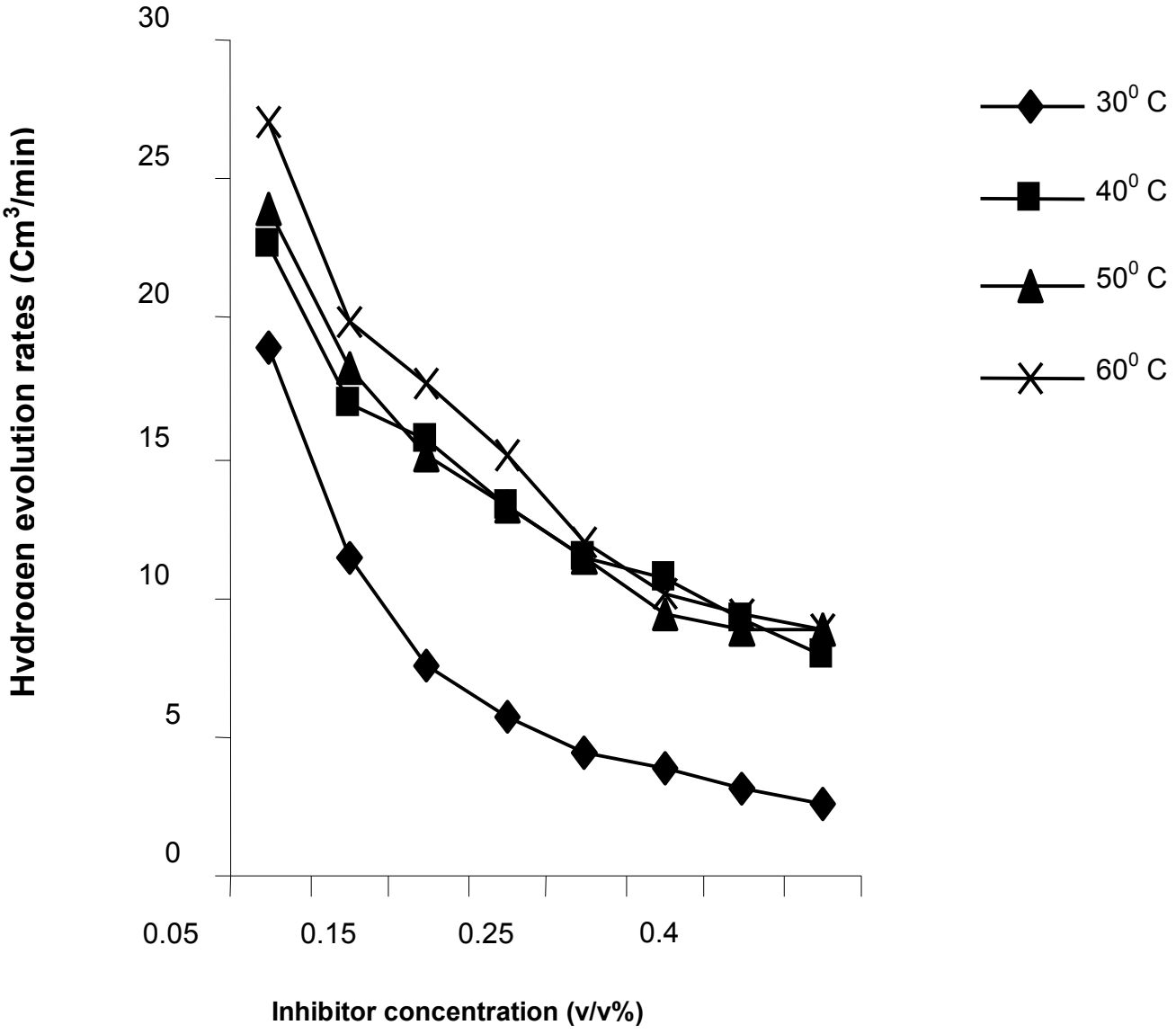


Fig. 4.25: Hydrogen evolution characteristics of the steel samples in different concentrations of *Piliostigma thonningii* at different temperatures

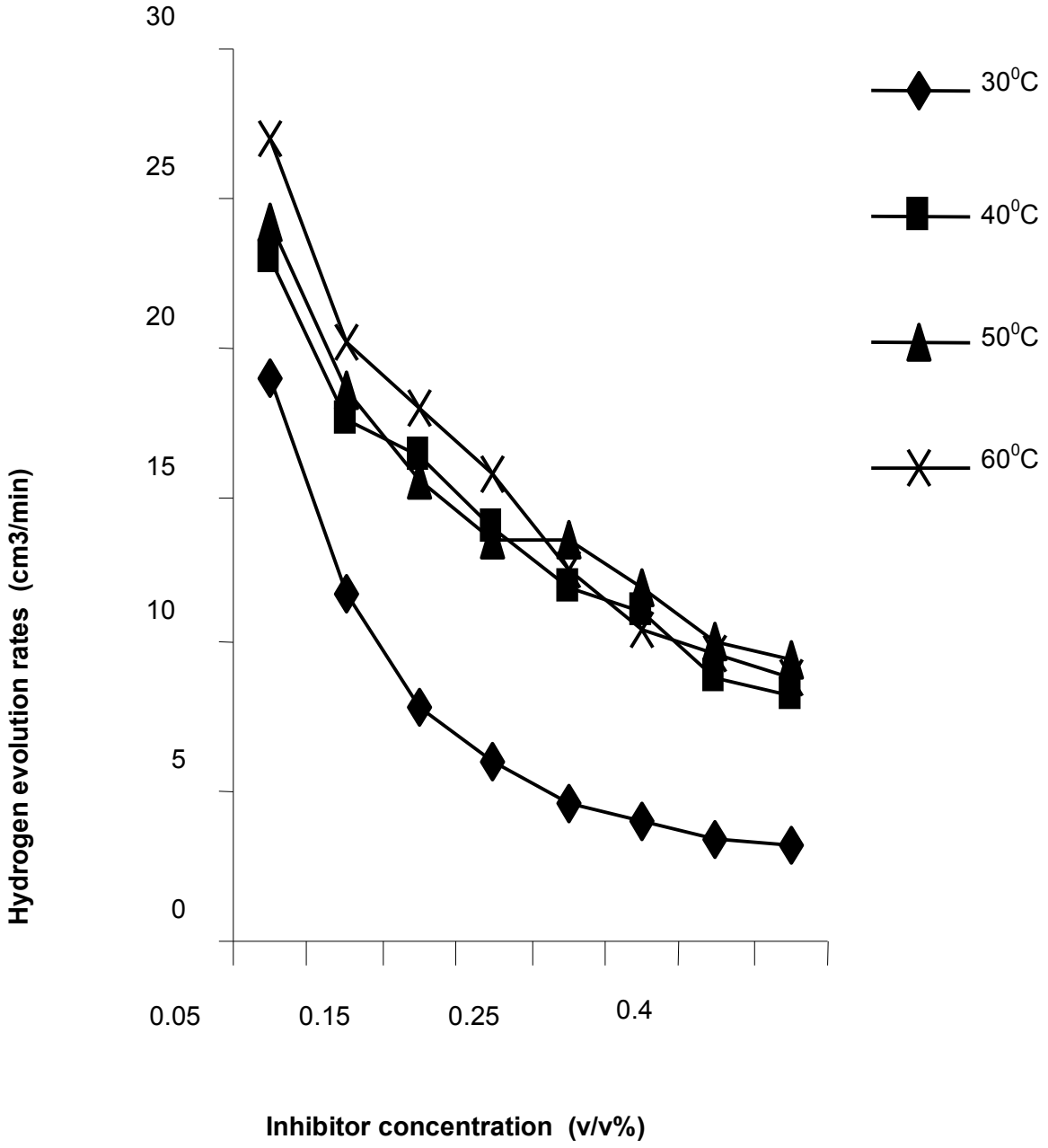


Fig. 4.26: Hydrogen evolution characteristics of the steel samples in different concentration of *Gmelina arborea* at different temperature

4.2 Discussion of results

4.2.1 Effect of the inhibitors on corrosion rate of steel.

To study the anti-corrosion properties of Neutral red, Methylene blue, *piliostigma thonningii* and *Gmelina arborea,* their concentration range was varied from 0.05 to 0.5v/v%. These corrosion properties were compared with those of a well known standard inhibitor, Sodium Benzoate. Figures 4.1-4.10 show the variation of corrosion rate with concentration at different temperatures studied (30, 40, 50, and 60^0C).

It is evident from these graphs that the corrosion rates of the steel samples increased with increasing temperature, and already in extremely low concentration (0.05v/v%) they were found to decrease the corrosion rate. From the figures (4.1-4.10) the corrosion rate of steel also decreased with increasing inhibitor concentration.

The extracts of *P. thonningii* with maximum corrosion rates of 0.0200g/m^2/min at 30^0C, 0.0205 g/m^2/min at 40^0C, 0.0215g/m^2/min at 50^0C, 0.0225g/m^2/ min at 60^0C; and *G. arborea* with corrosion rates of 0.0217g/m^2/ min at 30^0C, 0.0217g/m^2/ min at 40^0C, 0.0230g/m^2/ min at 50^0C and 0.0237g/m^2/ min at 60^0C compared favourably well with Sodium Benzoate having corrosion rates of 0.0371g/m^2/ min at

30^0C, 0.0379g/m^2/min at 40^0C, 0.0382g/m^2/min at 50^0C and 0.0392g/m^2/min at 0^0C. These good inhibition abilities of the extracts corroborates with other finding by Bouklah *et al.,* 2005 and could be attributed to the presence of Tannins.

4.2.2 Effects of inhibitor concentration and experimental temperatures on inhibition efficiencies

The inhibition efficiencies of the inhibitors were calculated using Equation 2.34. the maximum inhibition efficiency for Sodium Benzoate is 91.5% at 30^0C, 90.34% at 40^0C, 89.50% at 50^0C, 86.91% at 60^0C; for methylene blue: 90.96% at 30^0C, 89.79% at 40^0C, 84.39% at 50^0C and 84.57% at 60^0C; for neutral red 83.29% at 30^0C, 51.29-80.95% at 40^0C, 75.10% at 50^0C and 73.40 at 60^0C; for *P. thonningii* : 97.94% at 30^0C, 97.46% at 40^0C, 95.96% at 50^0C and 93.62% at 60^0C; for *G. arborea* 96.98% at 30^0C, 94.56% at 40^0C, 92.33% at 50^0C, 89.23% at 60^0C. It is clear that inhibition efficiency (**IE%)** increased with inhibitor concentration even at a low concentration. This could be attributed to the presence of Tannins, S, N, and O in the structures of the extracts, methylene blue, neutral red and sodium benzoate respectively as also reported by Martinez & Stern, (2003) and Bouklah *et al.,* (2005).

The decrease in inhibition efficiency (IE%) with temperatures is suggestive of the fact that at lower temperatures the inhibitor molecules adsorb onto the steel surfaces, and at higher temperatures desorption of the inhibitor molecules from the steel surface occur which conforms with earlier work by Tang *et al.* (2003).

4.2.3 Mechanism of the inhibition

The degrees of surface coverage (θ) for different concentrations of the inhibitors in 0.2M H_2SO_4 were evaluated from Equation 2.37. For the tabulated values of θ, the increase in θ with increasing inhibitor concentration could be attributed to more inhibitor molecules adsorption onto the steel surfaces when inhibitor concentration was increased which agrees with Tang *et al (* 2003).

a. Langmuir adsorption isotherm

Figures 4.11-4.15 are plots of log (θ/1- θ) against Log C, which were linear for all the inhibitors studied. These suggested that the adsorption of some of the inhibitor compounds on the steel samples follows the Langmuir adsorption isotherm. In this case, the adsorption of the inhibitor molecules belonged to a monolayer adsorption, assuming that the lateral interactions between the

inhibitor molecules are ignored; hence Equation 2.19 (the Langmuir equation) is obeyed.

b. Temkin adsorption isotherm

To further determine the mechanism of inhibitor, the degrees of coverage (θ) were evaluated by Equation 2.21. Testing a plot of θ against log C gives a straight line, suggesting that the adsorption of the Inhibitors Studied Conformed to the Temkin adsorption isotherm elucidated by Equation 2.21 (see figures 4.16- 4.20). The applicability of the Temkin isotherm supports the assumption of a monolayer adsorption on energetically uniform, inhomogeneous metal surface with an interaction in the adsorption layer.

4.2.4 Thermodynamic consideration

Thermodynamic model could well be used to explain the corrosion inhibition of the inhibitors. Thus, the adsorption heats (Q_{ads}) and adsorption free energies (ΔG_{ads}) were calculated, using Equations 2.31 and 2.32 respectively, and tabulated in the appendix (Table 4.34).

The negative values of the free energies of adsorption (ΔG_{ads}) suggested that the adsorption of the inhibitors onto the steel was a spontaneous process. Its increase with temperature revealed that the

adsorption was unfavorable with increase in experimental temperatures as a result of the adsorption of inhibitors from the surface of the steels as established by Tang *et al. (*2003). The ΔG_{ads} values obtained for all the inhibitors are less negative than -20 KJ/mol which suggests strong electrostatic interaction between the charged molecules and the charged metal, indicating physical adsorption as reported by Bilgic and Sahin (2001).

The values of the heats of adsorption as shown in the appendix (Table 4.34), suggested that the adsorption and hence inhibition efficiencies decrease with rise in temperature. This is in good agreement with earlier report by Ebenso *et al.,* 2004. The obtained values of heat of adsorption (Q_{ads}) values were less negative than -10KJ/mol for sodium Benzoate, Neutral red and methylene blue, suggesting probable physical adsorption while for the extracts of *Piliostigma thonningii and Gmelina arborea,* with values more negative than – 10KJ/mol, the adsorption is probably chemical as established by Monticelly *et al.,* (1986). Hence it could be concluded that the different values of ΔG_{ads} for the compounds is indicative that their inhibition properties depend on the ability of

hetero atoms in their molecules to donate electrons to the metal surface, thereby forming a coordinate bond.

4.2.5 Kinetic consideration

The Kinetic model is another useful tool for explaining the mechanism of corrosion inhibition by any inhibitor. The logarithm of corrosion rate could be represented as a straight line function of $^1/T$. The activation energy of the uninhibited system at room temperature (- 838.87 KJ/mol) was much more negative than those of the inhibited systems, which indicates that all the inhibitors are more effective at room temperature as suggested by Ita and Offiong (2001). Since the presence of the inhibitors caused a change in the values of the apparent activation energies, such a change indicated a change in the rate determining step brought about by the presence of various chemical components of the inhibitors. This means that the adsorption processes took place easily and the adsorption layers on the steel samples under test were stable as contained in earlier work by Chetouani *et al.* (2004).

4.2.6 Gasometric consideration

Inhibitors do not affect reactions to the same degree; some are more Anodic than Cathodic, others vice-versa (Hausler, 1979). The

gravimetric method is used to measure the extent of Anodic reaction/protection, while the gasometric (Hydrogen evolution) method determines the extent of cathodic reaction/protection.

Figures 4.22 – 4.26 are indicative of the fact that as the concentrations of the organic resins and plant extracts increased from 0.05 – 0.5v/v%, the Hydrogen evolution rates decreased, which means they affected the cathodic reactions by retarding/stifling the evolution of Hydrogen. The ability of these resins and extracts to retard the evolution of Hydrogen could be due to the formation of a protective thin film (which became more stable as the concentration increased from 0.05 – 0.5v/v%) that shielded the steel from the aggressive attack of the acid.

Since both the organic resins and plant extracts affected the cathodic (evolution of $H_{2)}$ and anodic reaction (dissolution of iron), they are **mixed – type** inhibitors of acid pickling g of medium carbon steel in 0.2M H_2SO_4..

CHAPTER FIVE

5.0 Conclusions and recommendations

5.1 Conclusions

From the obtained results, the following conclusions were arrived at:

1. Sodium Benzoate, Neutral red, Methylene blue, *piliostigma thonningii* and *Gmelina arborea* are effective inhibitors for corrosion of Medium Carbon steel in 0.2M H_2SO_4 pickling acid solution.

2. The inhibition efficiencies (IE%) of the compounds tested in 0.2M H_2SO_4 acid increased with decrease in temperature and increased progressively in the order: Methylene blue (83.29%), Neutral red (90.96%), Sodium Benzoate (91.50%), *Gmelina arborea* (96.98%) and *Piliostigma thonnnigii* (97.94%) at the temperature and concentration ranges studied.

3. The inhibitors retard the anodic and cathodic reactions at varying degrees, thereby implying that they are mixed type inhibitors, affecting both cathodic and anodic reactions/dissolutions.

4. The inhibitors lowered the corrosion rates of the steel by adsorption mechanism which obeyed Langmuir and Temkin adsorption isotherms.

5. The adsorption of the inhibitors onto the steel surfaces is an Exothermic process, and in the process both physical and chemical adsorption takes place.

5.2 Recommendations

1. The effect of varying acid concentration on the inhibiting action of the inhibitors can be investigated.

2. Potentiodynamic polarization studies of the action of the inhibitors in H_2SO_4 acid is recommended so as to verify the kinetic and thermodynamic models arrived at in this work.

3. The extracts of *Piliostigma thonningii* and *Gmelina arborea* could be used as corrosion inhibitors in the processes of chemical cleaning, acid pickling and descaling of medium carbon steels.

4. Since Nigeria is blessed with varied and abundant natural plants, effort should be made to identify more natural plants which could be used as corrosion inhibitors.

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APPENDIX

Table 4.3: Corrosion behaviour of medium carbon steel samples in 0.2M H_2SO_4 in the absence of any inhibitor at different temperatures

Temperatures (^{0}C)	Initial weight (g)	Final weight (g)	Weight loss (g)	Corrosion rate (g/m^2/min)
30	18.4434	18.4202	.0232	0.0730
40	18.4235	18.4001	0.0234	0.0735
50	18.442	18.4184	0.0236	0.0743
60	18.4375	18.4136	0.0239	0.0752

Table 4.4: Corrosion behaviour of medium carbon steel samples in 0.2M H_2SO_4 with the addition of varying concentration of sodium benzoate at 30^{0}C

Inhibitor concentration(v/v%)	Initial weight (g)	Final weight (g)	Weight loss (g)	Corrosion rate (g/m^2/min)
0.05	18.4033	18.3915	0.0118	0.0371
0.10	18.4077	18.3986	0.0091	0.0285
0.15	18.4137	18.4073	0.0064	0.0202
0.20	18.4055	18.3999	0.0056	0.0175
0.25	18.4049	18.3994	0.0055	0.0172
0.30	18.4172	18.4136	0.0036	0.0113
0.40	18.4093	18.4072	0.0021	0.0067
0.50	18.4137	18.4117	0.0020	0.0062

Table 4.5: Corrosion behaviour of medium carbon steel samples in 0.2M H_2SO_4 with the addition of varying concentration of sodium benzoate at 40^{0}C

Inhibitor concentration(v/v%)	Initial weight (g)	Final weight (g)	Weight loss (g)	Corrosion rate (g/m^2/min)
0.05	18.4115	18.3994	0.00121	0.0379
0.10	18.4344	18.4249	0.0095	0.0300
0.15	18.4109	18.4040	0.0069	0.0216
0.20	18.4115	18.4050	0.0065	0.0205
0.25	18.4099	18.4041	0.0058	0.0183
0.30	18.4131	18.4095	0.0036	0.0112
0.40	18.4210	18.4186	0.0024	0.0074
0.50	18.4182	18.4159	0.0023	0.0071

Table 4.6: Corrosion behaviour of medium carbon steel samples in 0.2M H_2SO_4 with the addition of varying concentration of sodium benzoate at 50^0C

Inhibitor concentration(v/v%)	Initial weight (g)	Final weight (g)	Weight loss (g)	Corrosion rate ($g/m^2/min$)
0.05	18.4133	18.4012	0.0021	0.0382
0.10	18.4077	18.3980	0.0097	0.0305
0.15	18.4137	18.4058	0.0079	0.0247
0.20	18.4095	18.4026	0.0069	0.0216
0.25	18.4249	18.4189	0.0060	0.0188
0.30	18.4172	18.4129	0.0043	0.0135
0.40	18.4093	18.4056	0.0037	0.0117
0.50	18.4137	18.4112	0.0025	0.0078

Table 4.7: Corrosion behaviour of medium carbon steel samples in 0.2M H_2SO_4 with the addition of varying concentration of sodium benzoate at 60^0C

Inhibitor concentration(v/v%)	Initial weight (g)	Final weight (g)	Weight loss (g)	Corrosion rate ($g/m^2/min$)
0.05	18.4134	18.4009	0.0125	0.0392
0.10	18.4117	18.4024	0.0093	0.0292
0.15	18.4092	18.4007	0.0085	0.0267
0.20	18.4186	18.4116	0.0070	0.0220
0.25	18.4045	18.3984	0.0061	0.0193
0.30	18.4095	18.4043	0.0052	0.0165
0.40	18.4135	18.4100	0.0035	0.0121
0.50	18.4015	18.3984	0.0031	0.0098

Table 4.8: Inhibition efficiencies obtained from the corrosion rates for different concentrations of sodium benzoate in 0.2M H_2SO_4 at different temperatures

Inhibitor concentration(v/v%)	30^0C	40^0C	50^0C	60^0C
0.05	49.1781	484354	48.5868	47.8723
0.10	60.9590	59.1837	58.9502	61.1702
0.15	72.3288	70.6122	66.7564	64.4947
0.20	76.0274	72.1088	70.9287	70.7446
0.25	76.4384	75.1020	74.6972	74.3351
0.30	84.5205	84.7619	81.8304	78.0585
0.40	90.8219	89.9320	84.2530	83.9095
0.50	91.5068	90.3400	89.5020	86.9681

Table 4.9: Values of coverage obtained from corrosion rates for different concentrations of sodium benzoate in 0.2m h_2so_4 at different temperatures

Inhibitor concentration(v/v%)	30^0C	40^0C	50+C	60^0C
0.05	0.4918	0.4844	0.4859	0.4787
0.10	0.6096	0.5918	0.5895	0.6117
0.15	0.7233	0.7061	0.6676	0.6450
0.20	0.7603	0.7211	0.7093	0.7075
0.25	0.7644	0.7510	0.7470	0.7434
0.30	0.8452	0.8476	0.8183	0.7806
0.40	0.9082	0.8993	0.8425	0.8391
0.50	0.9151	0.9034	0.8950	0.8697

Table 4.10: Corrosion behaviour of medium carbon steel samples in 0.2M H_2SO_4 with the addition of varying concentration of methylene blue at 30^0C

Inhibitor concentration(v/v%)	Initial weight (g)	Final weight (g)	Weight loss (g)	Corrosion rate (g/m2/min)
0.05	18.3995	18.3875	0.0120	0.0377
0.10	18.4100	18.4005	0.0095	0.0299
0.15	18.4095	18.4030	0.0065	0.0204
0.20	18.4009	18.3949	0.0060	0.0189
0.25	18.4201	18.4141	0.0060	0.0189
0.30	18.3999	18.3975	0.0025	0.0079
0.40	18.4000	18.3975	0.0025	0.0079
0.50	18.4230	18.4209	0.0021	0.0066

Table 4.11: Corrosion behaviour of medium carbon steel samples in 0.2M H_2SO_4 with the addition of varying concentration of methylene blue at 40^0C

Inhibitor concentration(v/v%)	Initial weight (g)	Final weight (g)	Weight loss (g)	Corrosion rate (g/m2/min)
0.05	18.3897	18.3776	0.0121	0.0381
0.10	18.4040	18.3940	0.0100	0.0314
0.15	18.4541	18.4466	0.0075	0.0236
0.20	18.3995	18.3921	0.0074	0.0232
0.25	18.4222	18.4160	0.0060	0.0195
0.30	18.4195	18.3795	0.0040	0.0126
0.40	18.4001	18.3976	0.0025	0.0076
0.50	18.4115	18.4091	0.0024	0.0075

Table 4.12: Corrosion behaviour of medium carbon steel samples in 0.2M H_2SO_4 with the addition of varying concentration of methylene blue at 50^0C

Inhibitor concentration(v/v%)	Initial weight (g)	Final weight (g)	Weight loss (g)	Corrosion rate ($g/m^2/min$)
0.05	18.4142	18.4023	0.0119	0.0374
0.10	18.3279	18.3177	0.0102	0.0321
0.15	18.4210	18.4128	0.0082	0.0258
0.20	18.3715	18.3640	0.0075	0.0236
0.25	18.4000	18.3935	0.0065	0.0204
0.30	18.3705	18.3660	0.0045	0.0142
0.40	18.4005	18.3963	0.0042	0.0132
0.50	18.3905	18.3868	0.0037	0.0116

Table 4.13: Corrosion behaviour of medium carbon steel samples in 0.2M H_2SO_4 with the addition of varying concentration of methylene blue at 60^0C

Inhibitor concentration(v/v%)	Initial weight (g)	Final weight (g)	Weight loss (g)	Corrosion rate ($g/m^2/min$)
0.05	18.4617	18.4492	0.0125	0.0393
0.10	18.3092	18.3007	0.0085	0.0267
0.15	18.5092	18.5022	0.0070	0.0220
0.20	18.3786	18.3719	0.0067	0.0211
0.25	18.5001	18.4941	0.0060	0.0189
0.30	18.2975	18.2925	0.0050	0.0157
0.40	18.4045	18.4003	0.0042	0.0132
0.50	17.9987	17.9950	0.0037	0.0116

Table 4.14: Inhibition efficiencies obtained from the corrosion rates for different concentrations of methylene blue in 0.2M H_2SO_4 at different temperatures

Inhibitor concentration(v/v%)	30^0C	40^0C	50^0C	60^0C
0.05	48.3562	48.1632	49.6635	47.7394
0.10	59.0411	57.2789	56.7968	64.4947
0.15	72.0548	67.8912	65.2760	70.7447
0.20	74.1096	68.4354	68.2369	71.9415
0.25	74.1096	73.4694	72.5437	74.8670
0.30	84.9315	82.8571	80.8883	79.7872
0.40	89.1781	89.2517	82.2342	82.4468
0.50	90.9589	89.7960	84.3876	84.5745

Table 4.15: Values of coverage obtained from corrosion rates for different concentrations of methylene blue in 0.2M H_2SO_4 at different temperatures

Inhibitor concentration(v/v%)	30^0C	40^0C	50^0C	60^0C
0.05	0.4836	0.4816	0.4966	0.4774
0.10	0.5904	0.5728	0.5680	0.6450
0.15	0.7206	0.6789	0.6528	0.7-74
0.20	0.7411	0.6844	0.6824	0.7194
0.25	0.7411	0.7347	0.7254	0.7484
0.30	0.8493	0.8286	0.8089	0.7979
0.40	0.8918	0.8925	0.8223	0.8245
0.50	0.9096	0.8977	0.8439	0.8458

Table 4.16: Corrosion behaviour of medium carbon steel samples in 0.2M H_2SO_4 with the addition of varying concentration of neutral red at 30^0C

Inhibitor concentration(v/v%)	Initial weight (g)	Final weight (g)	Weight loss (g)	Corrosion rate ($g/m^2/min$)
0.05	18.4265	18.4152	0.0113	0.0355
0.10	18.4637	18.4546	0.0091	0.0286
0.15	18.5003	18.4920	0.0083	0.0261
0.20	18.4616	18.4547	0.0069	0.0217
0.25	18.4052	18.3977	0.0065	0.0204
0.30	18.4806	18.4746	0.0060	0.0189
0.40	18.4450	18.4405	0.0045	0.0142
0.50	18.4629	18.4590	0.0039	0.0122

Table 4.17: Corrosion behaviour of medium carbon steel samples in 0.2M H_2SO_4 with the addition of varying concentration of neutral red at 40^0C

Inhibitor concentration(v/v%)	Initial weight (g)	Final weight (g)	Weight loss (g)	Corrosion rate ($g/m^2/min$)
0.05	18.4344	18.4230	0.0114	0.0358
0.10	18.4109	18.4017	0.0092	0.0288
0.15	18.4615	18.4529	0.0086	0.0270
0.20	18.4424	18.4352	0.0072	0.0227
0.25	18.4421	18.4351	0.0070	0.0220
0.30	18.4108	18.4044	0.0064	0.0200
0.40	18.4425	18.4374	0.0051	0.0160
0.50	18.4430	18.4385	0.0045	0.0140

Table 4.18: Corrosion behaviour of medium carbon steel samples in 0.2M H_2SO_4 with the addition of varying concentration of neutral red at 50^0C

Inhibitor concentration(v/v%)	Initial weight (g)	Final weight (g)	Weight loss (g)	Corrosion rate (g/m²/min)
0.05	18.4232	18.4116	0.0116	0.0365
0.10	18.4210	18.4116	0.0094	0.0295
0.15	18.4090	18.4002	0.0088	0.0276
0.20	18.4120	18.4044	0.0076	0.0240
0.25	18.4095	18.4020	0.0075	0.0235
0.30	18.4095	18.4024	0.0071	0.0222
0.40	18.4215	18.4150	0.0065	0.0205
0.50	18.4115	18.4056	0.0059	0.0185

Table 4.19: Corrosion behaviour of medium carbon steel samples in 0.2M H_2SO_4 with the addition of varying concentration of neutral red at 60^0C

Inhibitor concentration(v/v%)	Initial weight (g)	Final weight (g)	Weight loss (g)	Corrosion rate (g/m2/min)
0.05	18.4212	18.4090	0.0122	0.0385
0.10	18.4185	18.4090	0.0095	0.0300
0.15	18.4160	18.4069	0.0091	0.0285
0.20	18.4321	18.4237	0.0084	0.0265
0.25	18.4025	18.3948	0.0077	0.0242
0.30	18.4112	18.4037	0.0075	0.0237
0.40	18.4005	18.3937	0.0068	0.0215
0.50	18.4202	18.4138	0.0064	0.0200

Table 4.20: Inhibition efficiencies obtained from the corrosion rates for different concentrations of neutral red in 0.2M H_2SO_4 at different temperatures

Inhibitor concentration(v/v%)	30^0C	40^0C	50^0C	60^0C
0.05	51.3699	51.2925	50.8748	48.8032
0.10	60.8219	60.8163	60.2961	60.1064
0.15	64.2465	63.2653	62.8533	62.1011
0.20	70.2740	69.1156	67.6985	64.7606
0.25	72.0548	70.0680	68.3715	67.8192
0.30	74.1096	72.7891	70.1211	68.4840
0.40	80.5480	78.2313	72.4092	71.4096
0.50	83.2877	80.9523	75.1010	73.4043

Table 4.21: Values of coverage obtained from corrosion rates for different concentrations of neutral red in 0.2M H_2SO_4 at different temperatures

Inhibitor concentration(v/v%)	30^0C	40^0C	50^0C	60^0C
0.05	0.5137	0.5129	0.5087	0.4880
0.10	0.6082	0.6082	0.6030	0.6011
0.15	0.6425	0.6329	0.6285	0.6210
0.20	0.7027	0.6912	0.6770	0.6476
0.25	0.7206	0.7007	0.6837	0.6782
0.30	0.7411	0.7279	0.7012	0.6848
0.40	0.8055	0.7823	0.7241	0.7141
0.50	0.8329	0.8095	0.7510	0.7340

Table 4.22: Corrosion behaviour of medium carbon steel samples in 0.2M H2SO4 with the addition of varying concentration of *Piliostigma thonningii* at 30^0C

Inhibitor concentration(v/v%)	Initial weight (g)	Final weight (g)	Weight loss (g)	Corrosion rate ($g/m^2/min$)
0.05	18.4115	18.4051	0.0064	0.0200
0.10	18.4410	18.4375	0.0037	0.0115
0.15	18.3999	18.3967	0.0032	0.0100
0.20	18.4019	18.3995	0.0024	0.0075
0.25	18.4430	18.4410	0.0019	0.0060
0.30	18.4424	18.4480	0.0016	0.0050
0.40	18.4629	18.4549	0.0080	0.0025
0.50	18.4410	18.4362	0.0048	0.0015

Table 4.23: Corrosion behaviour of medium carbon steel samples in 0.2M H_2SO_4 with the addition of varying concentration of *Piliostigma thonningii* at 40^0C

Inhibitor concentration(v/v%)	Initial weight (g)	Final weight (g)	Weight loss (g)	Corrosion rate ($g/m^2/min$)
0.05	18.4040	18.3975	0.0065	0.0205
0.10	18.4100	18.4063	0.0037	0.0117
0.15	18.4000	18.3968	0.0032	0.0100
0.20	18.4115	18.4090	0.0025	0.0075
0.25	18.4222	18.4201	0.0021	0.0067
0.30	18.3995	18.3977	0.0018	0.0057
0.40	18.4142	18.4132	0.0010	0.0032
0.50	18.4045	18.3997	0.0048	0.0015

Table 4.24: Corrosion behaviour of medium carbon steel samples in 0.2M H_2SO_4WITH THE addition of varying concentration of *Piliostigma thonningii* at 50^0C

Inhibitor concentration(v/v%)	Initial weight (g)	Final weight (g)	Weight loss (g)	Corrosion rate ($g/m^2/min$)
0.05	18.4115	18.4047	0.0068	0.0215
0.10	18.4109	18.4064	0.0045	0.0140
0.15	18.4255	18.4213	0.0042	0.0132
0.20	18.4250	18.4215	0.0035	0.0109
0.25	18.4321	18.4297	0.0024	0.0075
0.30	18.4291	18.4271	0.0020	0.0062
0.40	18.4280	18.4267	0.0013	0.0041
0.50	18.4188	18.4187	0.0010	0.0030

Table 4.25: Corrosion behaviour of medium carbon steel samples in 0.2M H_2SO_4 with the addition of varying concentration of *Piliostigma thonningii* at 60^0C

Inhibitor concentration(v/v%)	Initial weight (g)	Final weight (g)	Weight loss (g)	Corrosion rate ($g/m^2/min$)
0.05	18.4215	18.4143	0.0072	0.0225
0.10	18.4353	18.4300	0.0053	0.0165
0.15	18.4350	18.4307	0.0043	0.0135
0.20	18.4360	18.4324	0.0036	0.0113
0.25	18.4265	18.4236	0.0029	0.0092
0.30	18.4175	18.4151	0.0024	0.0075
0.40	18.4500	18.4479	0.0021	0.0065
0.50	18.4275	18.4261	0.0014	0.0045

Table 4.26: Inhibition efficiencies obtained from the corrosion rates for different concentrations of *Piliostigma thonningii* in 0.2M H_2SO_4 t different temperatures

Inhibitor concentration (v/v%)	30^0C	40^0C	50^0C	60^0C
0.05	72.6027	72.1088	71.0633	70.0798
0.10	84.2466	84.0816	81.1575	78.0585
0.15	86.3014	86.3946	82.2342	82.0479
0.20	89.7260	89.1156	85.3297	84.9734
0.25	91.7808	90.8844	89.9058	87.7660
0.30	93.1507	92.2449	91.6555	90.0266
0.40	96.5753	95.6463	94.4818	91.3564
0.50	97.9452	97.9600	95.9623	93.6176

Table 4.27: Values of coverage obtained from corrosion rates for different concentrations of *Piliostigma thonningii* IN 0.2M H_2SO_4 at different temperatures

Inhibitor concentration (v/v%)	30^0C	40^0C	50^0C	60^0C
0.05	0.7260	0.7211	0.7106	0.7008
0.10	0.8425	0.8408	0.8116	0.706
0.15	0.8630	0.8640	0.8223	0.8205
0.20	0.8973	0.8912	0.8533	0.8497
0.25	0.9178	0.9088	0.8991	0.8777
0.30	0.9315	0.9225	0.9166	0.9003
0.40	0.9658	0.9565	0.9448	0.9136
0.50	0.9795	0.9796	0.9596	0.9362

Table 4.28: Corrosion behaviour of medium carbon steel samples in 0.2M H_2SO_4 with the addition of varying concentration of *Gmelina arborea* at 30^0C

Inhibitor concentration(v/v%)	Initial weight (g)	Final weight (g)	Weight loss (g)	Corrosion rate (g/m2/min)
0.05	18.3997	18.3928	0.0072	0.0217
0.10	18.4005	18.3625	0.0038	0.0119
0.15	18.4101	18.4068	0.0033	0.0103
0.20	18.4125	18.4100	0.0025	0.0080
0.25	18.4205	18.4183	0.0022	0.0069
0.30	18.4115	18.4096	0.0019	0.0061
0.40	18.4005	18.3993	0.0012	0.0037
0.50	18.4123	18.4116	0.0007	0.0022

Table 4.29: Corrosion behaviour of medium carbon steel samples in 0.2M H_2SO_4 ith the addition of varying concentration of *Gmelina arborea* at 40^0C

Inhibitor concentration(v/v%)	Initial weight (g)	Final weight (g)	Weight loss (g)	Corrosion rate ($g/m^2/min$)
0.05	18.4028	0.0072	0.0227	0.0217
0.10	18.4410	18.4372	0.0038	0.0121
0.15	18.4220	18.4183	0.0037	0.0115
0.20	18.4005	18.3975	0.0030	0.0093
0.25	18.4112	18.4089	0.0023	0.0072
0.30	18.4095	18.4074	0.0021	0.0067
0.40	18.4187	18.4169	0.0018	0.0058
0.50	18.4155	18.4142	0.0013	0.0040

Table 4.30: Corrosion behaviour of medium carbon steel samples in 0.2M H_2SO_4 with the addition of varying concentration of *Gmelina arborea* at 50^0C

Inhibitor concentration (v/v%)	Initial weight (g)	Final weight (g)	Weight loss (g)	Corrosion rate ($g/m^2/min$)
0.05	18.2995	18.2922	0.0073	0.0230
0.10	18.4314	18.4272	0.0042	0.0131
0.15	18.2212	18.2173	0.0039	0.0121
0.20	18.4597	18.4562	0.0035	0.0111
0.25	18.3252	18.3220	0.0032	0.0101
0.30	18.3975	18.3945	0.0030	0.0093
0.40	18.3005	18.2982	0.0023	0.0072
0.50	18.3009	18.2991	0.0018	0.0057

Table 4.31: Corrosion behaviour of medium carbon steel samples in 0.2M H_2SO_4 with the addition of varying concentration of *Gmelina arborea* at 60^0C

Inhibitor concentration(v/v%)	Initial weight (g)	Final weight (g)	Weight loss (g)	Corrosion rate ($g/m^2/min$)
0.05	18.4230	18.4155	0.0075	0.0237
0.10	18.3120	18.3072	0.0048	0.0151
0.15	18.4995	18.4951	0.0044	0.0137
0.20	18.4990	18.4952	0.0038	0.0119
0.25	18.3125	18.3090	0.0035	0.0110
0.30	18.4235	18.4203	0.0032	0.0099
0.40	18.4355	18.4326	0.0029	0.0090
0.50	18.3105	18.3079	0.0026	0.0081

Table 4.32: Inhibition efficiencies obtained from the corrosion rates for different concentrations of *Gmelina arborea* IN 0.2M H_2SO_4 at different temperatures

Inhibitor concentration (v/v%)	30^0C	40^0C	50^0C	60^0C
0.05	70.2740	69.1156	69.0444	68.4840
0.10	83.6986	83.5374	82.3688	799202
0.15	85.8904	84.3537	83.7147	81.7819
0.20	89.0411	87.3470	85.0606	84.1755
0.25	90.5480	90.2041	86.4065	85.3723
0.30	91.6438	90.8844	87.4832	86.8351
0.40	94.9315	92.1088	90.3090	88.0319
0.50	96.9863	94.5578	92.3281	89.2287

Table 4.33: Values of coverage obtained from corrosion rates for different concentrations of *Gmelina arborea* in 0.2M H_2SO_4 at different temperatures

Inhibitor concentration (v/v%)	30^0C	40^0C	50^0C	60^0C
0.05	0.7027	0.6212	0.6904	0.6848
0.10	0.8370	0.8354	0.8237	0.7992
0.15	0.8590	0.8435	0.8372	0.8178
0.20	0.8904	0.8735	0.8506	0.8418
0.25	0.9055	0.9020	0.8641	0.8537
0.30	0.9164	0,9088	0.8748	0.8684
0.40	0.9493	0.9211	0.9031	0.8803
0.50	0.9699	0.9456	0.9233	0.8923

Table 4.34: Kinetic and thermodynamic parameters of the various inhibitors at different temperatures in 0.2M H_2SO_4 pickling acid solution

Sample inhibitor	Activation energy (KJ/Mol)	ΔG_{ads} (KJ/Mol) at 30 ^{0}C	ΔG_{ads} (KJ/Mol) at 40 ^{0}C	ΔG_{ads} (KJ/Mol) at 50 ^{0}C	ΔG_{ads} (KJ/Mol) at 60 ^{0}C	Heat of adsorption Q $_{ads}$ (KJ/mol)
Sodium benzoate	-5.20097	-16.4684	-16.8187	-17.1020	-17.4971	-6.08004
Methylene blue	-3.07898	-16.3180	-16.6040	-16.8491	-17.6493	-2.87256
Neutral red	-5.05615	-15.7567	-16.1224	-16.3513	-16.6914	-6.31835
Piliostigma thonningii	-9.90352	-18.9485	-19.4482	-19.5549	-19.7712	-10.64651
Gmelina arborea	-10.16140	-18.6620	-18.9584	-19.1464	-19.4107	-11.10380

Table 4.35:. Hydrogen evolution characteristics of the steel samples in different concentrations of $C_7H_5O_2Na$ at different temperatures

	H_2 Evolution rate (cm^3 $min.^{-1}$)			
Inhibitor Concentration (v/v%)	**30^0C**	**40^0C**	**50^0C**	**60^0C**
0.05	20.44	24.53	25.79	30.19
0.10	12.58	18.87	22.01	23.27
0.15	8.81	17.92	16.67	20.75
0.20	6.92	16.04	13.84	18.87
0.25	5.35	13.84	12.58	16.98
0.30	5.03	12.90	11.95	15.09
0.40	4.72	12.26	11.64	12.58
0.50	4.40	11.95	11.00	11.95

Table 4.36: Hydrogen evolution characteristics of the steel samples in different concentrations of neutral red at different temperatures

	H_2 Evolution rate (cm^3 $min.^{-1}$)			
Inhibitor concentrtion(v/v%)	**30^0C**	**40^0C**	**50^0C**	**60^0C**
0.05	19.81	23.27	25.16	28.30
0.10	11.95	18.24	18.87	19.50
0.15	8.81	16.35	16.35	17.92
0.20	6.29	13.84	13.84	16.03
0.25	5.66	11.95	12.58	14.15
0.30	4.40	11.32	11.32	12.58
0.40	3.77	9.75	10.69	11.01
0.50	3.77	9.75	10.69	11.01

Table 4.37: Hydrogen evolution characteristics of the steel samples in different concentrations of methylene blue at different temperatures

	H_2 Evolution rate (cm^3 $min.^{-1}$)			
Inhibitor concentration (v/v%)	**30^0C**	**40^0C**	**50^0C**	**60^0C**
0.05	20.44	23.58	25.47	28.93
0.10	12.58	18.24	19.50	20.13
0.15	8.81	16.67	16.98	18.55
0.20	6.92	14.46	14.46	16.67
0.25	6.29	12.58	13.21	14.78
0.30	5.66	11.95	11.95	13.52
0.40	5.66	10.70	11.31	11.95
0.50	4.40	10.70	11.31	11.64

Table 4.38: Hydrogen evolution characteristics of the steel samples in different concentrations of *Piliostigma thonningii* at different temperatures

	H_2 Evolution rate (cm^3 $min.^{-1}$)			
Inhibitor concentration (v/v%)	**30^0C**	**40^0C**	**50^0C**	**60^0C**
0.05	18.87	22.64	23.90	27.04
0.10	11.32	16.98	18.24	19.81
0.15	7.55	15.72	15.09	17.61
0.20	5.66	13.21	13.21	15.10
0.25	4.40	11.32	11.32	11.91
0.30	3.78	10.70	9.43	10.06
0.40	3.14	9.12	8.81	9.43
0.50	2.52	7.86	8.81	8.81

Table 4.39: Hydrogen evolution characteristics of the steel samples in different concentrations of *Gmelina arborea* at different temperatures

	H_2 Evolution rate (cm^3 $min.^{-1}$)			
Inhibitor concentration (v/v%)	**30^0C**	**40^0C**	**50^0C**	**60^0C**
0.05	18.87	22.96	24.21	27.04
0.10	11.64	17.61	18.55	20.13
0.15	7.86	16.35	15.41	17.92
0.20	5.95	13.84	13.52	15.72
0.25	4.72	11.95	13.52	12.58
0.30	4.09	11.00	11.95	10.38
0.40	3.50	8.81	10.06	9.75
0.50	3.14	8.18	9.43	8.81