CORROSION INHIBITION WITH PARTS OF PLANT PRODUCTS AT MILD STEEL SURFACES IN ACIDIC MEDIA

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By

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2020

CERTIFICATE

We feel great pleasure in certifying that the thesis entitled "**CORROSION INHIBITION WITH PARTS OF PLANT PRODUCTS AT MILD STEEL SURFACES IN ACIDIC MEDIA**" submitted by Mr. Rakesh kumar dubey is an original piece of research work carried out under our guidance and supervision. He has completed the following requirements as per Ph.D regulations of the university.

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(3) Regulary submitted annual progress report.
(4) Presented her work in the departmental committee.
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ABSTRACT

As a contribution to the current interest in finding out environment friendly more efficient corrosion inhibitors the present study aims to carry out extensive physiochemical studies regarding the corrosion inhibition efficiencies of various parts of plant products on mild steel surfaces in acidic media at different temperatures and periods of contact. Thermodynamic and kinetic parameters also determined in order to define the surface mechanism.

The exploration of natural products of plant origin as corrosion inhibitors is becoming the subject of extensive investigations due to low cost and eco-friendliness of these products and are fast replacing the synthetic, expensive and toxic organic inhibitors.

The protection of metals against corrosion has been a matter of great industrial concern. Corrosion is a surface phenomenon known as attack on metal or alloy by their environment such as air, water or soil or electrochemical reaction to form more stable compound. It causes gradual deterioration of material usually metals. The chemical reaction is generally an electrochemical oxidation on reacting with an oxidant such as oxygen forming iron oxide. Corrosion can also occur in materials other than metals, such as ceramic and polymer.

A corrosion inhibitor is a chemical compound or substance added to corrosive medium to reduce the corrosion rate of metal or an alloy. The effectiveness or corrosion inhibition efficiency of a corrosion inhibitor in a liquid or fluid is a function of many factors like fluid composition, quantity of water, flow regime etc. some of the mechanisms of its effect are formation of passivation layer inhibiting either the oxidation or reduction part of the redox corrosion system (anodic and cathodic inhibitors) or scavenging dissolved oxygen. Inhibitors slow corrosion processes by either increasing the anodic or cathodic polarization behavior, reducing the movement or diffusion of ions to the metallic surfaces or increasing the electrical resistance of metallic surface.

CANDIDATE'S DECLARATION

I hereby certify that the work, which is being presented in this thesis, entitled "**CORROSION INHIBITION WITH PARTS OF PLANT PRODUCTS AT MILD STEEL SURFACES IN ACIDIC MEDIA**" in partial fulfillment of the requirement for the award of the Degree of Doctor of Philosophy, carried under the supervision of Dr.S.M.Nafees and co-supervision of Dr. (Mrs.) Kalpana and submitted to University of Kota, Kota represents my ideas in my own words and where other ideas or words have been included. I have adequately cited and referenced the original sources. The work presented in this thesis has not been submitted elsewhere for the award of any other degree or diploma from any institution.

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ABBREVIATIONS

1. AAS : Atomic Absorption Sprectoscopy

2. AEZJL : Aqueous extract of *Ziziphus jujuba* leaves

3. AEZJS : Aqueous extract of *Ziziphus jujuba* stem

4. AEZJR : Aqueous extract of *Ziziphus jujuba* roots

5. AEZJF : Aqueous extract of *Ziziphus jujuba* fruits

6. AFM : Atomic force microscopy

7. AO : Argan oil

8. CC : Commiphora caudata

9. EDX : Energy-Dispersive X-ray Analysis

10. EFM : Electron Frequency Modulation

11. EIS : Electron Impedance Sprectoscopy

12. FITR : Fourier Transform Infrared Spectroscopy

13. GA : Gum Arabic

14. GIE : Garcina indica extract

15. HE : Hydrogen Evolution

16. LD : *Lavandula dentata*

17. ML : Mass Loss

18. OCP : Open Circuit Potential

19. PDP : Potentiodynamic Polarization

20. SEM : Scanning Electron Microscopy

21. TA : Tryptamine

22. TSC : Tri Sodium Citrate

23. XRD : X-Ray Diffraction

24. BLE : Breadfruit leaves extract

CHAPTER – 1

INTRODUCTION AND REVIEW OF LITERATURE

Due to many remarkable features like low cost, easy availability, high strength and durability mild steel is the commonly used alloy in industries. Mild steel largely used in designing various vessels for aggressive solutions like acidic & basic solutions, salt solutions, reagents for reactions and tanks for handling various corrosive liquids. Acid solutions are generally used for descaling, cleaning, pickling, and in various petrochemical processes. Acids like hydrochloric acid, acetic acid and sulphuric acid are widely used in the pickling process [42]. These acids are also largely used for drilling fracturing and acid simulations at various stages in oil exploration, production and descaling operations and have many other industrial applications [85]

Corrosion is a natural and electrochemical phenomenon caused by potential difference between metal surface and its environmental viz. acid[10]. In acid solution H^+ ions and dissolved oxygen are natural motors of corrosion [21] It is a continuous process and cannot be stopped completely but can be slowed down. Application of corrosion inhibitors in industries and in different fields is the most effective method to slow down the reaction and protect the metal [12]. Corrosion inhibitors are compounds those cause lowering in the corrosion rates of a metal, when added in suitable amounts without significantly changing the concentration of other agents [217].

To study corrosion inhibition of mild steel large number of corrosion inhibitors have been studied so far in acidic media. Most of the well known corrosion inhibitors are those organic compounds containing N, O, S, P and multiple bond or aromatic rings in their structure [91,188,187,195]. Loosely bonded π electrons and lone pairs in these functional groups are key feature which determine the corrosion inhibition efficiency [35, 97, 208]. The organic compounds present in the inhibitors adsorb on the metal surface and block the active sites and thus reduce the corrosion rate considerably [174]. Besides having good corrosion inhibition efficiency they are costly, non biodegradable and harmful for life and environment. The above drawbacks of synthetic corrosion inhibitors provoked the researchers to search for the new cheap, non-toxic, eco-friendly, green, naturally occurring plant products as corrosion inhibitors. Natural products have been reported as corrosion inhibitor for different metals [41, 61, 170, 227]. Extracts of pant roots, seeds, leaves, bark, fruits etc. have been reported in acidic media as corrosion inhibitors [3, 148, 149, 152]. The inhibitive action of natural plant products is reported due to the presence of organic compounds such as tannins, alkaloids, steroids, amino acids, flavonoids etc. [44, 62, 130]. Researchers have studied that inhibitive effect of some plant extracts is due to the adsorption of some phytochemicals present in the extract and formation of protective film on the metal [60, 146,223].

Metallic corrosion has been studied in different acidic, basic and neutral media using different gravimetric and electrochemical methods and different techniques. Hesham T.M., Abdel-Fatah et al. reported Miswak (*Salvadora persica*) aqueous root extract in 1.0 N sulfamic acid solution using mass loss and EIS techniques at 303-313 K temperatures [3]. Pandian Bothi Raja et al. studied *Neolamarckia cadamba* extract in 1M HCl medium using PDP, EIS & SEM techniques [171]. Aqueous extract of LD (*Lacendula dentata*) was investigated in 1M HCl solution by weight loss, EIS and petentiodynamic polarization measurements and shown 95% efficiency at 2% by weight extract concentration. Polarisation studies indicate that phytochemicals present in LD extract acts as mixed type of inhibitors [36].

Raphia hookeri (RH) gum exudate was studied in H_2SO_4 solution by weight loss and hydrogen evolution technique and 71.9% efficiency was obtained at 0.5g/L at 30^oC [208]. Ehteram A. Noor investigated fenugreek leaves extract in 2M HCl & 2M H_2SO_4 solution and found Langmuir adsorption in HCl and Temkin adsorption isotherms in H_2SO_4 solution are followed [139]. *Hibiscus cannabinus* extract inhibitor for mild steel corrosion is reported by M.Ramanand Singh et al. in 0.5 M H_2SO_4 [194]. Ecofriendly Quinazoline derivative was studied by A.S. Fouda et al in

2M HCl solution using EIS, PDP electrochemical frequency modulation weight loss technique and observed 93.8% inhibition efficiency at 30°C[67].

Sesbania sesban extract (SSE) for carbon steel was reported as inhibitor in 1M HCl. 91.08% efficiency was obtained at 2.00g/L at 25°C [17]. *Mentha rotundigolia* leaves extract for steel in 1M HCl in the range 298K-338K of temperature was studied as corrosion inhibitor [98]. Inhibitive effect of gramine was studied in 1M HCl by PDP, EIS & gravimetric measurements [165]. *Calotropis gifantea* leaves extract was studied by using weight loss and electrochemical techniques in 1M HCl solution [50]. P.S. Desai investigated *Hibiscus rosa sinensis* leaves extract for mild steel in 1M HCl using gravmetric & electrochemical techniques [49]. Eddy and Mamza studied ethanolic extract of seeds and leaves of *Azadirachta indica* in H_2SO_4 solution using gravimetric, gasometric and IR methods [55]

90% inhibition efficiency was obtained in mild steel corrosion inhibition in 1N H_2SO_4 solution using *Nyctanthes arbortristis* leaves extract [177]. Aqueous extract of *Ammodaucus leucotrichus* fruit was reported as inhibitor for C38 steel in 1M HCl solution using EIS, EDP & weight loss method [127]. Maria V. Fiori Bimbi et al. studied pentin as eco friendly corrosion inhibitor [66]. Bei Ojan studied inhibitive effect of tannic acid on mild steel corrosion in sea water wet/dry cyclic conditions using weight loss & electrochemical methods [164]. Banana peel extract gave 98% inhibition efficiency at Zn^{+2} (15ppm) by weight loss method [176].

Alka Singh and Kalpana S. have reported corrosion inhibition at iron surfaces by fenugreek leaves in acetic acid & citric acid solutions by weight loss method [191, 192]. Leaves extract of *Gossipum hirsutum L.* was studied by Olusegun K. Abiola et al. as green corrosion inhibitor for alluminium in HCl solution. They employed weight loss method for corrosion inhibition studies and observed 92% inhibition efficiency at 30°C [7].

Corrosion inhibitor for mild steel in 0.5M H_2SO_4 and 1M HCl solution was investigated by P.R. Vijayalakshmi, T. Rajakshmi and S. Subhashini using weight loss and electrochemical measurement techniques. The plant material taken was *Borassus flabellifer Linn.* (palmyra palm) shell extract 97.65% and 98.11% inhibition efficiencies were observed in 0.5 M H_2SO_4 and 1M HCl solutions respectively at 3% (v/v) concentration of extract [215].

D.G. Ladha et al. evaluated corrosion inhibition properties of aqueous extract of fenugreek seeds (FSE) (*Trigonella foenum graecum*) for aluminum in hydrochloric acid medium using gravimetric, galvanostatic polarization and EIS techniques. Results showed that presence of phytochemical constituents such as trigonelline present in extract adsorbs at the metal sites. Adsorption process follows Langmuir adsorption isotherm [113].

Anticorrosive behavior of *Glycine max* (L.) oil has been investigated in 2M H_2SO_4 solution by Bhawsar Jeetendra et al. using weight loss method for mild steel. 47.98% inhibition efficiency was obtained for 20g/L at 298 K [34]. Abdul Rasoul Salih Mahdi and Shymma Kadhem Rahem Studied inhibitive properties of aqueous extract of leaves of herb *Thymus vulgarize* (thyme) for reinforced steel in simulated chloride contaminated concrete pore solution (SCP) using open circuit potential and potentiodynamic polarization technique [125].

R. Karthik et al. studied the anticorrosion activity of *Cassia senna* for mild steel in 1M hydrochloric acid using weight loss, potential dynamic polarization, electrochemical impendance spectroscopy (EIS), scanning electron microscopy (SEM), UV-visible spectroscopy and x-ray diffraction (XRD) studies [93].

Nutan Kumpawat et al. reported the anticorrosive behavior of *Holy Basil* (Tulsi) for tin metal in HNO_3 solution by using leaves and stem extracts of different varieties by weight loss technique [111]. It has been reported by Kanchan Agrawal that *Fenugreek* leaves and Lemon peel extracts are good corrosion inhibitors for mild steel in 1M HCl solution using weight loss and electrochemical methods [11].Inhibition efficiency of seed extract of Kuchla(*Strychnos nuxvomica*) has been reported for mild steel in hydrochloric acid solution by Ambrish Singh et al. [20]

The inhibitive effect of *Aloe vera barbadensis* gel was studied on copper metal in hydrochloric acid solution using weight loss technique [79]. The inhibitive effect of leaves extract of African bread fruit in 1M H_2SO_4 solution was investigated by P.M. Ejikeme et al. for mild steel and aluminum metal [57]. They obtained 70.55% inhibition efficiency for mild steel and 78.65% inhibition efficiency for Al at 30^oC in 5g/L concentration of BLE.

Extract of areal parts of *Daucus carota* plant was investigated as green corrosion inhibitor for mild hydrochloric acid medium using weight loss method and on theoretical analysis [96] maximum 95.72% inhibition efficiency was achieved at 2% (v/v) DCA extract at 5h of immersion at 30^oC. Cantaloupe (*Cucumis melo*) juice and seed extracts has been investigated for cast iron corrosion inhibition in 1M hydrochloric acid solution [64] using hydrogen evolution measurements (HEM) and mass loss measurements. Adsorption process followed Langmuir adsorption isotherm.

It has been found that *Polyalthia longifolia* leaves extract is a good corrosion inhibitor for mild steel. 92% inhibition efficiency was observed at 1.5% (v/v) concentration of extract in sulphuric acid medium and 87% inhibition efficiency was observed at 1.5% (v/v) concentration of extract in hydrochloric acid medium [212, 213]. I.J. Alinnor and P.M. Ejikeme investigated aquesous, ethanolic and acidic leaves extract of *Ocimum gratissimum* for corrosion inhibition of aluminum in hydrochloric acid medium using gravimetric method [15]. Narayana Hebbar et al. revealed the anticorrosion behavior of anti inflammatory ketosulfone drug for Zn in acidic medium by polarization and AC-impedance technique at 303-333K. Tafel plots were drawn in experiments which indicated that the drug is a mixed type inhibitor [80].

S. Aejitha, P.K. Kasthuri and P.Geethamani studied the corrosion inhibition efficiency of acidic leaves extract of *Commiphora caudate* (CC) in 1M HCl and1M H_2SO_4 solutions separately using weight loss and electro chemical techniques. [9].Results showed that inhibitive property of CC is greater in hydrochloric acid solution. Extract of rice husk ash was studied as a good corrosion inhibitor for mild steel in 1M H_2SO_4 and HCl solution. The study was carried out using mass loss and atomic absorption spectroscopy (AAS) [13]. Iroha et al. revealed anticorrosive behavior of acetone extract of red onion skin for aluminum in 2M hydrochloric acid solution using weight loss method. [86].

Yaro and Ibraheem revealed the inhibition effect of Peach juice on low carbon steel corrosion in hydrochloric acid at different temperatures using weight loss and polarization techniques. 91% inhibition efficiency was obtained at 50^oC in $50cm^3/L$ inhibitor concentration [221]. E.E. Oguzie studied corrosion inhibitor effect of leaves extract of *Sansevieria trifasciata* on aluminum metal by gasometric technique [147].

It has been reported by L.Y.S. Helen et al. that *Aquilaria crassna* leaves extract is a good corrosion inhibitor for mild steel in 1M HCl medium using gravimetric method (weight loss method) [81]. Potato peel extract was investigated as an effective naturally available corrosion inhibitor for mild steel in 2M HCl by Taleb H. Ibrahim at al. [85]

Gopal Ji et al. studied corrosion inhibition effect of root extract of *Chlorophytum borivilianum* on mild steel in HCl and H_2SO_4 solution using various techniques viz. weight loss, electrochemical impedance spectroscopy, Tafel polarization and scanning electron microscopy [75].

Inhibition effect of biomass extract of *Petersianthus macrocarpus* plant was revealed by gravimetric, electrochemical impedance and potentiodynamic methods on mild steel corrosion in HCl and H_2SO_4 solutions [12]. Saedah R. Al-Mhyawi found anticorrosive behavior of *Juniperus* plant extract for mild steel in H_2SO_4 solution using chemical (HE and WL) and electrochemical (PDP and EIS) methods [16].

M. Dekmouche et al. investigated corrosion inhibition effect of ethyl acetate extract of *Pistacia atlantica* gals in hydrochloric acid solution for mild steel using weight loss, polarization and AC impedance methods [48]. O. Benali et al. revealed the corrosion inhibition effect of tannin extract of *Chamaerops humilis* plant and potassium iodide on the corrosion of mild steel in 0.5M H_2SO_4 solution using electrochemical method [30]. S.A. Umoren at al. investigated synergistic inhibition effect between naturally occurring exudate gum and halide ions on mild steel corrosion in H_2SO_4 medium by hydrogen evolution techniques [209].

L. Afia et al. studied anticorrosive property of Argan Oil (AO) on corrosion of C38 steel by weight loss, electrochemical polarization and EIS methods [10]. Taleb Ibrahim et al. revealed that leaves extract showed 84% corrosion inhibition efficiency in 2M HCl solution for mild steel by using weight loss measurement and various electrochemical techniques [84].

Osmanthus fragran leaves extract was studied as corrosion inhibitor for carbon steel in hydrochloric acid medium using potentiodynamic polarization, electrochemical impedance spectroscopy (EIS), atomic force microscopy (AFM), Fourier transform infrared spectroscopy (FTIR) and quantum chemical calculations [118]. Bamboo leaf extract was studied by Xianghong Li et al. as corrosion inhibitor for steel in HCl and H_2SO_4 solutions [121]. Xianghong Li et al. also studied bamboo leaves extract as corrosion inhibitor in citric acid solution for steel and zinc using weight loss, potentiodynamic polarization curves and electrochemical impedance spectroscopy (EIS) methods [122].

M. Faustin et al. investigated corrosion inhibition of C38 steel by *Geissospermum* leave alkaloids extract in hydrochloric acid solution using electrochemical studies [65]. Long chain alkyl carboxylates like stearate, palmitate and myristate were investigated as green corrosion inhibitor for magnesium alloy ZE41 corrosion in aqueous salt solution using potentiodynamic polarization, EIS, SEM and EDX analyses [51]. Black papper extract was studied by M.A. Quraishi, Dileep Kumar Yadav and Ishtiaque Ahamad as corrosion inhibitor for mild steel in hydrochloric acid solution using mass loss measurements, PDP, Linear polarization resistance and EIS [167]. Corrosion inhibition of aluminum by *Salvia Judica* extract was investigated in 1M NaOH solution by E.M. Nawafleh et al. using weight loss method at different temperatures [135].

Deepa prabhu and Padma latha Rao found *Garcina Indica* extract (GIE) as novel green inhibitor and 6063 aluminium alloy in 1.0M H_3PO_4 solution using potentiodynamic polarization, Tafel extrapolation technique and EIS technique [160].

Olasehinde E.F. et al. studied corrosion inhibition effect of *musa Sapientum* peels extract in HCl solution for mild steel using weight loss method [153]. I.E. Uwah, P.C. Okafor, V.E. Ebiekpe investigated corrosion inhibition effect of leaves, bark and roots extract of *Nauclea Latifolic*on for mild steel in H_2SO_4 solution using weight loss and gasometric techniques [211].

L. Barmmu et al. reported *Chenopodium ambrosiodes* extract as good corrosion inhibitor for steel l in suphuric acid solution using weight loss method, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) measurements 94% inhibition efficiency was obtained at 4g/L[25].

M.Dhamini et al. investigated black pepper extract and its piperine as a corrosion inhibitor for C38 steel in 1M HCl by weight loss method [46]. J. Halambek et al. reported natural oil extract from *Lavandula angustifolia* L. as corrosion inhibitor for A1-3Mg alloy by weight loss, polarization measurements and SEM [78].

Corrosion inhibition effect of *Phyllanthus amarus* extracts from leaves and seeds for mild steel corrosion in acidic media has been studied by P.C. Okafor at al.

[151]. M. Lebrini et al. reported *Oxandra asbeckii* alkaloids extract as an good corrosion inhibitor for C38 steel in 1M hydrochloric acid medium using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) [115].

A.K. Satapathy et. al. have been investigated the corrosion inhibition of mild steel by extract of *Justicia gandarussa* plant in hydrochloric acid solution by weight loss and electrochemical techniques. 93% inhibition efficiency was achieved with 150 ppm extract at 25^{o}C [179]. Shivakumar and mohana reported *Centella asiatica* extracts as green corrosion inhibitor for mild steel in 0.5 M sulphuric acid medium using gravimateric, polarization and EIS measurements. 95.08% inhibition efficiency was obtained at 303K [186]. *Spirulina platensis* was reported as green corrosion inhibitor for mild steel by C.Kamal and M.G. Sethuraman using weight loss, PDP method, EIS and SEM analysis [92].

3-[(4-amino-2-methyl-5-pyrimidinyl)methyl]-5-(2-hydroxyethyl)-4-methylthiazoliumchloride hydrochloride was reported as green corrosion inhibitor for copper in HNO_3 solution by Olusegun K. Abiola et al. using weight loss method [6]. M. Behpour et al. investigated two aleo-gum resin exudates from *Ferula assafoetida* and *Dorema ammoniacum* as corrosion inhibitor for mild steel corrosion in acidic medium using weight loss, PDP and EIS methods [27]. Mahendra Yadav et al. reported synthesized thiourea derivatives for mild steel corrosion inhibition in 15% HCl solution using weight loss, PDP, EIS, techniques [220]. Punita Mourya, Sitashree Banerjee and M.M. Singh reported *Tagetes erecta* (marigold flower) extract as green corrosion inhibitor mild steel in 0.5 M H_2SO_4 solution using gravimetric, PDP and EIS measurements [132]. N.O. Obi-egbedi et al. investigated extracts of *Spondias mombin* L. as green corrosion inhibitor for aluminium in sulphuric acid medium using standard gravemetric technique [141].

L. Bammou et al. studied the corrosion inhibition effect of eco friendly cheap natural substance *Harmal* extract on C-steel in hydrochloric acid solution [24]. They used weight loss and electrochemical methods. Ambrish Singh et al. reported extract of *Zanthoxylum schinifolium* as an effective corrosion inhibitor for N80 steel in CO_2 *saturated 3.5% NaCl solution by using EIS ,PDP,XRD, SEM techniques[19]. Jambolana* on zinc were reported by P.D.Rani et al. in 1N HCl medium using mass loss measurement [144]. Olusegun K. Abiola and A.O. James studied corrosion inhibiting effect of *Aloe vera* leaves extract by weight loss techniques, on the corrosion of zinc in 2M HCl solution [5].

F. Silvio de Souza et al. evaluated caffeine as green corrosion inhibitor for copper using PDP and EIS techniques in aerated 0.1M H_2SO_4 solution [190]. A.S. Yaro et al. showed the inhibitive properties of Apricot juice in 1M phosphoric acid to protect mild steel from corrosion using weight loss technique at different temperatures [222]. S. sathiya, K. Bharathi and S. Geetha revealed corrosion inhibition of Al metal by *Datura metel* leaves extract in 1M HCl using chemical and electrochemical techniques [180].

S. Anath Kumar et al. studied aqueous extract of *Magnolia champaca* flower [107] as corrosion inhibitor for mild steel in 0.5 M H_2SO_4 solution and *Magnolia champaca* stem extract [109] using weight loss, PDP, EIS methods for metal steel in 1M HCl. *Tectona grandis* seed extract has shown a corrosion inhibiton properties for mild steel in HCl solution by G.R. Thusnavis et al. [205]. Gopal ji et al. studied corrosion inhibitive effect of *Argemone mexicana* plant leaves extract [74], *Capsicum annum* fruit extract [73], *Parthenium hysterophorus* plant leaves extract [75] for mild steel in HCl solution.

S. Ananth Kumar et al. also studied the leaves extract of *Oxystelma esculentum* plant as corrosion inhibitor for mild steel in 0.5 M H_2SO_4 solution using weight loss, EIS and polarization techniques [110]. It has been shown that ethanolic extract of *Ricinus commun* leaves is a good corrosion inhibitor for mild steel in 100 ppm NaCl solution [181]. Vitamin B-12 solution was tested by S. Ananth Kumar et al. as corrosion inhibitor in 0.5 M H_2SO_4 for mild steel using weight loss, PDP and

EIS measurements [22]. A.M. Al-Fakih, M.Aziz and H.M.Sirat reported the acidic extract of turmeric and ginger rhizomes separately as corrosion inhibitor for mild steel in 1M HCl solution using weight loss and PDP measurements. [14]. Aqueous extract of ginger has also been reported as inhibitor for mild steel in 1M HCl by weight loss, open circuit potential (OCP), linear and Tafel polarization techniques [63].

Methanolic extract of *Alpina galinga* was tested against mild steel in 0.5 N H_2SO_4 for corrosion inhibition by S.Ananth Kumar et al. using weight loss, PDP and electrochemical impedance measurements [108].

Bryophyllum pinnatum Leaves extract has been proved as a corrosion inhibitor for mild steel in 0.5 M HCl solution by Dakeshwar Kumar Verma and Fahmida Khan using gravimetric and scanning electron microscope technique [214]. Leaves extract of *Millingtonia hortensis* for mild steel corrosion in 1N HCl and 1N H_2SO_4 solutions using mass loss measurements was studied by S. Kulandai Therese and V.G. Vasudha [103].

E.L Ating et al. also studied leaves extract of *Ananas Sativum* as green inhibitor for aluminum in HCl solutions using weight loss and hydrogen evoluation method [23]. *Cocos nucifera* petiole extract was investigated as corrosion inhibitor for mild steel in 0.5M H_2SO_4 and 1M HCl solutions using mass loss, polarization and electrochemical impedance techniques [216]. The leaves extract of *Carcia papaya* and *Camellia sinensis* (green tea) extract were investigated as green corrosion inhibitors for $\alpha\,\beta$ (duplex) brass in 1M Nitric acid solution using weight loss and potential measurement techniques [123]. Extract of leaves and berries of *Solanum nigrum* were investigated as green inhibitor for zinc in 0.5N HCl [155] using weight loss, thermometric and gasometric methods. *Vernonia amygdalina* (bitter leaf) was tested for zinc plate corrosion inhibitor in 2M HCl solution by weight loss, gasometric and potentiostatic polarization [158].

A.Y. El-Etre et al. studied aqueous extract of *Lawsonia* (heena) leaves as corrosion inhibitor for C-steel, nickel and zinc in acidic, neutral and alkaline medium using polarization technique [62]. *Morinda tinctoria* leaves extract has shown corrosion inhibition property for mild steel in HCl medium using weight loss and AC impedance studies [102].

The corrosion controlling capacity of beet root extract was investigated in well water in the absence and presence of Zn^{+2} ion for carbon steel by mass loss method [182]. ethanolic extract of leaves and seeds *Azadiraciha indica*, were tested as corrosion inhibitor for mild steel in H_2SO_4 solution using weight loss and gasometric techniques [55]. A.S. Founda et al. studied methanolic extract of barks and rhizomes of *curcum* plant as a green inhibitor for steel in 3.5% NaCl and l6ppm Na_2S solution by PDP,EIS, electro chemical frequency modulation (EFM) techniques [68]. Corrosion inhibition by *Ficus aburiljfolia* plant extract on N-80 oil well tubular steel was studied by weight loss technique by G.Abubakar et al. [8] in 15% HCl solution. *Cassia auriculata* flowers extract was tested as corrosion inhibitor for Al and mild steel in 2M HCl solution by weight loss, polarization and impedance studies by A. Rajendran and C. Karthikeyan [172]. *Ginreng root* extract has been proved as eco-friendly corrosion inhibitor for AA 1060 aluminum alloy in HCl solution by weight loss method [142].

Hui Cang et al. studied *Aloe* leaves extract for mild steel corrosion in 1M HCl solution by weight loss PDP, EIS techniques [83]. S.M. Mahdi showed *pomegranate* peel powder as inhibitor for mild steel in 5% HCl and 5% H_2SO_4 solutions using weight loss method [126]. S*olanum trilobatum* was tested as green inhibitor for aluminum corrosion in 1M NaOH medium using weight loss, hydrogen evoluation, EIS and polarization methods [71]. F.S. de souza and A. Spinelli studied naturally occurring biological molecule caffeic acid as corrosion inhibitor for mild steel in 0.1 M H_2SO_4 solution using weight loss, PDP, EIS and Raman spectroscopy [47]. M.Znini et al. revealed the corrosion inhibition effect of essential oil obtained from

Salvia aucheri mesatlantica for mild steel corrosion in 0.5 M H_2SO_4 solution using weight loss and electrochemical polarization measurements [225].

A.S. Abdul rahman et al. have investigated corrosion inhibition of mild steel in sulphuric acid solution by leaves extract of *African prequentina* using gravimetric, gasometric and thermometric measurements [4].

Seed extract of *Psidium guajava* fruit (guava) was studied by K.P. Vinod Kumar et al. as inhibitor for Carbon steel in HCl medium using weight loss measurement [104]. S. Leelavathi and R. Rajalakshmi revealed the corrosion mitigating property of leaves extract of *Dodonaea viscosa* L. on mild steel corrosion in 1M HCl and 0.5M H_2SO_4 using mass loss and electrochemical measurements [116]. Nasrin Soltani et al. studied leaves extract of *Salvia officinalis* as inhibitor for 304 stainless steel corrosion in 1M HCl solution using weight loss, PDP, EIS and Tafel polarization studies [199]. M. Sangeetha et al tested aqueous extract of *asafoetida* for protection of mild steel corrosion in sea water using weight loss method [175]. Bentiss et al. studied 4H-1,2,3-triazole derivatives as corrosion inhibitors for mild steel in normal HCl solution by using weight loss and AC impedence measurements and polarisation curves. Results showed that 4H-1,2,3-triazole derivatives obeys Langmuir adsorption model on mild steel surface [31].

The corrosion inhibition efficiency of pyridazine compounds in 0.5M H_2SO_4 medium were studied by Bouklah et al. using weight loss method at various temperatures and revealed that inhibition efficiency increases with increase in concentration. Pyridazine compounds followed Langmuir adsorption isotherm on mild steel surface [37]. Corrosion inhibition of Armco iron in HCl solution was studied by using four surfactants: tetradecyl trimethyl ammonium iodide (TTAI), tetra decyl trimethyl ammonium brornide (TTAB), hexadecyl trimethyl ammonium bromide (HTAB) and dodecyl trimethyl ammonium bromide (DTAB). They observed that protection efficiency increases with increase in inhibitor concentration and length of alkyl chain and these surfactants followed Langmuir adsorption isotherm on Armco iron surface [39].

Cristofari et al. studied essential oil extracted from *Purlicaria mauritanica* as corrosion inhibitor for mild steel in 0.5M H_2SO_4 medium. They employed weight loss, EIS, electrochemical polarization methods. Carvatan acetone was found predominant component in essential oil in 87.3%. 91.5% inhibition efficiency was found at 2g/L essential oil concentration. Spontaneous adsorption of inhibitor was adsorption followed Langmuir adsorption isotherm [45].

Eddy investigated corrosion prevention properties of ethanolic extract of *Garcinia kola* and *Cola nitida* using weight loss and thermometric methods for mild steel in H_2SO_4 medium. Physical adsorption mechanism was proposed from inhibition efficiency trend with temperature but Langmuir adsorption isotherm was followed by inhibitor [56]. Ekanem et al. studied *pineapple* leaves extract as mild steel corrosion inhibitor in HCl solution at 30°C- 60°C temperature range using weight loss and hydrogen evolution methods. Inhibition efficiency increases with increase in temperature. Extract adsorption followed Langmuir isotherm and chemisorption is also proposed by the trend of inhibition efficiency with temperature [58].

4-phenylsemicarbazide (4PSC) and semicarbazide (SC) were found significant corrosion inhibitors for mild steel in HCl solution by Ita and Offlong. They used weight loss and hydrogen gas evolution measurements and found that 4PSC showed 82% inhibition efficiency and semicarbazide (SC) showed 66% inhibition efficiency [89].

Mimosa tannin was tested as corrosion inhibitor for low carbon steel in sulphuric acid medium by using weight loss method in the range of 20°C to 60°C temperatures and observed that adsorption of tannin followed Temkin, Frumkin and Freundlich adsorption isotherms [129]. Tryptamine (TA) was found an effective corrosion inhibitor for ARMCO iron in 0.5 M deaerated H_2SO_4 solution at 25°C-55°C temperature range. They employed potentiodynamic curves and electrochemical impedencc spectroscopy (EIS) methods. TA adsorption followed Bockris – Swiakels' adsorption isotherm (X=1) [131].

Corrosion inhibition efficiency of aqueous extract of *fenugreek* leaves and seeds were studied by Ehteram A. Noor in HCl and H_2SO_4 solutions for mild steel and revealed that both the extracts act as anodic type inhibitors. He observed that inhibition efficiency was greater in HCl than in H_2SO_4 solution. He employed electrochemical impedence spectroscopy and potentiodynamic polarization measurements for study [138].

Okafor et al. studied leaves (LV), root (RT) and seeds (SD) extract of *Azadirachta indica* as corrosion inhibitor for mild steel in H_2SO_4 solution using weight loss and gasometric techniques. Inhibition efficiency followed SD> RT> LV trend and increases with increase in extract concentrations. Adsorption followed Freundlich adsorption isotherm [150].

Leaves extract of *Brideiia retusa, Murraya koenigii, Embilica officinalis* were studied as corrosion inhibitor for mild steel in H_2SO_4 and HCl solutions respectively [156, 166, 178]. Sharma et al. have also studied mature leaves extract of *Azadirachta indica* as corrosion inhibitor for mild steel in 2N HNO_3 solution at 30°C and 60°C respectively and extract followed Frumkin adsorption isotherm [184].

Fruit extract of Shahjan (*Moringa olifera*) was investigated as a good corrosion inhibitor for mild steel corrosion in HCl solution using weight loss, EIS, linear polarization and potentiodynamic polarization techniques (Tafel). Inhibitor extract obeyed Langmuir adsorption isotherm [193].

The essential oils extracted from aerial parts of *Mentha spicata L.* and *Lavcrndula multijida L.* were observed as corrosion inhibitor for steel in 1M HCl and

0.5M H_2SO_4 solutions using weight loss method and electrochemical polarization measurements in studies by Znini et al. In studies they found that these natural oils act as mixed type of inhibitors and followed Langmuir adsorption isotherm [224, 226].

Rajendran has revealed that flower extract of *Nerium oleander* contains anticorrosive property for mild steel and aluminium in 2M HCl at$30^o \pm 1^oC$ and observed that inhibition percentage increases with extract concentration [173].

Corrosion inhibition property of aqueous extract of *water hyacinth* leaves extract-Zn^{+2} system with and without TSC (Tri Sodium Citrate) was studied by Kavitha and Manjula [95] and Kavitha et al. [94] respectively in aqueous environment containing 60 ppm chloride ion for mild steel. Shanab et al. studied *Eichhornia crassipes* as corrosion inhibitor for Magnesium alloy (AZ3 lE) in 3.5% NaCl solution [183] while Ulaeto et al. reported leaves and roots extract of *Eichhorina crassipes* as corrosion inhibitor for mild steel in hydrochloric acid medium using gasometric technique [206] and Oloruntoba Daniel Toyin investigated corrosion inhibitive property of leaves extract of *water hyacinth* for 1014 steel in chloride environment [154].

Jamiu K. Odusote reported that *Jatropha curcas* leaves extract act as a good corrosion inhibitor for mild steel in all concentration of the extract. [90]

The inhibitive performance of extract of leaves *Cissus quadrangularis* on the corrosion of mild steel in 0.3 M HCI was studied using mass loss and electrochemical measurments. [52]

The inhibiting effect of *cucumber* peel and seed extracts on corrosion of steel in 2 M solution of HCl at ambient temperature was studied using gravimetric and electrochemical measurments. It was observed that corrosion rates reduced with increase in extract concentration [219]

Maria Erna et al. reported that Amylose acetate / Carboxy methyl chitosan composites extract act as good corrosion inhibitor [128]. Lekan Taofeek Popoola reported mechanisms and active functional groups of the eco-friendly organic green corrosion inhibitors [117].

The corrosion inhibition effect of *Terminalia avicennioides* (TA) stem extract in 1M HCl solution was investigated using weight loss and electrochemical method from result 88.71% inhibition efficiency was obtained [70].

The inhibition of corrosion of mild steel in 1N H_2SO_4 solution using leaf extract of *Pongamia pinnata* investigated by T.K. Bhuvaneswari, V.S. Vasantha and C. Jeya Prabha [200]

The efficiency of the leaves extract of *Juniperus Procera* as a corrosion inhibitor against carbon steel and it's adsorption behavior were investigated in 1M HCl solution using mass loss process by Ismat H. Ali et al. Results revealed that inhibition efficiency increased with increase of the inhibitor's concentration [88]

The inhibitive performance of extract of *Adhatoda vasika* (AV) on the corrosion of mild steel in 0.5M HCl were studied using mass loss and electrochemical measurments by E. Dharmaraj et al. Result shown that extract of *Adhatoda Vasika* acts as an effective Corrosion inhibitor in the acid environment [53]

The inhibition performance and mechanisms of *Loquat* leaves extract for the corrosion of mild steel in H_2SO_4 was studied by Xingwen Zheng et. al [218]

L.R. Chauhan et al reported the inhibition effect of *Zenthoxylum alatum* plant extract on the corrosion of mild steel in HCl solution. They observed that inhibition efficiency increases with increase in plant extract concentration [112].

Sudesh Kumar and Suraj Prakash Mathur have investigated ethanolic extract of leaves, latex and fruit of *Calotropis procera* as corrosion inhibitor for aluminium in sulphuric acid medium [105] while Bharthi et al. reported leaves extract of *Calotropis procera* as corrosion inhibitor for aluminium in 1 M HCl solution [33]. Sudesh kumar et al. also studied corrosion controlling property of alcoholic extracts of leaves, latex and fruit extract of *Calotropis procera* and *Calotropis gigenrea* for mild steel in basic solution by mass loss method and thermometric method [106]. Raja and Sethuraman have also reported corrosion inhibitive property of *Calotropis procera* for mild steel in sulphuric acid medium [169].

Sharma et al. studied Ethanolic extract of leaves, stem bark and fruit of *Lantana camara* was studied as corrosion inhibitor for aluminium in different concentrations of sulphuric acid solutions [185], Petchiammi1 and Selvaraj have reported anticorrosive effect of fruit peel extract of *Lantana camara* in 1M HCl for mild steel and found maximum 85% inhibition efficiency [157]. Besides these Nkiko et al. also reported *Lantana camara* leaves extract as corrosion inhibitor for Zinc alloy in H_3PO_4 solution [136].

Priya bhardwaj, Seema Agarwal and S.Kalpana Studied aqueous extract of *Calotropis procera* leaves, *Nerium oleander* leaves as corrosion inhibitor for mild steel in 1M HCl Solution [161,162].They obtained maximum 60.86% Inhibition efficiencies with *Calotropis procera* and 83.76% inhibition efficiency with aqueous extract of leaves of *Nerium oleander* at 303K.

Although large amount of research studies have been done on corrosion inhibition at mild steel in aggressive media with various natural substances, but still there is thurst to search newer , better and cheaper green corrosion inhibitors. To keep this in view, the present work has been undertaken which enlightens, “Corrosion inhibition with parts of plant products at mild steel surfaces in acidic media”, for which no reference could be traced out in the literature reviewed so far.

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CHAPTER – 2

MATERIALS, METHODS AND METHODOLOGY

Materials:

Selection of plant as corrosion inhibitor:

Aqueous extract of *Ziziphus Jujuba leaves* (AEZJL), *Ziziphus Jujuba Stem* (AEZJS), *Ziziphus Jujuba Roots* (AEZJR) and *Ziziphus Jujuba Fruits* (AEZJF), 1M HCl solution, rectangular specimens of mild steel, borosil beakers (250 ml), volumetric flasks, measuring cylinders, different emery papers (Marks 80 to 120 grades), distilled water, electronic balance (Citizens model CY204), thermostat (12 holes double walled), electronic oven (14') and desiccators (210 ml).

After several trials on different plants *Ziziphus jujuba* has been choosen for detailed studies keeping in view its easy availability and better results and moreover due to utility of its all parts in corrosion inhibitor.

The details of the selected plant for corrosion studies on mild steel are as below.

1. Ziziphus Jujuba:

Plant classification

Kingdom : Plantae

Division : Magnoliophyta

Class : Magnoliopsida

Order : Rosales

Family : Rhamnaceae

Genus : Ziziphus

Species : *Ziziphus Jujuba*

Generally it is called jujube or red date. It’s precise natural distribution is uncertain due to extensive cultivation but it is thought to be in Southern Asia between Lebanon, Northern India and Southern and central china.

Ziziphus Jujuba is a small deciduous tree or shrub. It’s height is 5-12 metres, leaves are shiny green 2-7 cm long and 1-3cm wide with three conspicuous veins at the base and finely toothed margin.

The fruit is an edible oval shape when immature it is smooth green with taste of an apple. Maturing brown to purplish black and eventually wrinkled looking like a small date.

The tree tolerates a wide range of temperatures and rainfall though it requires hot summers and sufficient water for acceptable fruiting. Unlike most of other species in the genus. it tolerates fairly cold winters.

Fresh jujube fruit contain carbohydrate, protein and fat. Fresh fruit is rich source of vitamin C and contains several minerals calcium, iron, magnesium, manganese, phosphorus, potassium, sodium and zinc. It contains 77% water.

Acid selected as aggressive media:

1. Hydrochloric acid (HCl)

Hydrochloric acid is a pungent smelling colourless solution of HCl gas in water. It is monoprotic acid which gives one H^+ ion in solution. It is highly corrosive acid. The name “Hydrochloric Acid” was coined by Joseph Louis Gay-Lussac, the French chemist in 1814. Hydrochloric acid is a binary mixture (two-component) of HCl and H_2O has a constant boiling azeotrope at 20.2% HCl and 108.6°C (227 F). It is prepared in solutions up to 38% HCl (concentrated grade). Higher concentrations just over 40% has high evaporation rate and thus storage and handling is difficult. 38% HCl has 1.189 kg/L density, BP 48°C and viscosity 2.10 mPa.S. these above data are at 20°C and 1 atm pressure. Hydrochloric acid is used in pickling of steel , removing rust from iron, production of organic and inorganic compounds such as vinyl chloride, bisphenol A and numerous pharmaceutical products, iron (III) chloride, polyaluminium chloride (PAC) (both used as flocculation and coagulation agents in sewage treatment), calcium chloride salt, nickel (II) chloride, zinc chloride etc.

Methods:

The leaves, Roots, Stem & Fruits of *Ziziphus Jujuba* were collected form local area and near by area of Gangapur city, Rajasthan (India). These were washed and air-dried in shade for 6-7 days, crushed and grounded mechanically and converted into fine powder form.

Preparation of AEZJL

For preparation of stock solution of AEZJL (Aqueous Extract of the *Ziziphus Jujuba* Leaves): 20 g of dried and grounded *Ziziphus Jujuba* leaves powder in 500 ml of distilled water was heated between 70°C-80°C for one hour in round bottom flask fitted with air condenser. The extract was left overnight and then filtered and made upto 500 ml with distilled water.

Preparation of AEZJR :

Stock solution of AEZJR (Aqueous Extract of *Ziziphus Jujuba* Roots): 20 grams of dried grounded roots powder of *Ziziphus Jujuba* in 500 ml of distilled water was heated between 70°C-80°C for one hour in round bottom flask fitted with aircondenser. The extract was left overnight then filtered and made up to 500 ml with distilled water.

Preparation of AEZJS :

For preparation of the stock solution of AEZJS (Aqueous Extract of *Ziziphus Jujuba* Stem): 20g of dried grounded stem powder of *Ziziphus Jujuba* in 500 ml of distilled water was heated between 70°C-80°C for one hour in 500 ml round bottom flask fitted with air condenser. The extract was left overnight and then filtered and made up to 500 ml with distilled water.

Preparation of AEZJF :

For preparation of the stock solution of AEZJF (Aqueous Extract of *Ziziphus Jujuba* fruits): 20g of dried grounded fruits powder of *Ziziphus Jujuba Fruits* in 500 ml of distilled water was heated between 70^{o}C-80^{o}C for one hour in round bottom flask fitted with air condenser. The extract was left overnight am filtered and made up to 500 ml with distilled water.

Preparation of different acidic media:

Acidic media for corrosion studies of mild steel were prepared by AR grade HCl (Merck Ltd), 1M standard solution of acid was prepared using de-ionized distilled water.

Determination of weight loss:

For corrosion studies of mild steel specimens gravimetric technique for weight loss described by Mattson [97] was used. For weight loss rectangular mild steel sheeth(0.03cm Thickness) specimens of various dimensions (5 cm in length and 1 cm in width), (4.8 cm in length and 1.5 cm width), (4.9 cm in length and 0.70 cm in width), (4.8 cm in length and 0.60 cm in width) were taken. The above specimens were abraded with different emery papers, degreased in acetone and washed with distilled water dried and the constant weight (W_1) was recorded by electronic balance.

Rectangular mild steel specimens were hanged with the plastic thread and glass rod in 100 ml of acidic media in 250 ml borosil glass beakers, containing specific amount of aqueous extracts of different parts of *Ziziphus jujuba* plant.

After one hour of immersion time the specimens were taken out from acidic media, washed with distilled water, dried and again softly abraded mildly with emery paper to remove the upper material and weighed accurately (W_2) by electronic balance. Weight loss (ΔW) is calculated by (W_1-W_2). Employed concentration range of the aqueous extracts of different parts of the plant were 1%-8% (v/v) for each extracts viz. AEZJL, AEZJR, AEZJS and AEZJF. The Corrosion inhibition experiments were performed at four different temperatures (30°C, 40°C, 50°C and 60°C).

Determination of Corrosion Rates:

In 1M HCl values of Corrosion Rates (CR) for mild steel specimens in different concentrations of inhibitors at four different studied temperatures were calculated by following equation (1) [139].

$$CR = \left(\frac{\Delta W}{At} \right) \qquad (1)$$

Where ΔW is the weight loss calculated by the difference of initial weight (W_1) and final weight (W_2) of mild steel specimens after treating with different acidic media containing different concentrations of inhibitor solutions. A is the surface area of different specimens and t is immersion time in minute.

Determination of Inhibition Efficiencies (IE %):

From the above calculated corrosion rate values (CR) the inhibition efficiencies for the mild steel specimens in 1M HCl solution containing different amount of inhibitor solutions at different temperatures are calculated by the following equation (2) [139,220].

$$\text{IE \%} = \left(\frac{\text{CR}_{\text{blank}} - \text{CR}_{\text{inh}}}{\text{CR}_{\text{blank}}}\right) \times 100 \qquad (2)$$

Where CR_{blank} and CR_{inh} are the corrosion rates in the absence and presence of the different inhibitors at different concentrations.

Determination of Kinetic Parameters:

Kinetic parameters K (rate constant) and B (reaction constant) are calculated by the straight lines obtained in the graph between the log of inhibitor concentrations and the log of corrosion rate values at different temperstures. The following equation (3) is used to determine the kinetic parameters [100,140].

$$\log CR = \log K + B \log C_{inh} \qquad (3)$$

where, K is the rate constant and equals to CR when the inhibitor concentration is unity. B is the reaction constant which is the measure of inhibitor effectiveness and CR_{inh} is the concentration in (v/v %) (ml/ l00ml) of four different inhibitors.

Determination of the thermodynamic and activation parameters:

The thermodynamic and activation parameters like Activation Energy (E_{act}), enthalpy of activation (ΔH^*) and entropy of activation (ΔS^*) were calculated for mild steel dissolution process.

Activation energy (E_{act}):

Activation energy was calculated using the Arrhenius equation (4) [207,220].

$$\log CR = \log A - \left(\frac{Eact}{2.303\, R\, T}\right) \qquad (4)$$

Where A is the Arrhenius pre exponential factor, CR is corrosion rate, T is absolute temperature in Kelvin and R is the universal gas constant The slope of graph plotted between log CR and 1/T gives the value of activation energy at various studied temperatures.

Enthalpy of activation (ΔH^*) and entropy of activation (ΔS^*):

The value of enthalpy of activation (ΔH^*) entropy of activation (ΔS^*) can be calculated by the following transition state equation (5) [207,220].

$$\log \left(\frac{CR}{T}\right) = [(\log \left(\frac{R}{Nh}\right) + \left(\frac{\Delta S^*}{2.303R}\right)] - [\left(\frac{\Delta H^*}{2.303RT}\right)] \qquad (5)$$

Where, CR is corrosion rate, N is Avogadro’s number, T is absolute temperatur R is the universal gas constant and h is Planck’s constant.

A plot between log (CR/T) and (1/T) gives a straight line with slope of and intercept of $[(\log \left(\frac{R}{Nh}\right) + \left(\frac{\Delta S^*}{2.303R}\right)]$ from which the values of enthalpy of activation (ΔH^*). and entropy of activation (ΔS^*) are calculated.

Adsorption Isotherms:

Adsorption has significant role in corrosion inhibition processes. Inhibitors generally physically or chemically adsorbed on metal surface and slow down metal dissolution process. To understand the nature of adsorption, the obtained surface coverage θ were fitted different adsorption isotherms like Langmuir adsorption isotherm, Temkin adsorption isotherm, Freundlich adsorption isotherm.

Many researchers have use the Langmuir adsorption isotherm to study the adsorption process. The mathematical expression for Langmuir adsorption isotherm is according to equation (6) [28, 69, 161, 165, 213]

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \qquad (6)$$

Rearranging the above equation (6)

$$\frac{\theta}{1-\theta} = K_{ads} \,.\, C_{inh} \qquad (7)$$

$$\log\left(\frac{\theta}{1-\theta}\right) = \log(K_{ads}) + \log(C_{inh}) \qquad (8)$$

Where C_{inh} is the inhibitor concentration in (ml/L) and K_{ads} ($ml^{-1}L$) is the equilibrium constant of adsorption, θ is the degree of surface coverage and is equal to IE% / 100. A straight line is obtained between (C_{inh}/θ) and C_{inh} or between log (C_{inh}/θ) and log C_{inh}, values, if the adsorption process follows Langmuir adsorption isotherm.

Freundlich adsorption isotherm is given by the following equation (9) and (10)[101].

$$\theta = K_{ads} \,.\, C_{inh} \qquad (9)$$

$$\log\theta = \log(K_{ads}) + n\log(C_{inh}) \qquad (10)$$

Where θ<n<1, θ is the degree of surface coverage and C_{inh} is the concentration of the inhibitor, K_{ads} is the equilibrium constant in the adsorption process. A straight line is obtained between the logarithm of degree of surface coverage (θ) and logarithm of inhibitor concentration C_{inh} in Freundlich isotherm.

Temkin adsorption is given by the following equation (11) [133, 151]

$$-2a\theta = 1og(K_{ads}) + \log(C_{inh}) \qquad (11)$$

Where a is the molecular interaction factor in adsorbed layer, K_{ads} is equilibrium constant and C_{inh}, is the inhibitor concentration and θ is the degree of surface coverage.

Determination of Adsorption Parameters:

Gibbs Energy ΔG_{ads}:

The values of K_{ads} obtained from adsorption isotherms is related to Gibbs energy by the following equation (12) [99,139].

$$K_{ads} = \frac{1}{C} \exp(\Delta G_{ads}/RT) \qquad (12)$$

It can also be written as

$$\Delta G_{ads} = -2.303RT \log (K_{ads}.C_{H2O}) \qquad (13)$$

Where. C_{H2O} is the concentration of water in (ml/L) at metal solution surface, R is Universal gas constant and T is the absolute temperature.

Determination of Enthalpy of Adsorption(ΔH_{ads}) and Entropy of Adsorption(ΔS_{ads}):

Enthalpy of adsorption (ΔH_{ads}) and entropy of adsorption (ΔS_{ads}) are calculated by the following basic equation (14) [59,l39].

$$\Delta G_{ads} = \Delta H_{ads} - T\Delta S_{ads} \qquad (14)$$

The intercept of the graph between the ΔG_{ads} and absolute temperature T, gives the values of ΔH_{ads}. Values of ΔS_{ads} were obtained by putting the values of ΔH_{ads} in equation (14) at different temperatures.

Methodology

For investigating the more efficient eco-friendly, cost effective natural corrosion inhibitor for mild steel four different parts of plant species *Ziziphus Jujuba* were selected. The plant leaves, roots, stem and fruits of this plant were collected form local land area of Gangapur city.

Each part of plant washed, air dried in shade for 6-7 days, crushed mechanically into fine powder and their aqueous extracts were prepared by heating specified quantity of leaves powder, stem powder, roots powder and fruits powder in distilled water separately in round bottom flask between 70°C-80°C for one hour. The extracts were left overnight and then filtered and made up to the mark by adding required volume of distilled water. Analytical grade hydrochloric acid (Merek Ltd) was taken to prepare acidic media.Standarised 1M solution of HCl was prepared in distilled water for experimental studies. The weight loss method, described by Mattson [97] was used to calculate the corrosion rates. For the purpose rectangular mild steel specimen of different dimensions were taken range of 5 cm to 4.8 cm in length and 1.5 cm to 0.6 cm in width respectively each of .03 cm of thickness. These rectangular specimens were abraded with series of emery papers degreased with acetone and washed thoroughly with distilled water and finally dried in hot air till constant weight (W_1) Weight was recorded on electronic balance (Citizen model CY 204). These specimens were hanged with plastic thread and glass rod in 100 ml acidic solution for 1 hour in 250 ml borosil beaker in presence and absence of different concentrations (v/v %) of aqueous extracts of inhibitors at different temperatures. After one hour specimens were removed, washed with distill water, dried and again abraded softly with emery paper and finally weighed with electronic balance (W_2). Thus weight loss (W_1-W_2) is obtained in grams. The employed concentration range of extracts of each part of plant was 1%-8% (v/v %). The experiments were repeated at 30°C, 40°C, 50°C, 60°C temperatures. The temperatures are mainted constant ($\pm$1°C) by carrying out experiments in constant temperatures water bath.

From the above obtained weight loss data, corrosion rates (CR) were calculated by using equation (1). Similarly inhibition efficiencies were calculated using equation (2), Kinetic parameters were calculated by using equation (3), thermodynamic parameters and activation energies were calculated applying equations (4) and (5). The different adsorption isotherms were plotted by using the equations (8), (10) and (11). Gibbs energy of adsorption, entropy of adsorption were calculated by equations (13) and (14).

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CHAPTER – 3

OBSERVATIONS AND RESULTS

The results obtained from gravimetric (weight loss) method, are used for calculating Corrosion rates, Inhibition efficiencies, Kinetic parameters, Apparent activation energy (E_{act}), Enthalpy of activationΔH^*, Entropy of activation (ΔS^*) and Gibbs Energy(ΔG_{ads}) Enthalpy of Adsorption (ΔH_{ads}) and Entropy of Adsorption (ΔS_{ads}). These data are summarized as tabular (Table 1 to 20) and graphical (Figure 1 to 28) from under well defined headings for four different plant extracts i.e. AEZJR, AEZJL, AEZJS, AEZJF in selected acid. Concentrations of extracts prepared are expressed in % (v/v). Langmuir, Freundlich and Temkin adsorption isotherms are drawn for different parts of plant materials.

Table 1. Mild steel corrosion rates in 1 M HCl solution in absence and presence of different concentrations of AEZJL at different temperatures

C_{inh} in (v/v)%	CR x 10^{-3} (g cm^{-2} min^{-1})			
	30°C	40 °C	50 °C	60 °C
0	0.96	1.53	2.19	2.76
1	0.73	1.14	2.03	2.64
2	0.57	0.87	1.94	2.59
3	0.39	0.73	1.83	2.53
5	0.27	0.57	1.74	2.47
8	0.11	0.39	1.58	2.38

Table 2. Inhibition efficiencies of AEZJL at different concentrations and temperatures in 1 M HCl solution

C_{inh} in (v/v)%	I E (%)			
	30°C	40 °C	50 °C	60 °C
1	23.9583	25.4902	7.30594	4.34783
2	40.625	43.1373	11.4155	6.15942
3	59.375	52.2876	16.4384	8.33333
5	71.875	62.7451	20.548	10.5073
8	88.5417	74.5098	27.8539	13.7681

Table 3. Kinetic parameters for mild steel corrosion in 1 M HCl solution with AEZJL

Temperature (^oC)	Kinetic Parameters	
	B	K x 10^{-3} (g cm^{-2} min^{-1})
30 ^oC	-0.049	2.66073
40 ^oC	-0.118	2.06538
50 ^oC	-0.502	1.20226
60 ^oC	-0.876	1.11173

Table 4. Activation and thermodynamic parameters for mild steel corrosion in 1 M HCl solution with AEZJL

C_{inh} in (v/v)%	E_{act} (kJ/mol)	ΔH^* (kJ/mol)	ΔS^* (J/mol/K)
0	29.68	27.12	-200.82
1	37.26	34.76	-179.88
2	44.86	42.36	-175.67
3	54.89	52.42	-162.88
5	65.23	62.77	-149.57
8	89.51	87.08	-117.92

Table 5. Adsorption parameters for mild steel corrosion in 1 M HCl solution with AEZJL

Temperature (^{o}C)	ΔG_{ads} (kJ/mol)	ΔH_{ads} (kJ/mol)	ΔS_{ads} (J/mol/K)
30 ^{o}C	-8.0684	-56.44	-159.642
40 ^{o}C	-8.5385		-153.04
50 ^{o}C	-5.2613		-158.448
60 ^{o}C	-3.9195		-157.719

Table 6. Mild steel corrosion rates in 1 M HCl solution in absence and presence of different concentrations of AEZJS at different temperatures

C_{inh} in (v/v)%	CR x 10^{-3} (g cm^{-2} min^{-1})			
	30°C	40 °C	50 °C	60 °C
0	0.82	1.41	2.11	2.78
1	0.59	1.21	1.87	2.65
2	0.42	1.03	1.64	2.49
3	0.37	0.91	1.47	2.37
5	0.27	0.78	1.31	2.21
8	0.18	0.66	1.22	2.15

Table 7. Inhibition efficiencies of AEZJS at different concentrations and temperatures in 1 M HCl solution

C_{inh} in (v/v)%	I E (%)			
	30°C	40 °C	50 °C	60 °C
1	28.04	14.18	11.37	4.68
2	48.78	26.95	22.27	10.43
3	54.88	35.46	30.33	14.75
5	67.07	44.68	37.91	20.50
8	78.05	53.19	42.18	22.66

Table 8. Kinetic parameters for mild steel corrosion in 1 M HCl solution with AEZJS

Temperature (^{o}C)	Kinetic Parameters	
	B	K x 10^{-3} (g cm^{-2} min^{-1})
30 ^{o}C	-0.552	0.6209
40 ^{o}C	-0.291	1.2359
50 ^{o}C	-0.212	1.8707
60 ^{o}C	-0.105	2.6546

Table 9. Activation and thermodynamic parameters for mild steel corrosion in 1 M HCl solution with AEZJS

C_{inh} in (v/v)%	E_{act} (kJ/mol)	ΔH^* (kJ/mol)	ΔS^* (J/mol/K)
0	34.22	31.64	-221.9
1	41.63	39.17	-182.12
2	48.92	46.64	-171.58
3	50.95	48.81	-138.46
5	57.52	55.54	-43.23
8	67.93	66.02	-43.23

Table 10. Adsorption parameters for mild steel corrosion in 1 M HCl solution with AEZJS

Temperature (^{o}C)	ΔG_{ads} (kJ/mol)	ΔH_{ads} (kJ/mol)	ΔS_{ads} (J/mol/K)
30 ^{o}C	-8.5325	-45.43	-121.774
40 ^{o}C	-7.0761		-122.536
50 ^{o}C	-6.7765		-119.67
60 ^{o}C	-4.5762		-122.684

Table 11. Mild steel corrosion rates in 1 M HCl solution in absence and presence of different concentrations of AEZJF at different temperatures

C_{inh} in (v/v)%	CR x 10^{-3} (g cm^{-2} min^{-1})			
	30°C	40 °C	50 °C	60 °C
0	0.86	1.46	2.17	2.89
1	0.64	1.31	2.11	2.76
2	0.57	1.17	2.03	2.67
3	0.47	1.12	1.87	2.61
5	0.39	1.01	1.78	2.54
8	0.27	0.73	1.63	2.47

Table 12. Inhibition efficiencies of AEZJF at different concentrations and temperatures in 1 M HCl solution

C_{inh} in (v/v)%	I E (%)			
	30°C	40 °C	50 °C	60 °C
1	25.5814	10.274	2.76498	4. 49827
2	33.7209	19.863	6.45161	7.61246
3	45.3488	23.2877	13.8249	9.68858
5	54.6512	30.8219	17.9724	12.1107
8	68.6047	50	24.8848	14.5329

Table 13. Kinetic parameters for mild steel corrosion in 1 M HCl solution with AEZJF

Temperature (^oC)	Kinetic Parameters	
	B	K x 10^{-3} (g cm^{-2} min^{-1})
30 ^oC	-0.053	2.76058
40 ^oC	-0.125	2.15278
50 ^oC	-0.255	1.38676
60 ^oC	-0.407	0.70146

Table 14. Activation and thermodynamic parameters for mild steel corrosion in 1 M HCl solution with AEZJF

C_{inh} in (v/v)%	E_{act} (kJ/mol)	ΔH^* (kJ/mol)	ΔS^* (J/mol/K)
0	33.93	31.25	-199.27
1	40.99	38.4	-186.02
2	43.69	41.17	-185.61
3	47.7	45.26	-144.85
5	52.2	49.81	-134.45
8	62.71	60.34	-126.74

Table 15. Adsorption parameters for mild steel corrosion in 1 M HCl solution with AEZJF

Temperature (^oC)	ΔG_{ads} (kJ/mol)	ΔH_{ads} (kJ/mol)	ΔS_{ads} (J/mol/K)
30 ^oC	-8.0162	-51.26	-143.709
40 ^oC	-6.0573		-145.376
50 ^oC	-2.9421		-150.52
60 ^oC	-4.2383		-142.107

Table 16. Mild steel corrosion rates in 1 M HCl solution in absence and presence of different concentrations of AEZJR at different temperatures

C_{inh} in (v/v)%	CR x 10^{-3} (g cm^{-2} min^{-1})			
	30°C	40 °C	50 °C	60 °C
0	0.67	1.33	2.27	3.04
1	0.56	1.24	2.13	2.82
2	0.37	1.1	1.89	2.74
3	0.35	0.94	1.86	2.69
5	0.29	0.85	1.81	2.61
8	0.25	0.69	1.59	2.53

Table 17. Inhibition efficiencies of AEZJR at different concentrations and temperatures in 1 M HCl solution

C_{inh} in (v/v)%	I E (%)			
	30°C	40 °C	50 °C	60 °C
1	16.4179	6.76692	6.1674	7.23684
2	44.7761	17.2932	16.7401	9.86842
3	47.7612	29.3233	18.0617	11.5132
5	56.7164	36.0902	20.2643	14.1447
8	62.6866	48.1203	29.956	16.7763

Table 18. Kinetic parameters for mild steel corrosion in 1 M HCl solution with AEZJR

Temperature (°C)	Kinetic Parameters	
	B	K x 10^{-3} (g cm^{-2} min^{-1})
30 °C	-0.372	0.52723
40 °C	-0.278	1.27938
50 °C	-0.124	2.11836
60 °C	-0.052	2.83139

Table 19. Activation and thermodynamic parameters for mild steel corrosion in 1 M HCl solution with AEZJR

C_{inh} in (v/v)%	E_{act} (kJ/mol)	ΔH^* (kJ/mol)	ΔS^* (J/mol/K)
0	42.72	39.88	-177.64
1	45.46	42.8	-170.56
2	55.28	52.72	-143.63
3	57.35	54.8	-137.55
5	61.98	59.47	-130.48
8	65.5	63.03	-118.53

Table 20. Adsorption parameters for mild steel corrosion in 1 M HCl solution with AEZJR

Temperature (^{o}C)	ΔG_{ads} (kJ/mol)	ΔH_{ads} (kJ/mol)	ΔS_{ads} (J/mol/K)
30 ^{o}C	-8.0888	-31.13	-76.0435
40 ^{o}C	-5.2933		-82.5453
50 ^{o}C	-5.3882		-79.6959
60 ^{o}C	-5.4275		-77.1846

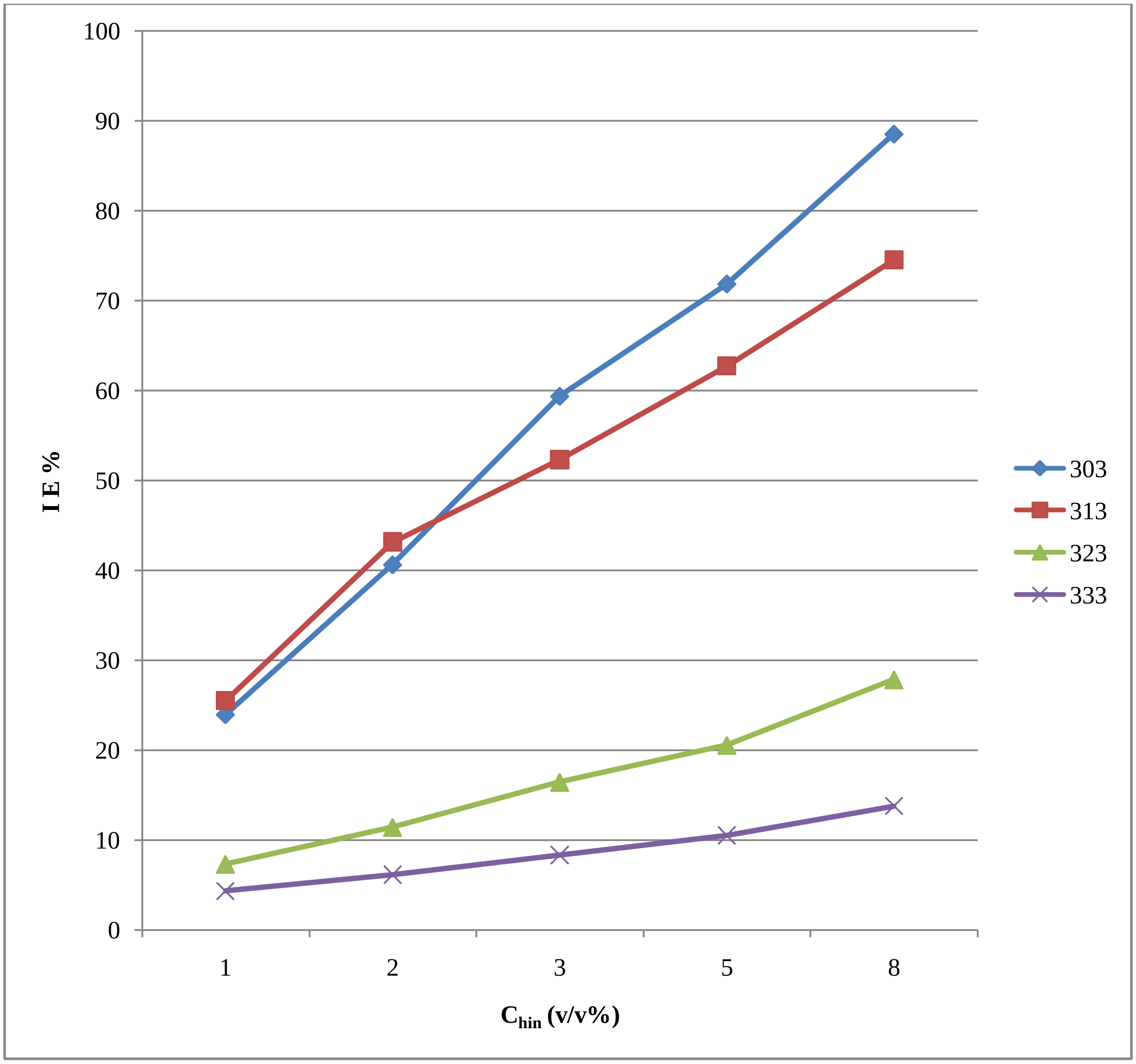

Figure1. Variation in I E % for mild steel corrosion in 1M HCl at different concentration of AEZJL at different studied temperatures

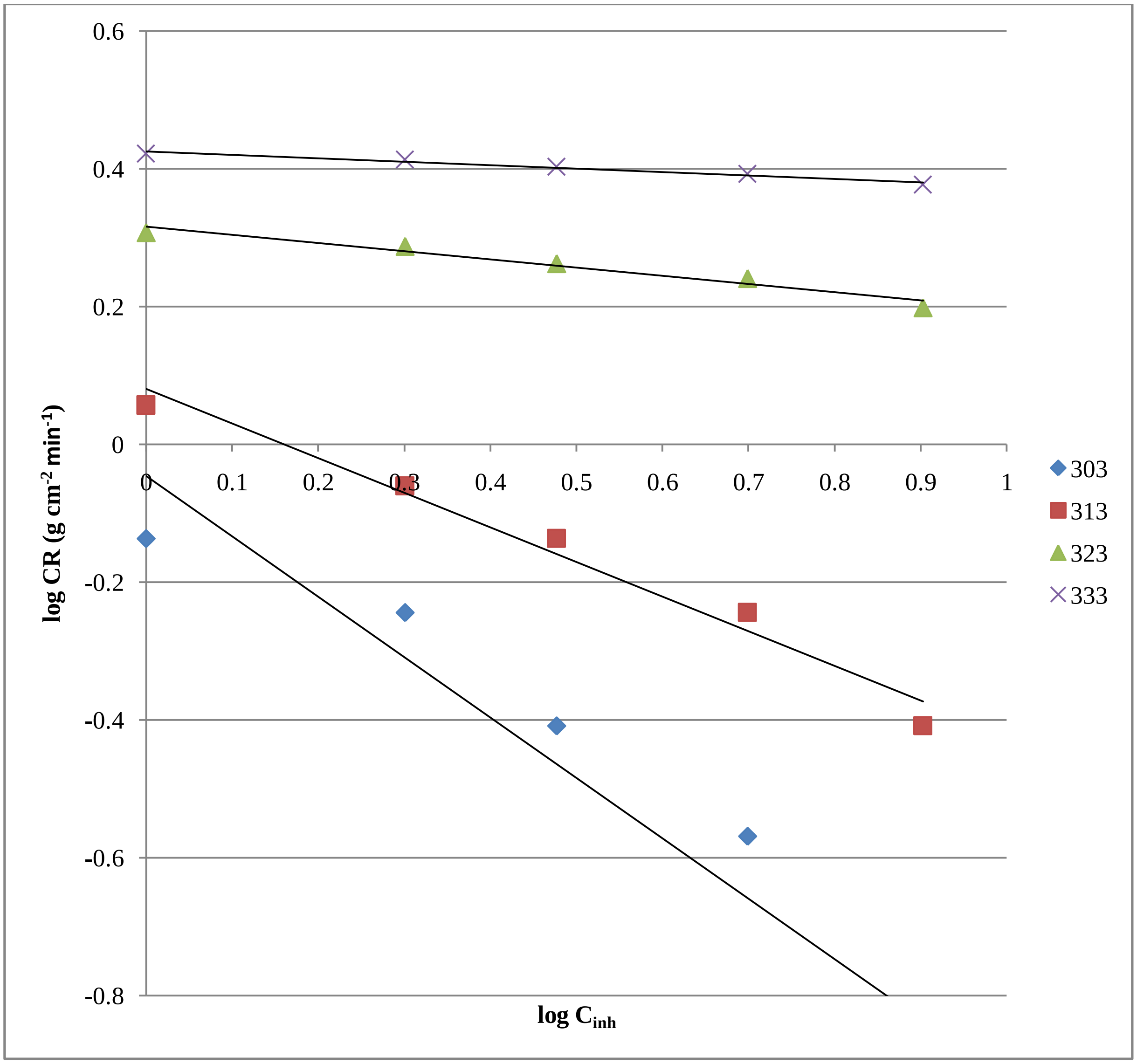

Figure2. Variation in log CR with log C_{inh} for mild steel corrosion in 1M HCl in presence of different concentration of AEZJL at various studied temperatures

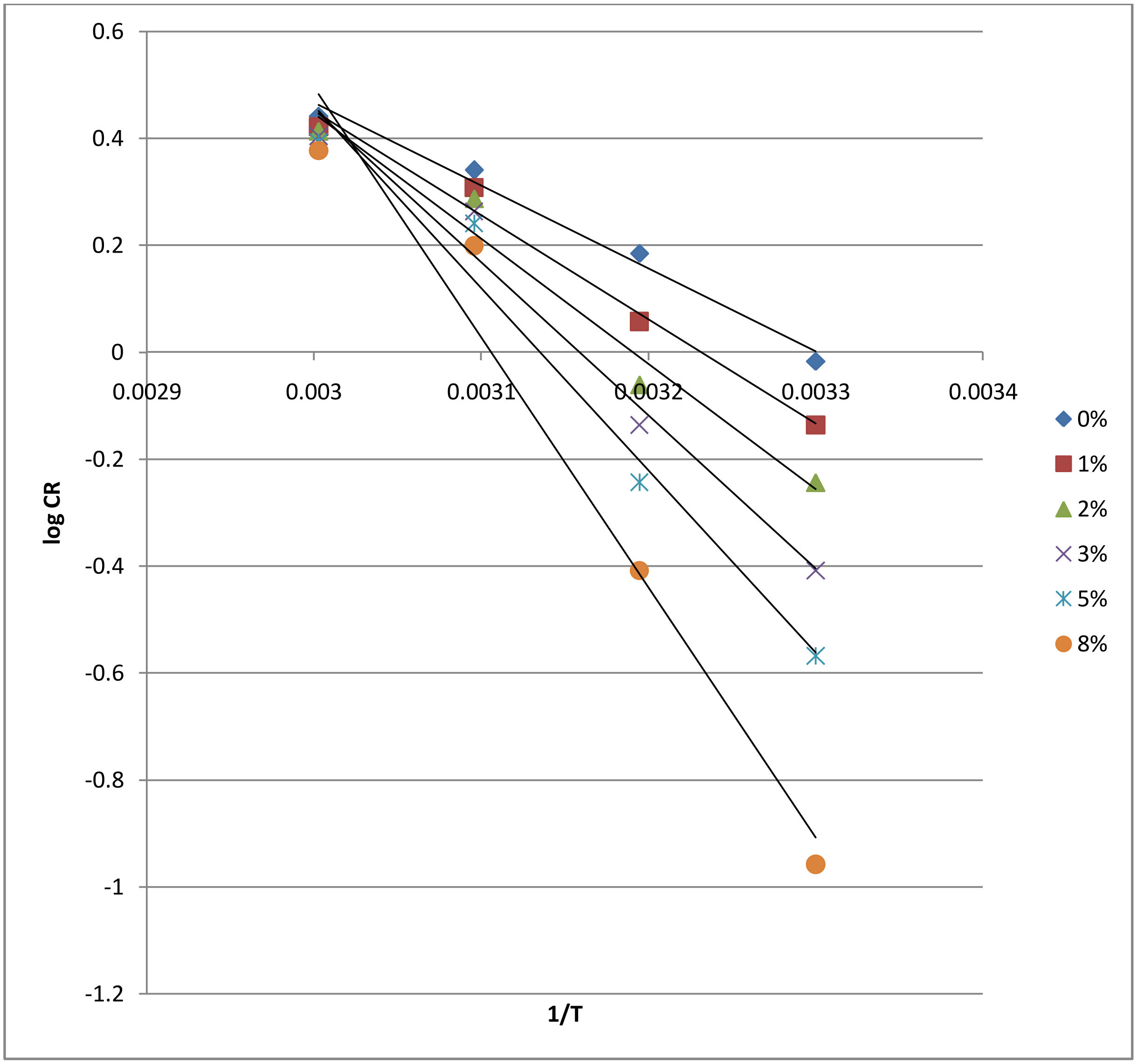

Figure3. Arrhenius plots for mild steel corrosion in 1M HCl in absence and presence of various concentration of AEZJL

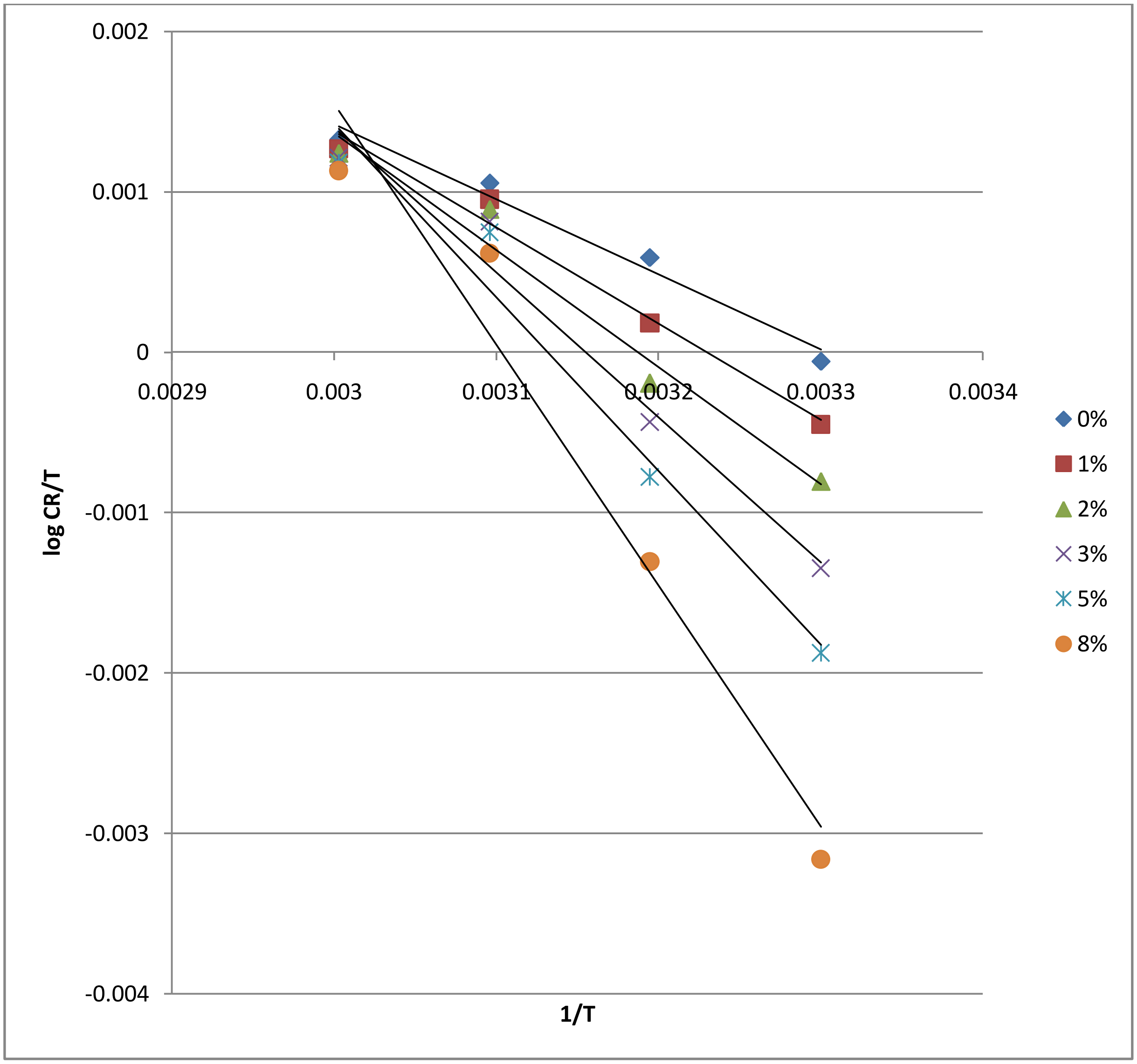

Figure4. Transition-state plots for mild steel corrosion in 1M HCl in absence and presence of various concentration of AEZJL

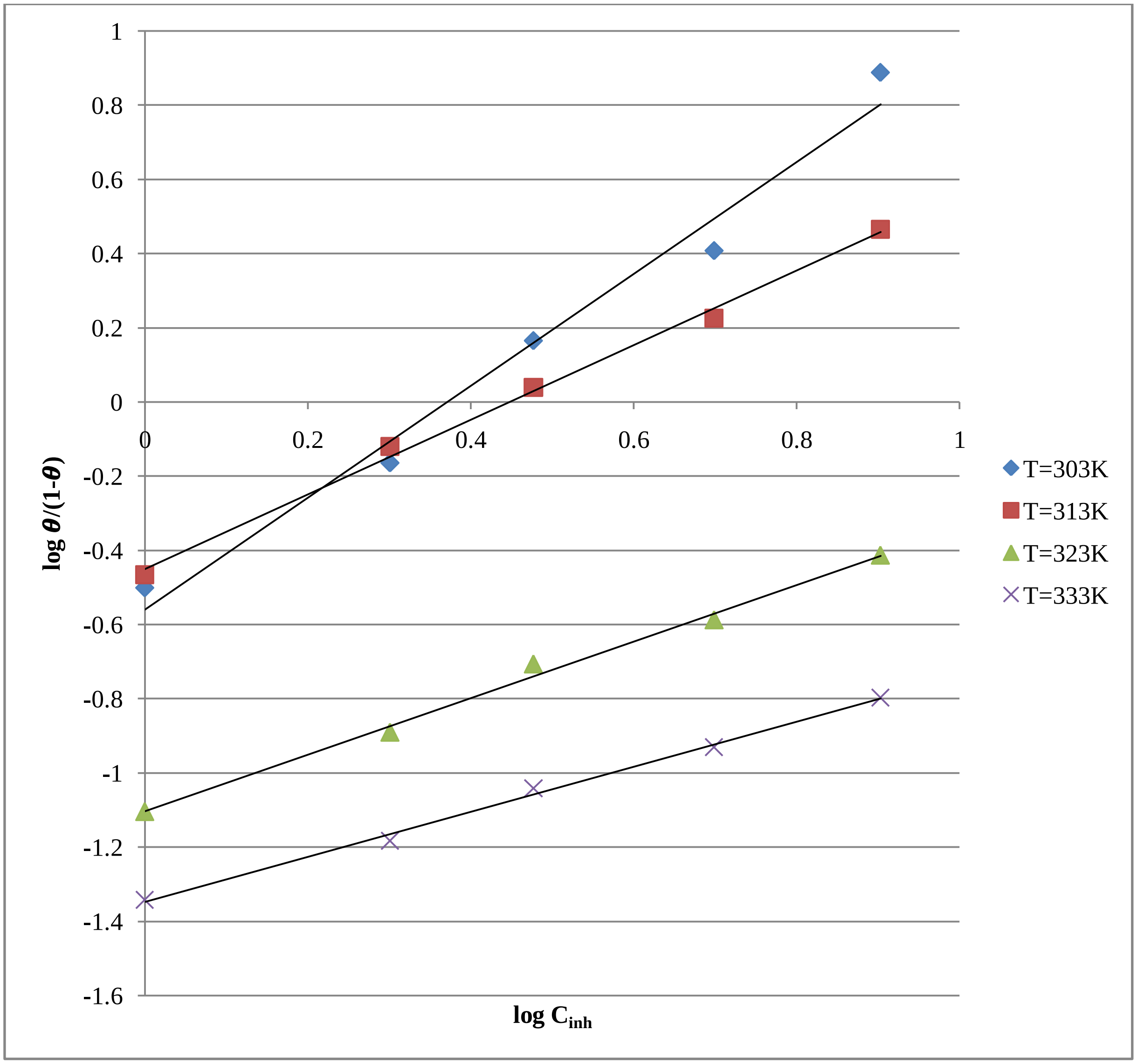

Figure5. Langmuir adsorption isotherms of AEZJL on mild steel surface in 1M HCl at different studied temperatures

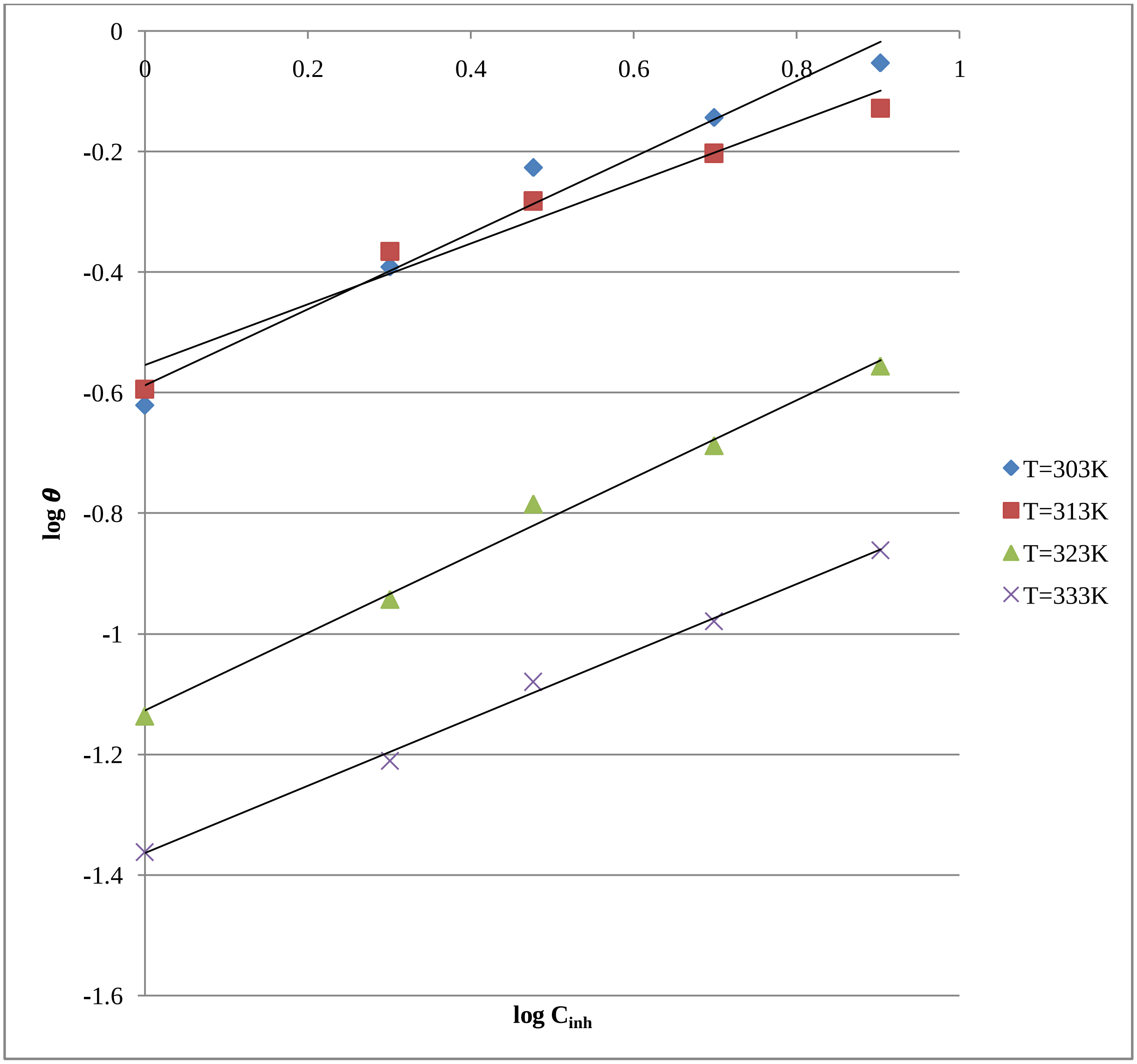

Figure6. Freundlich adsorption isotherms of AEZJL on mild steel surface in 1M HCl at different studied temperatures

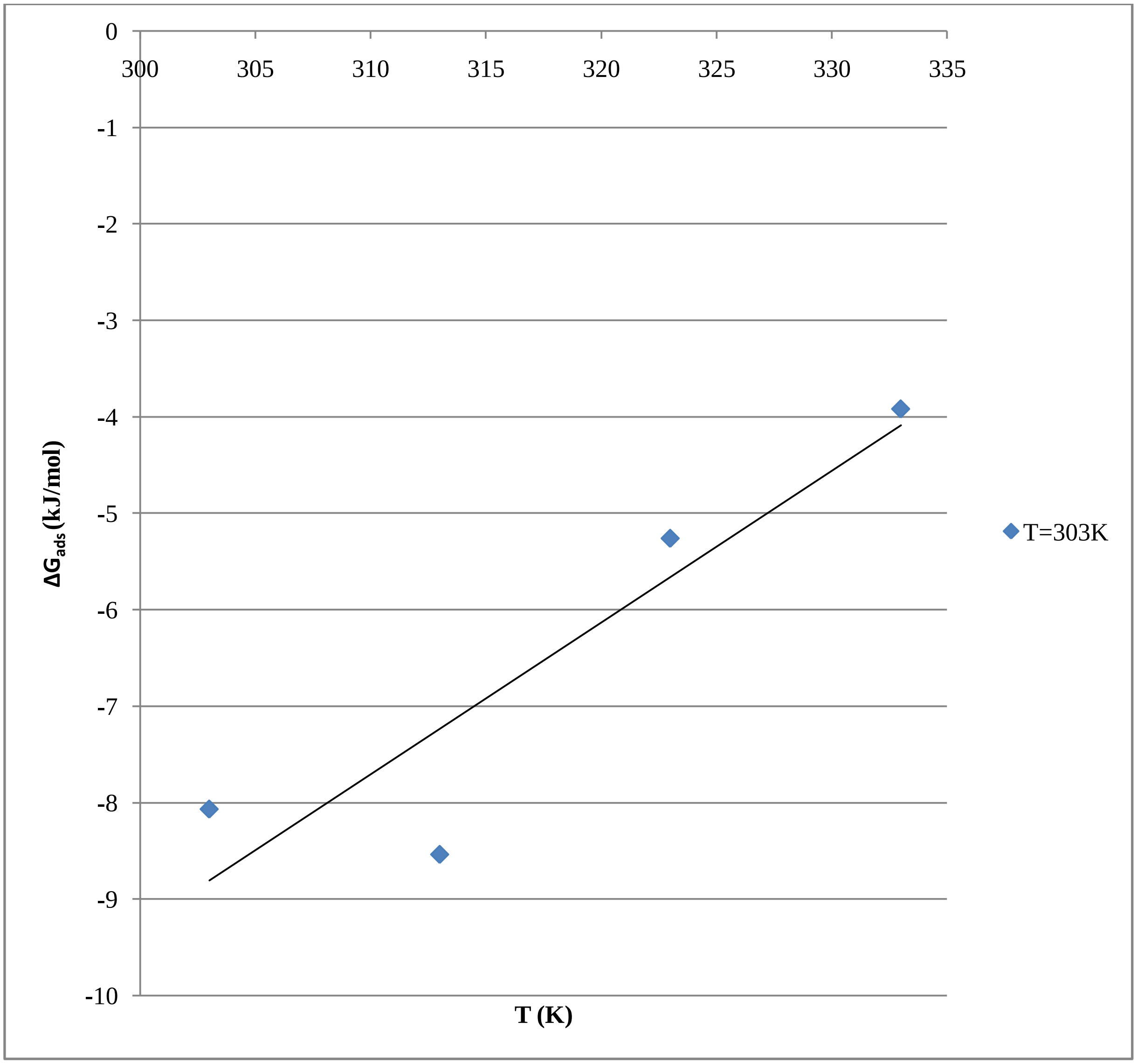

Figure7. The Variation of ΔG_{ads}(kJ/mol) with T (K) for mild steel corrosion in 1M HCl solution with AEZJL

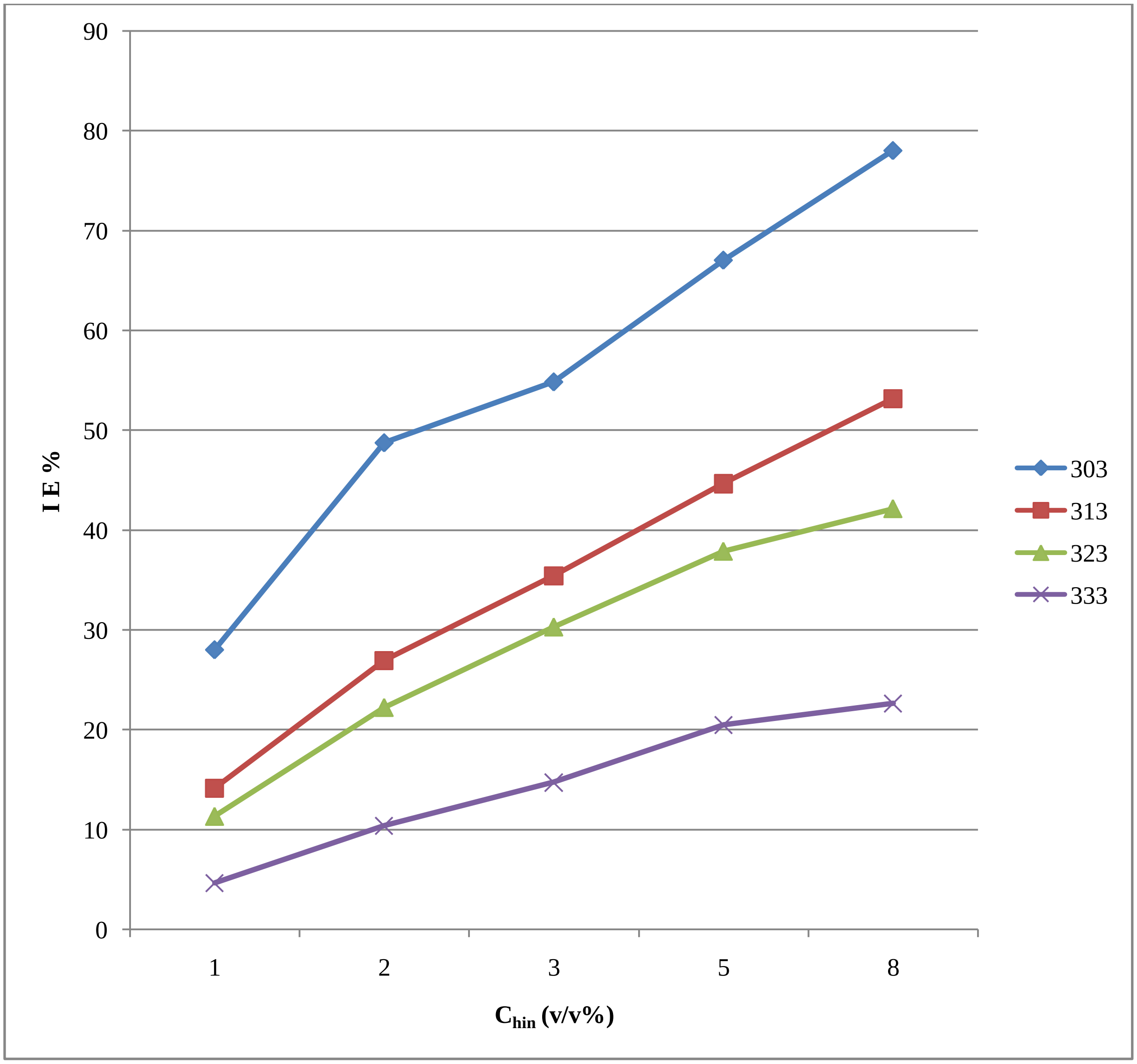

Figure8. Variation in I E % for mild steel corrosion in 1M HCl at different concentration of AEZJS at different studied temperatures

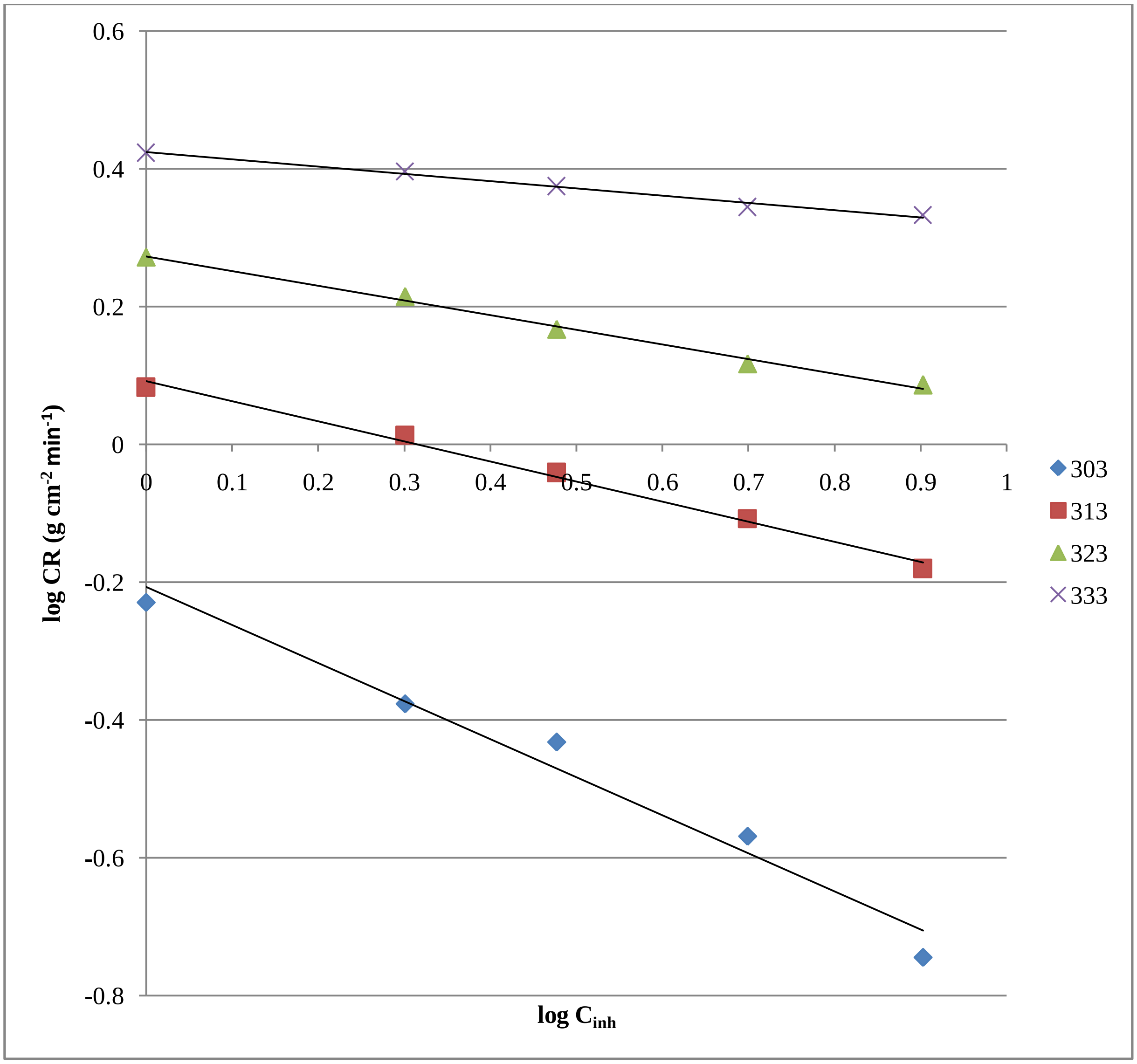

Figure9. Variation in log CR with log C_{inh} for mild steel corrosion in 1M HCl in presence of different concentration of AEZJS at various studied temperatures

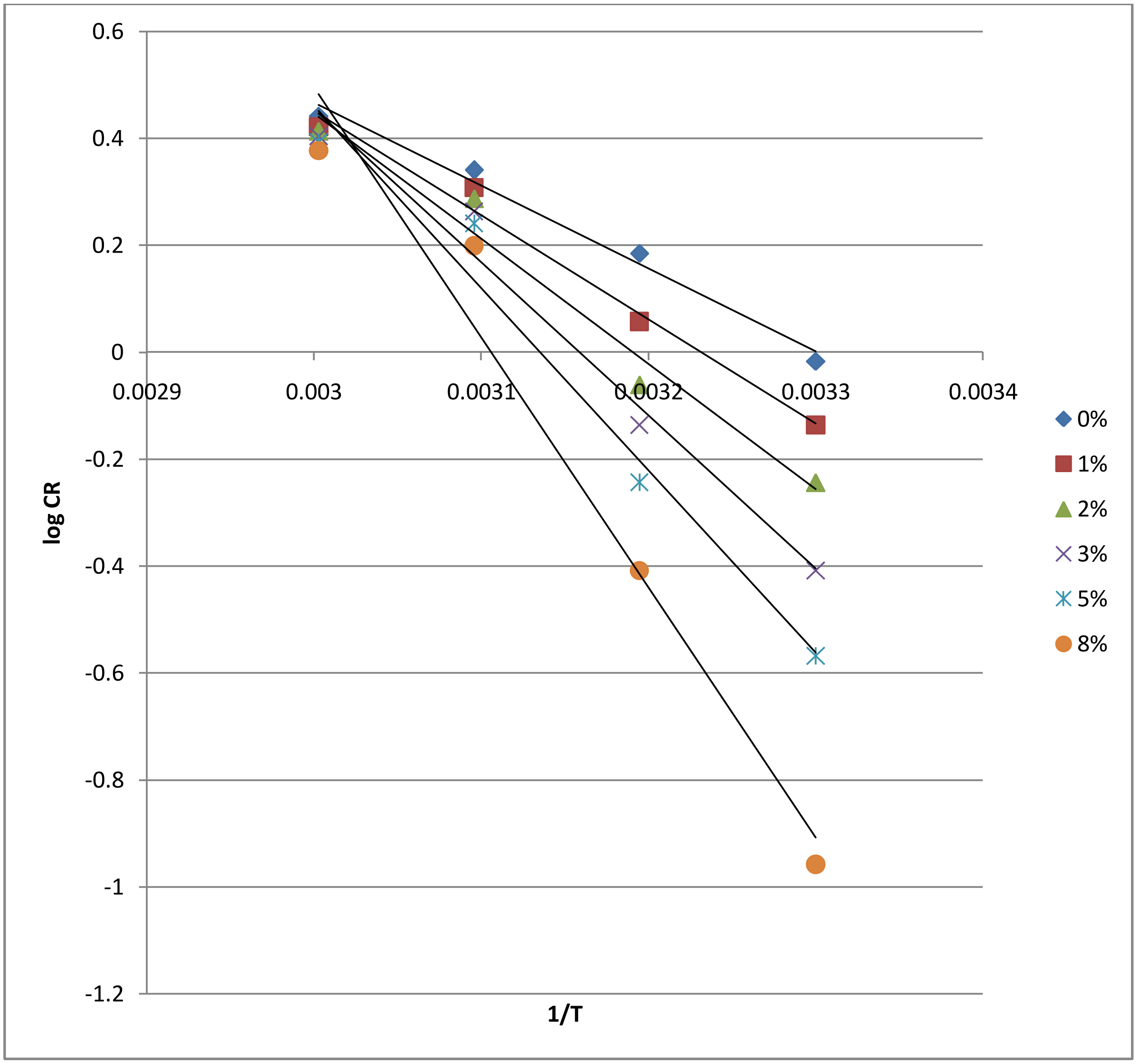

Figure10. Arrhenius plots for mild steel corrosion in 1M HCl in absence and presence of various concentration of AEZJS

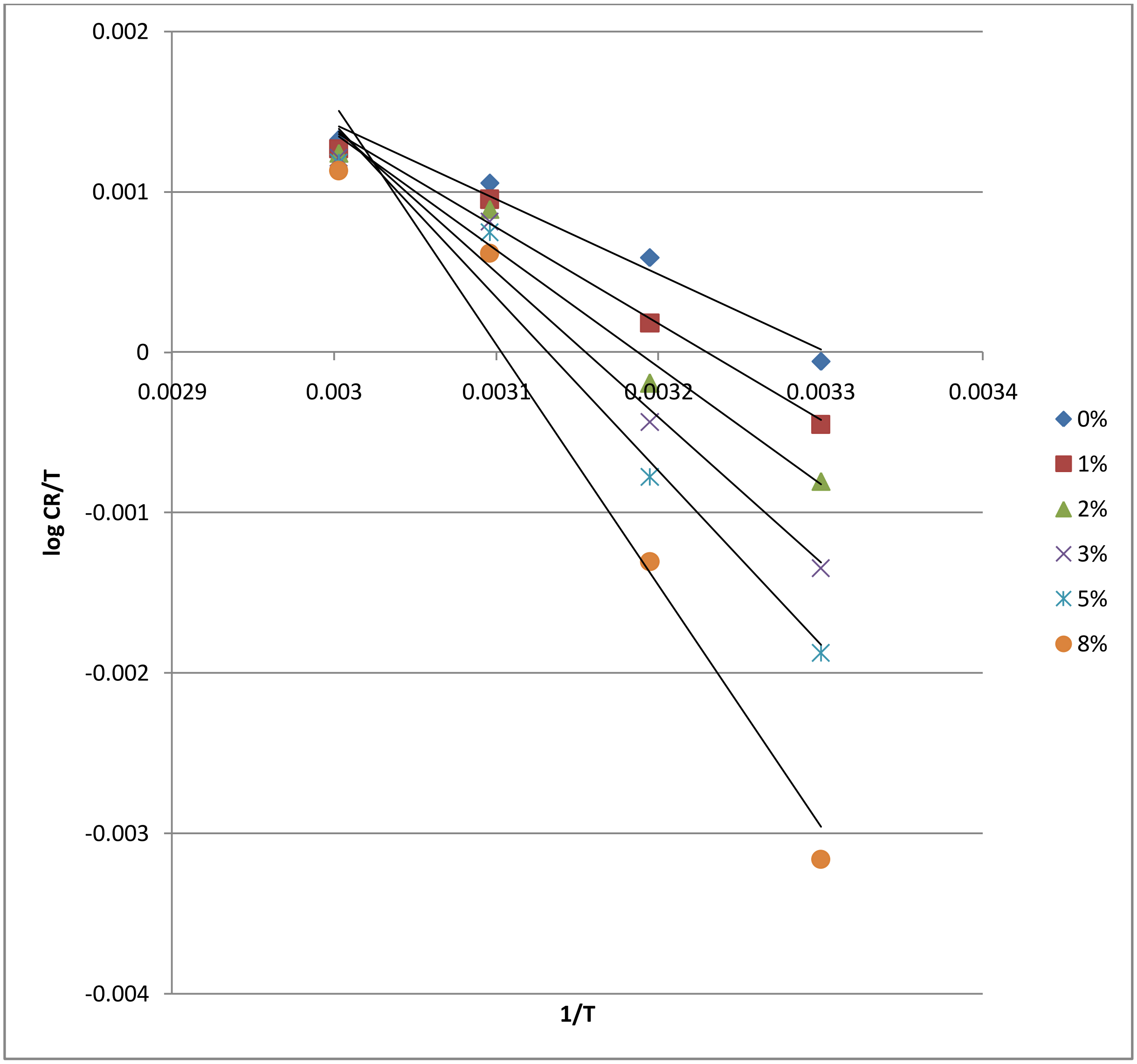

Figure11. Transition-state plots for mild steel corrosion in 1M HCl in absence and presence of various concentration of AEZJS

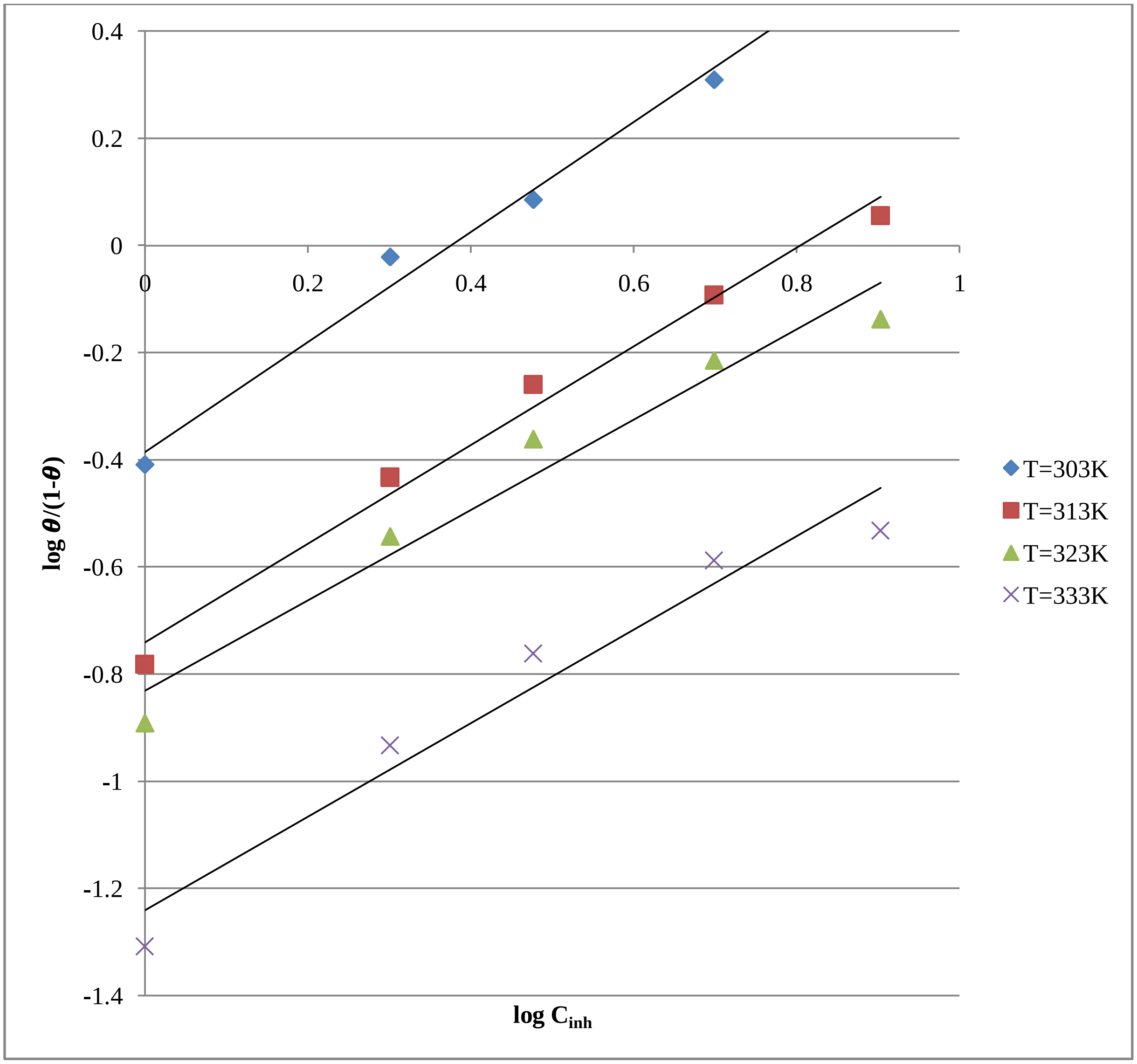

Figure12. Langmuir adsorption isotherms of AEZJS on mild steel surface in 1M HCl at different studied temperatures

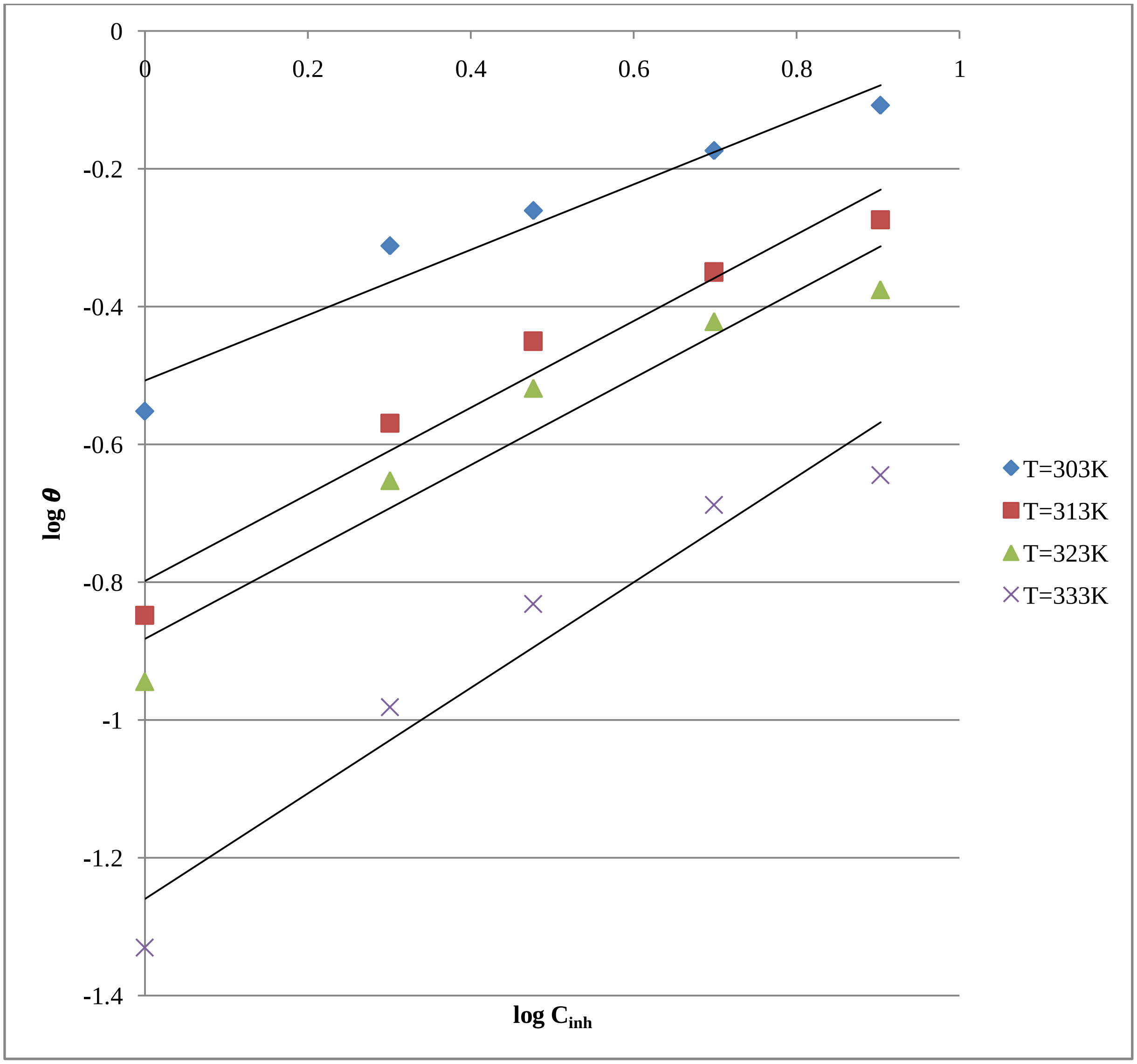

Figure13. Freundlich adsorption isotherms of AEZJS on mild steel surface in 1M HCl at different studied temperatures

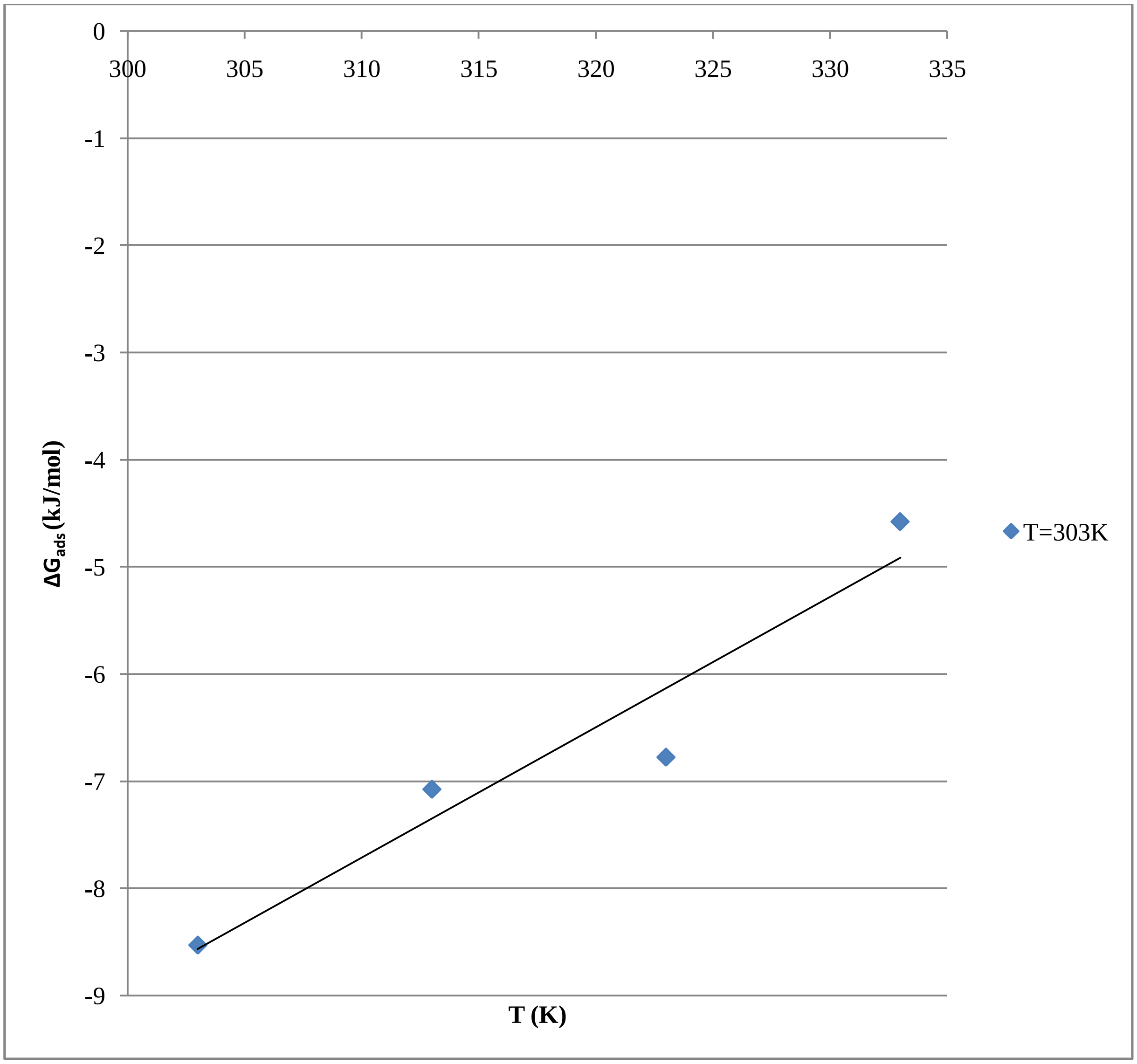

Figure14. The Variation of ΔG_{ads}(kJ/mol) with T (K) for mild steel corrosion in 1M HCl solution with AEZJS

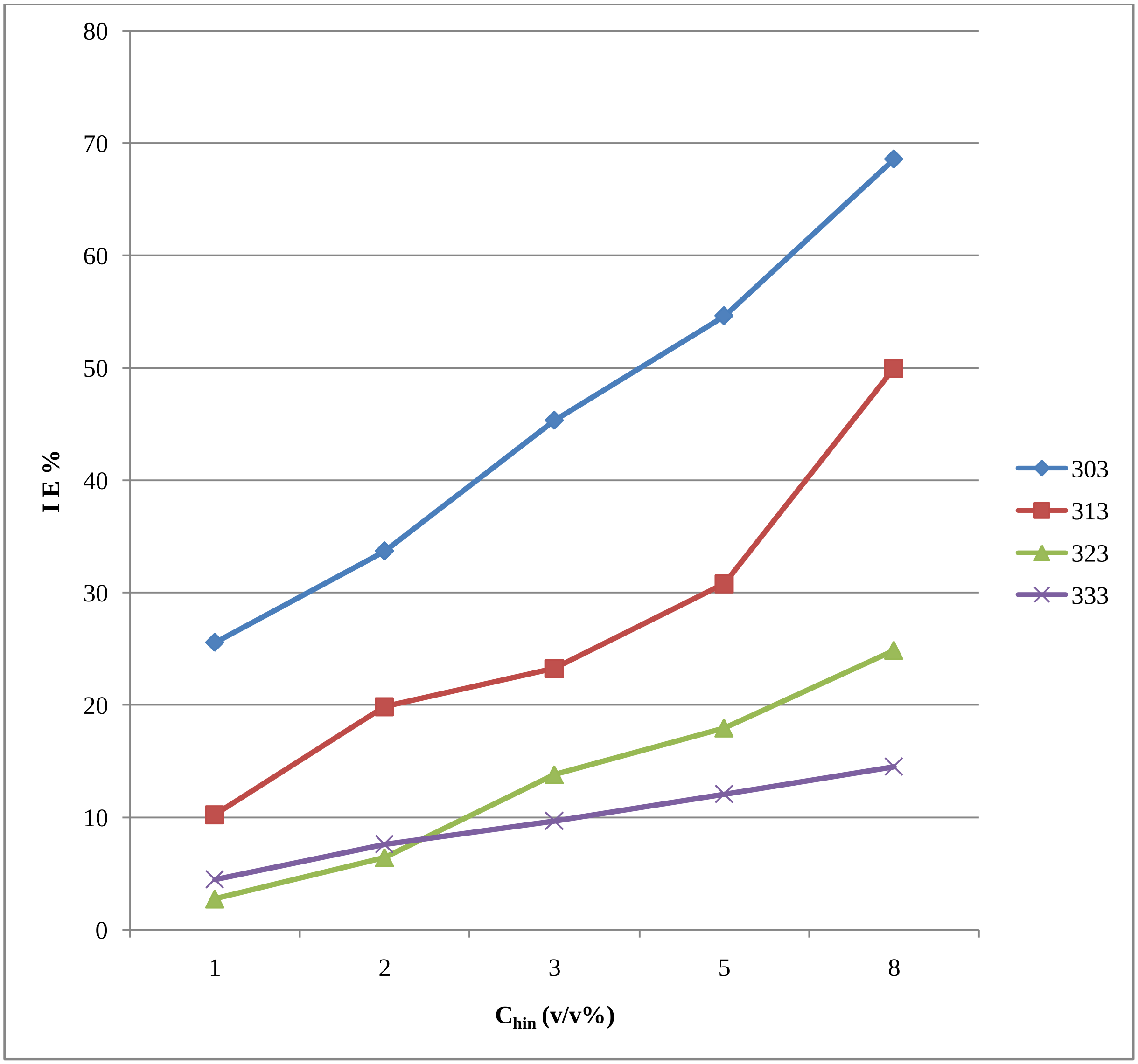

Figure15. Variation in I E % for mild steel corrosion in 1M HCl at different concentration of AEZJF at different studied temperatures

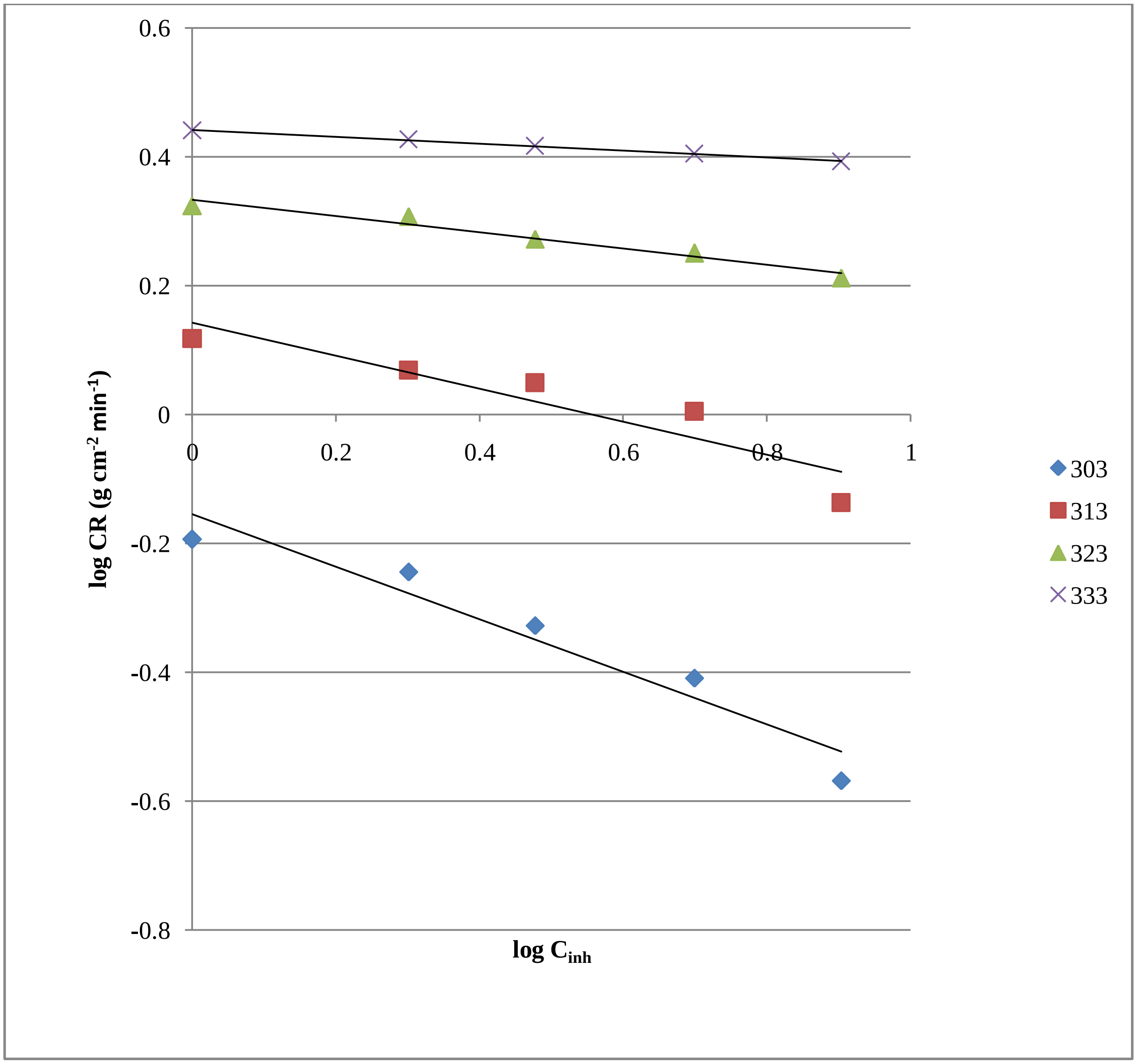

Figure16. Variation in log CR with log C_{inh} for mild steel corrosion in 1M HCl in presence of different concentration of AEZJF at various studied temperatures

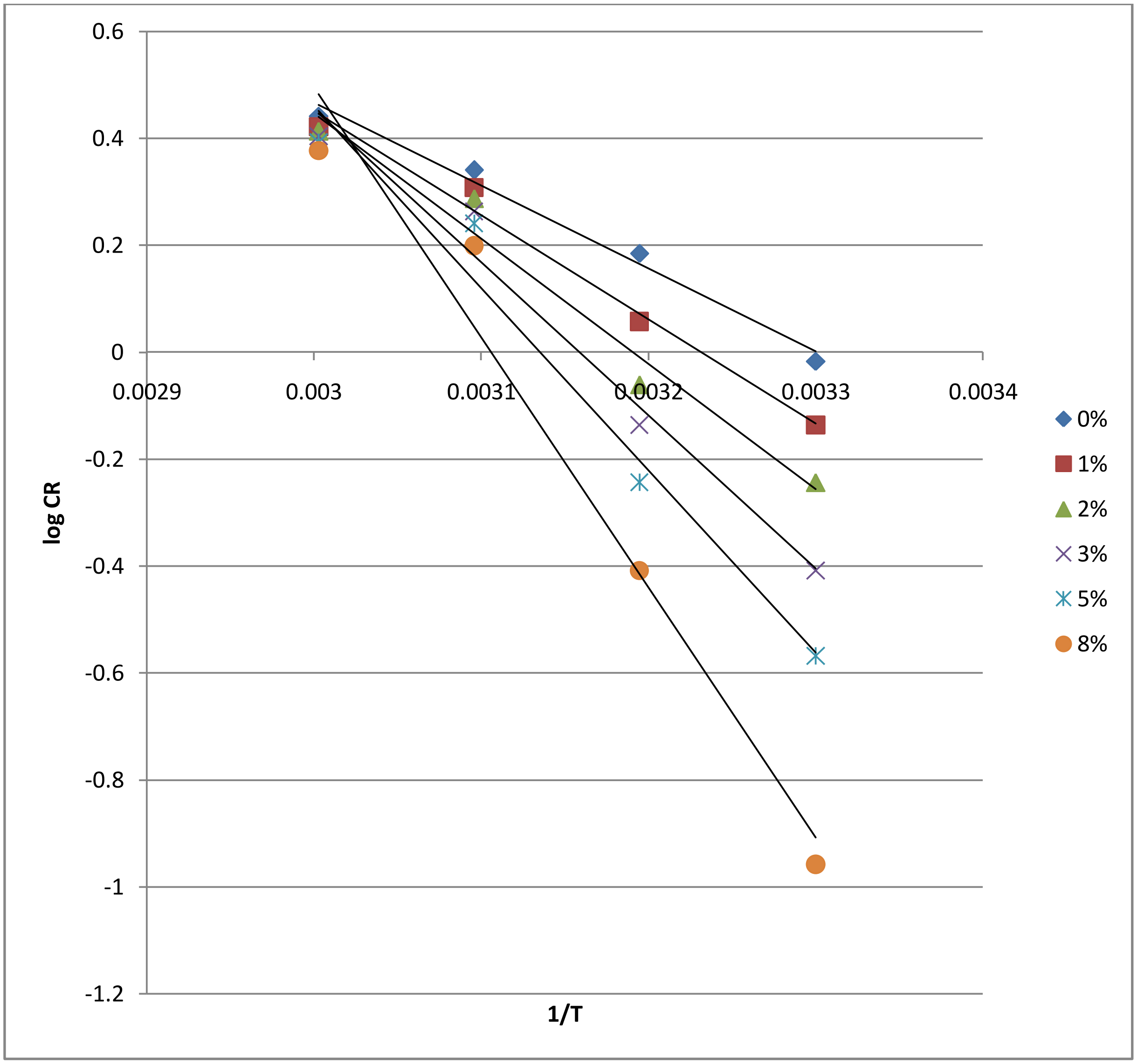

Figure17. Arrhenius plots for mild steel corrosion in 1M HCl in absence and presence of various concentration of AEZJF

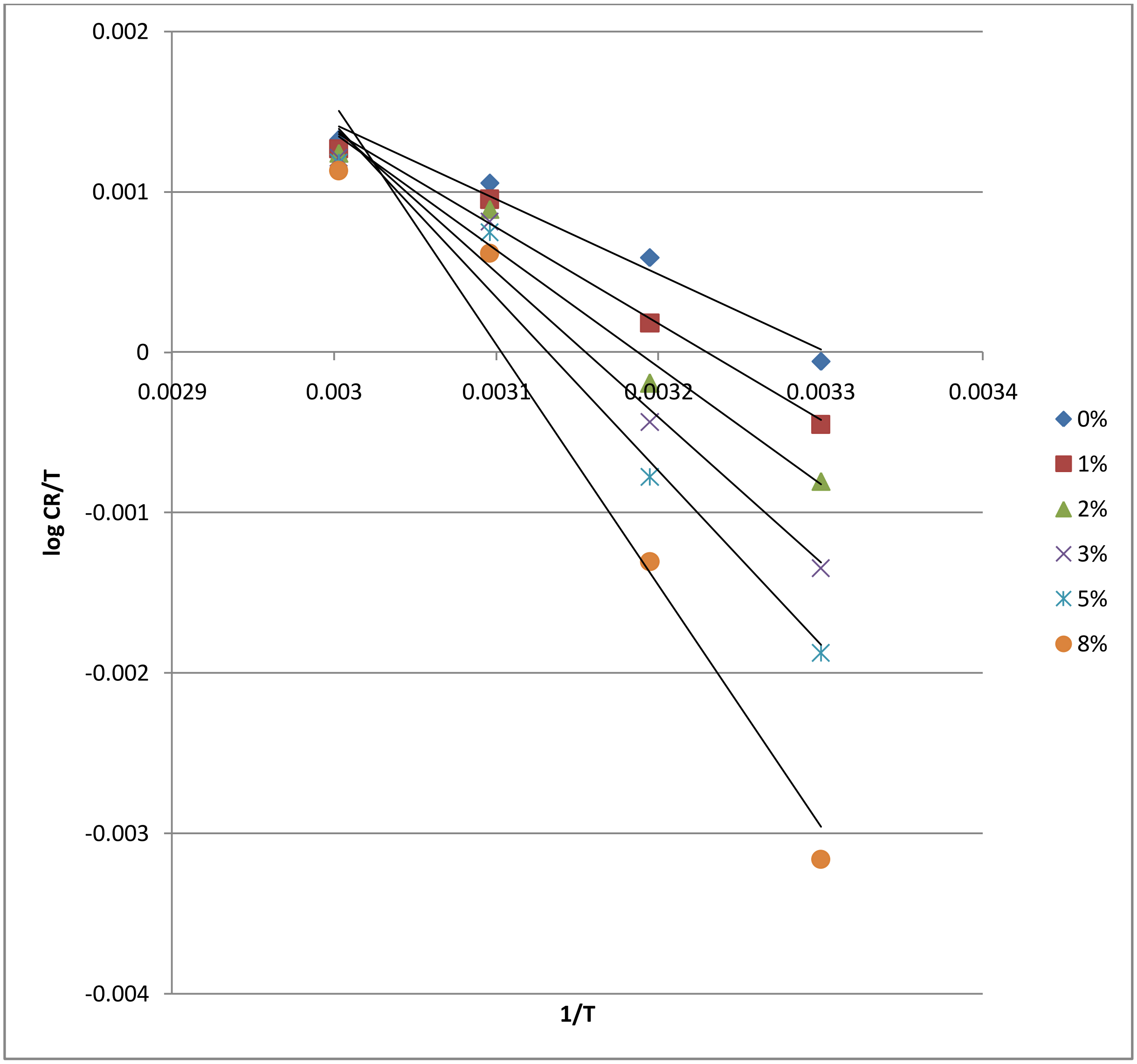

Figure18. Transition-state plots for mild steel corrosion in 1M HCl in absence and presence of various concentration of AEZJF

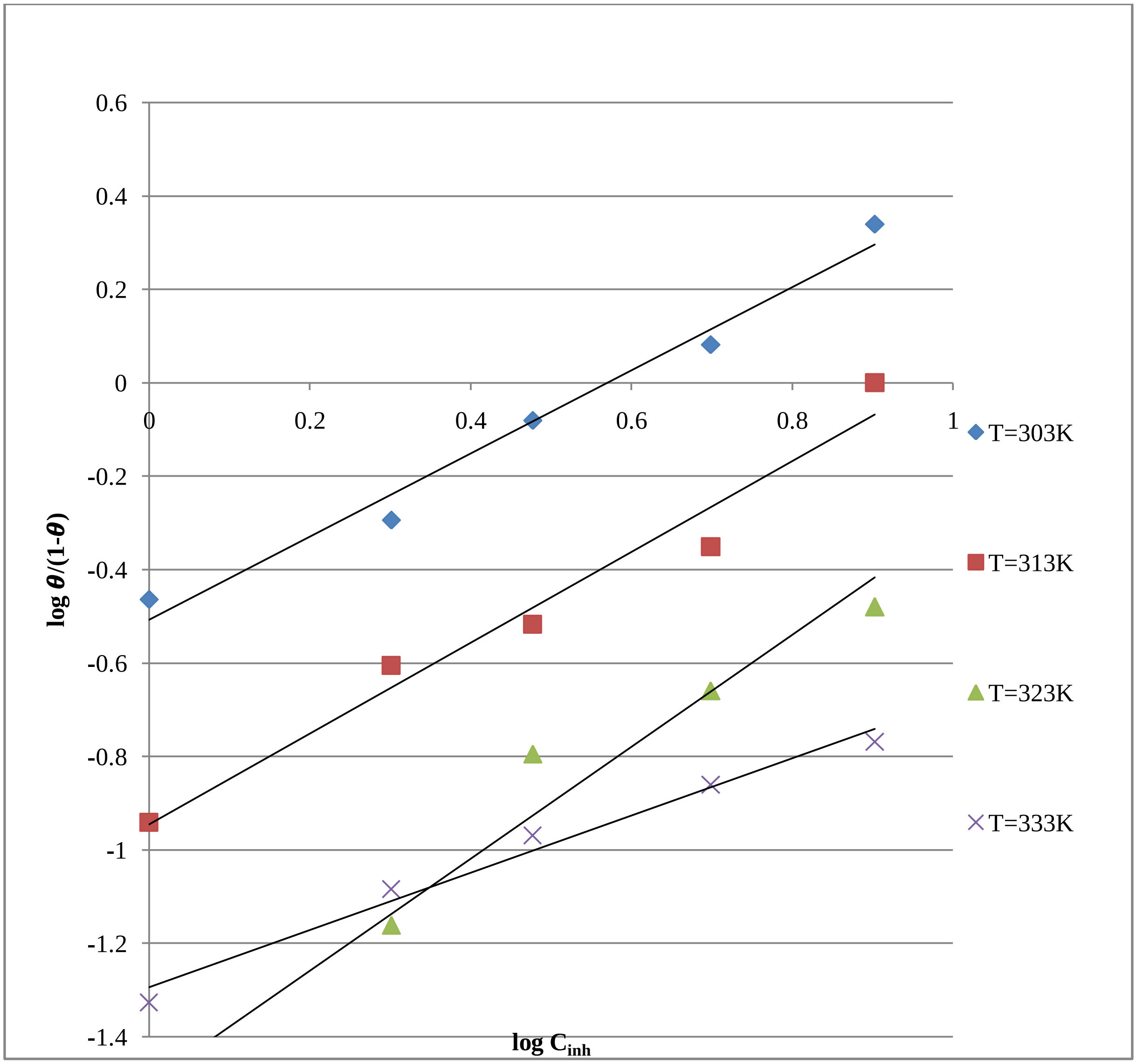

Figure19. Langmuir adsorption isotherms of AEZJF on mild steel surface in 1M HCl at different studied temperatures

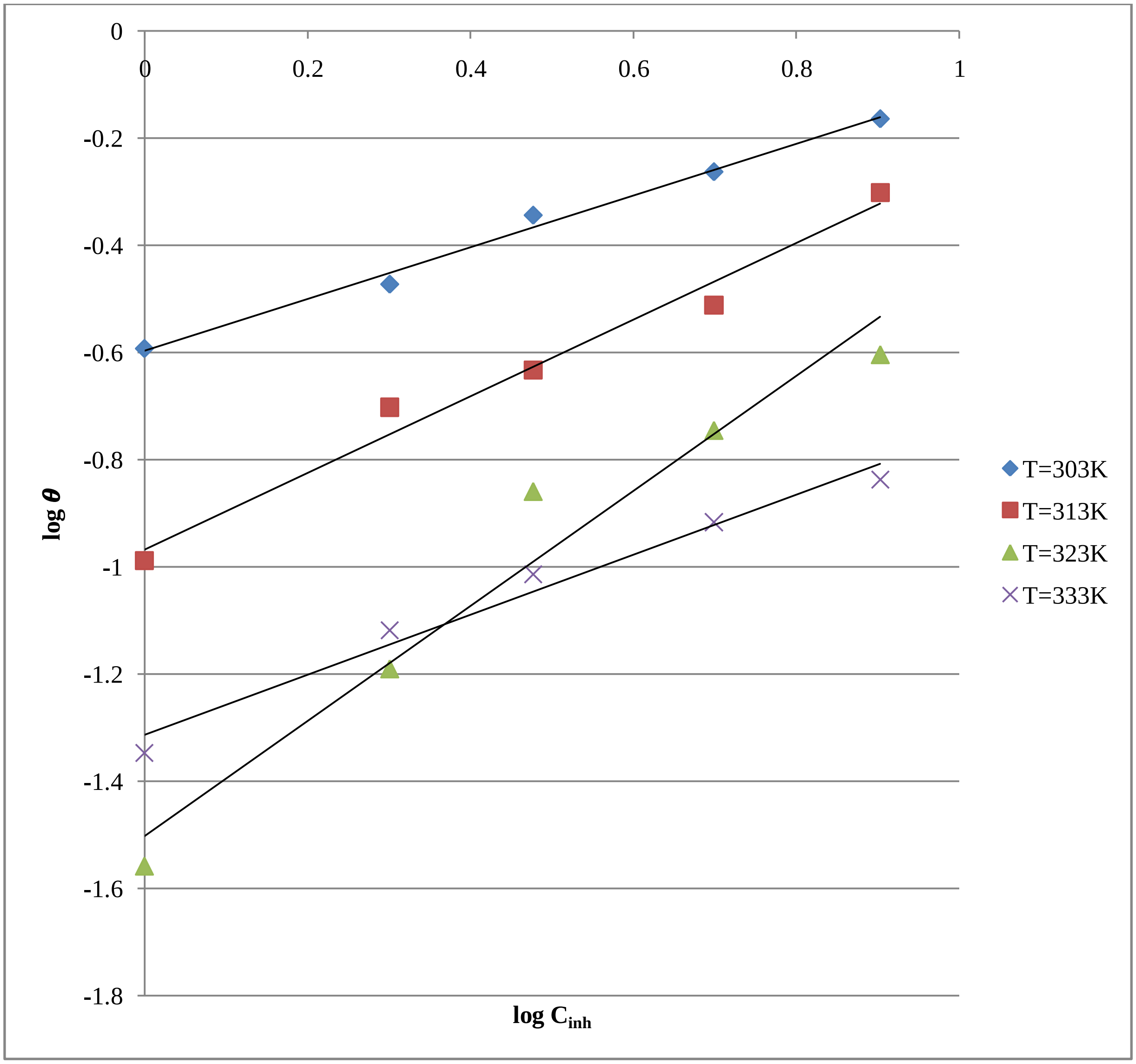

Figure20. Freundlich adsorption isotherms of AEZJF on mild steel surface in 1M HCl at different studied temperatures

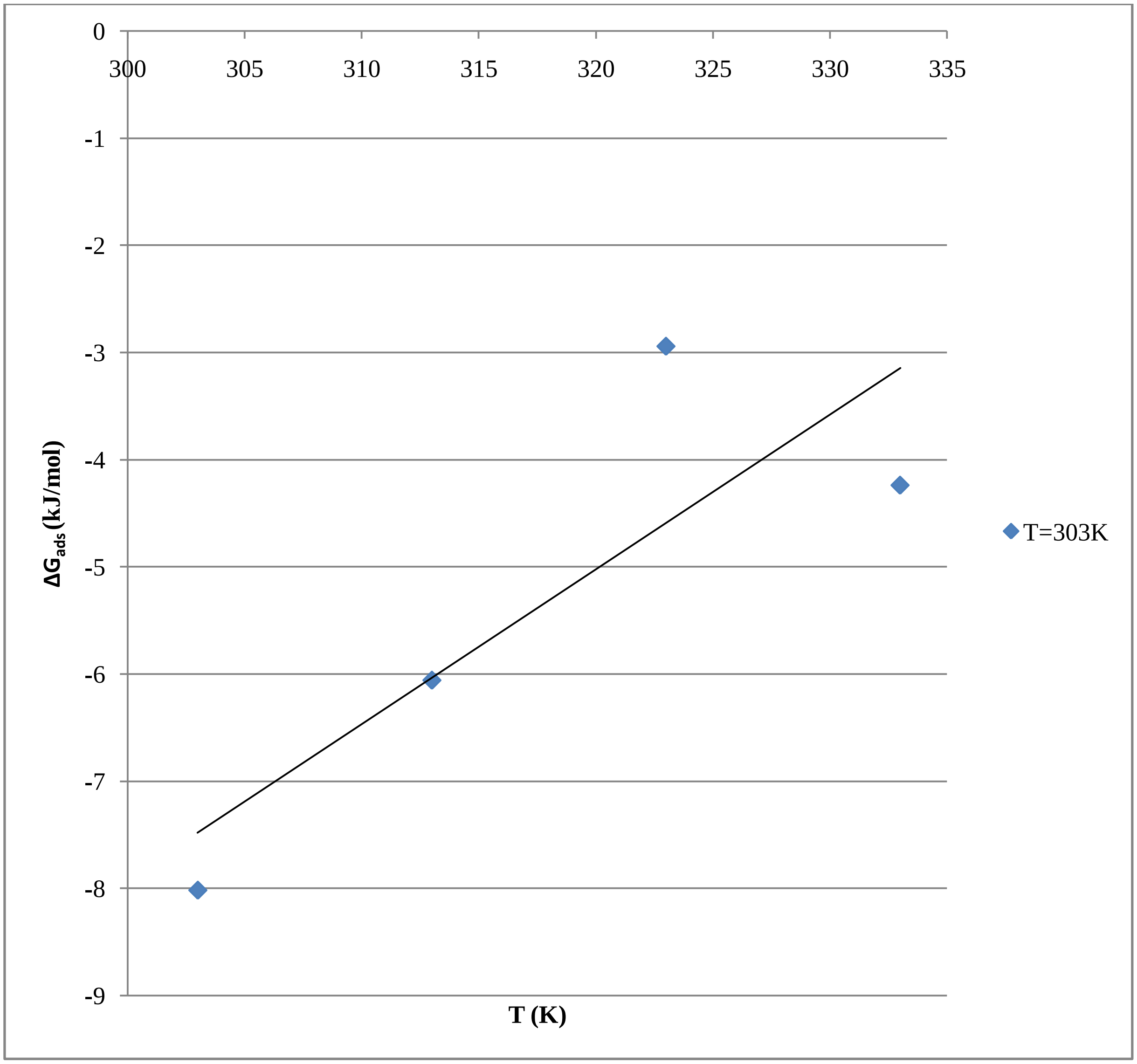

Figure21. The Variation of ΔG_{ads}(kJ/mol) with T (K) for mild steel corrosion in 1M HCl solution with AEZJF

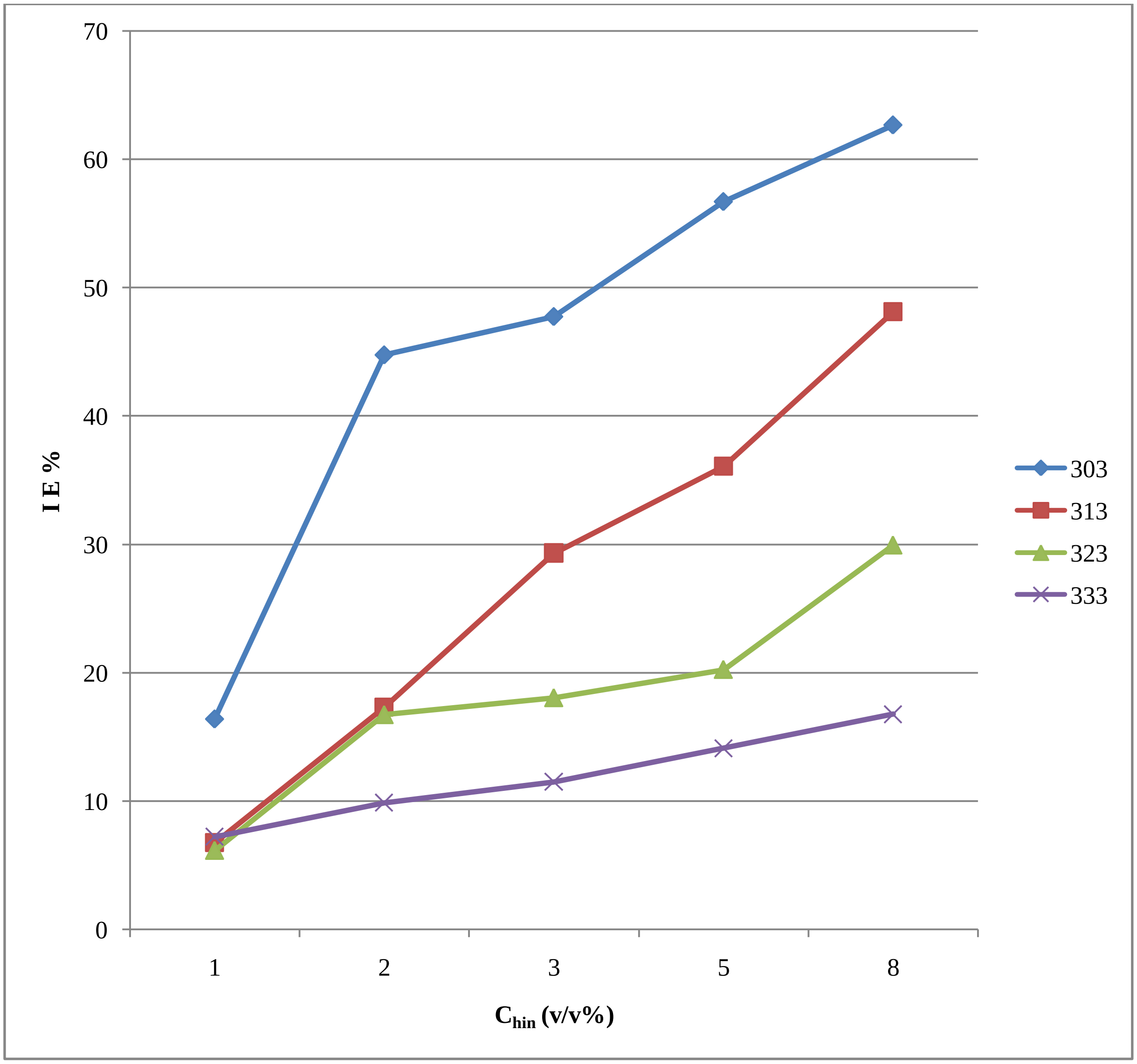

Figure22. Variation in I E % for mild steel corrosion in 1M HCl at different concentration of AEZJR at different studied temperatures

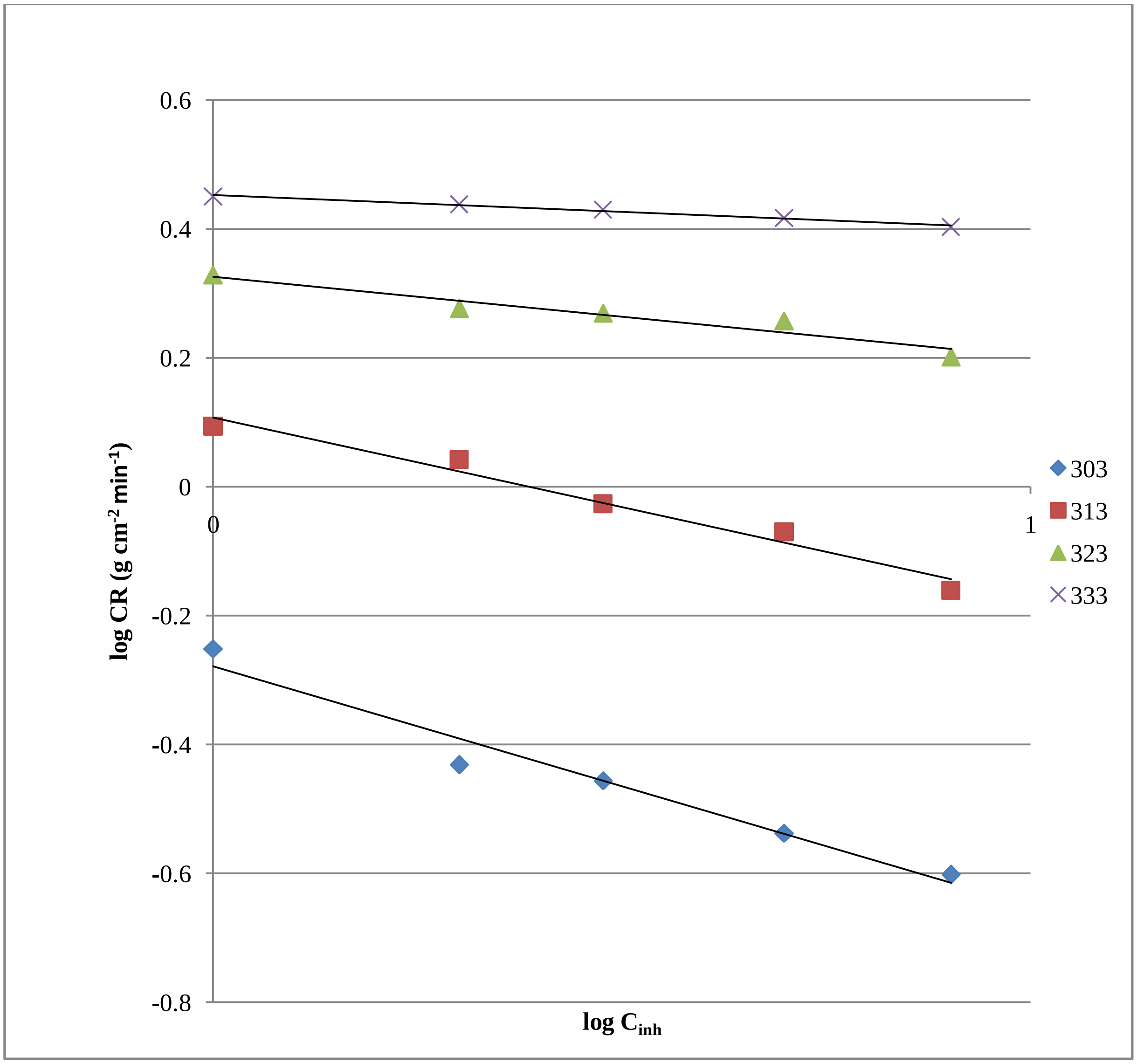

Figure23. Variation in log CR with log C_{inh} for mild steel corrosion in 1M HCl in presence of different concentration of AEZJR at various studied temperatures

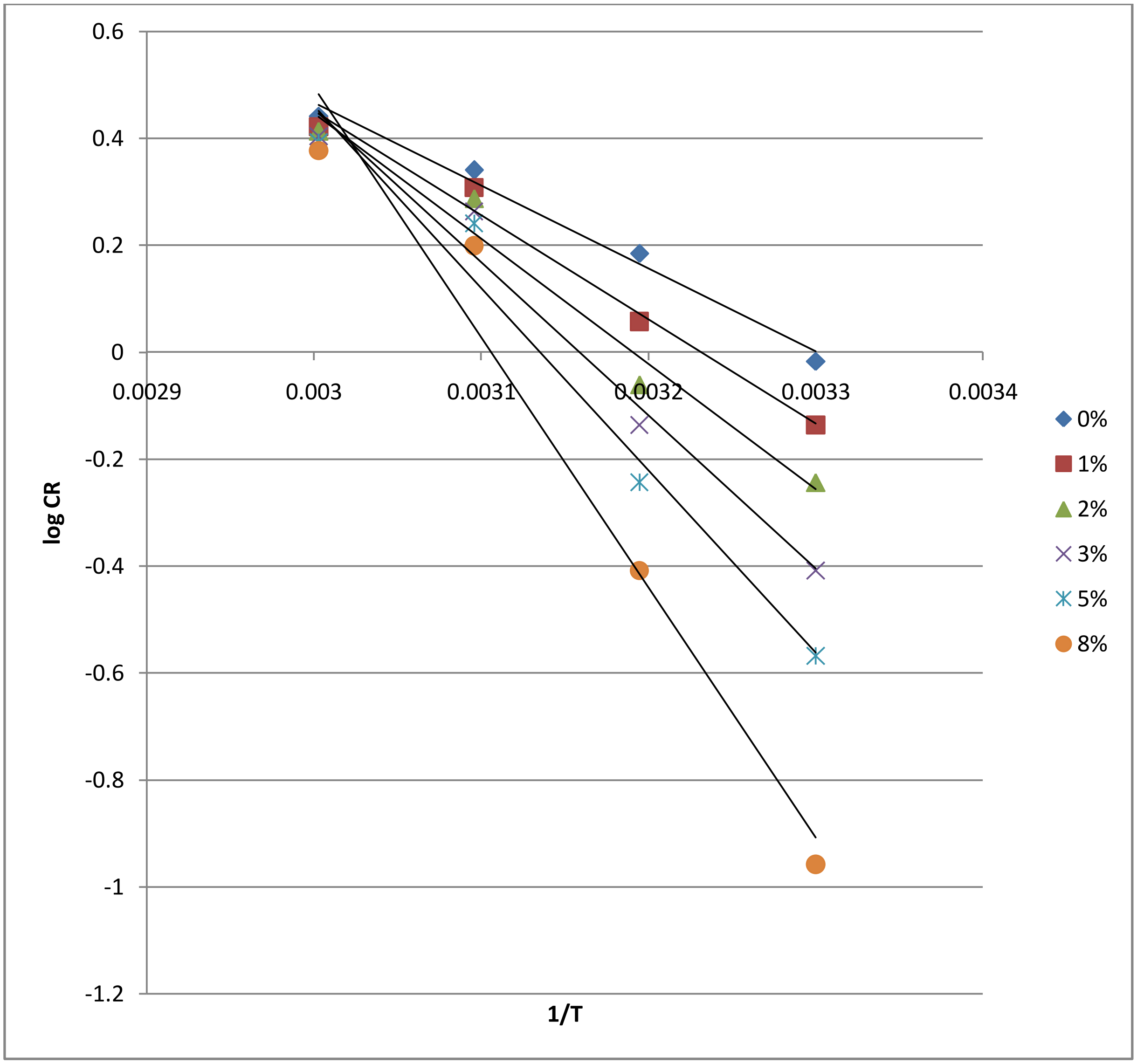

Figure24. Arrhenius plots for mild steel corrosion in 1M HCl in absence and presence of various concentration of AEZJR

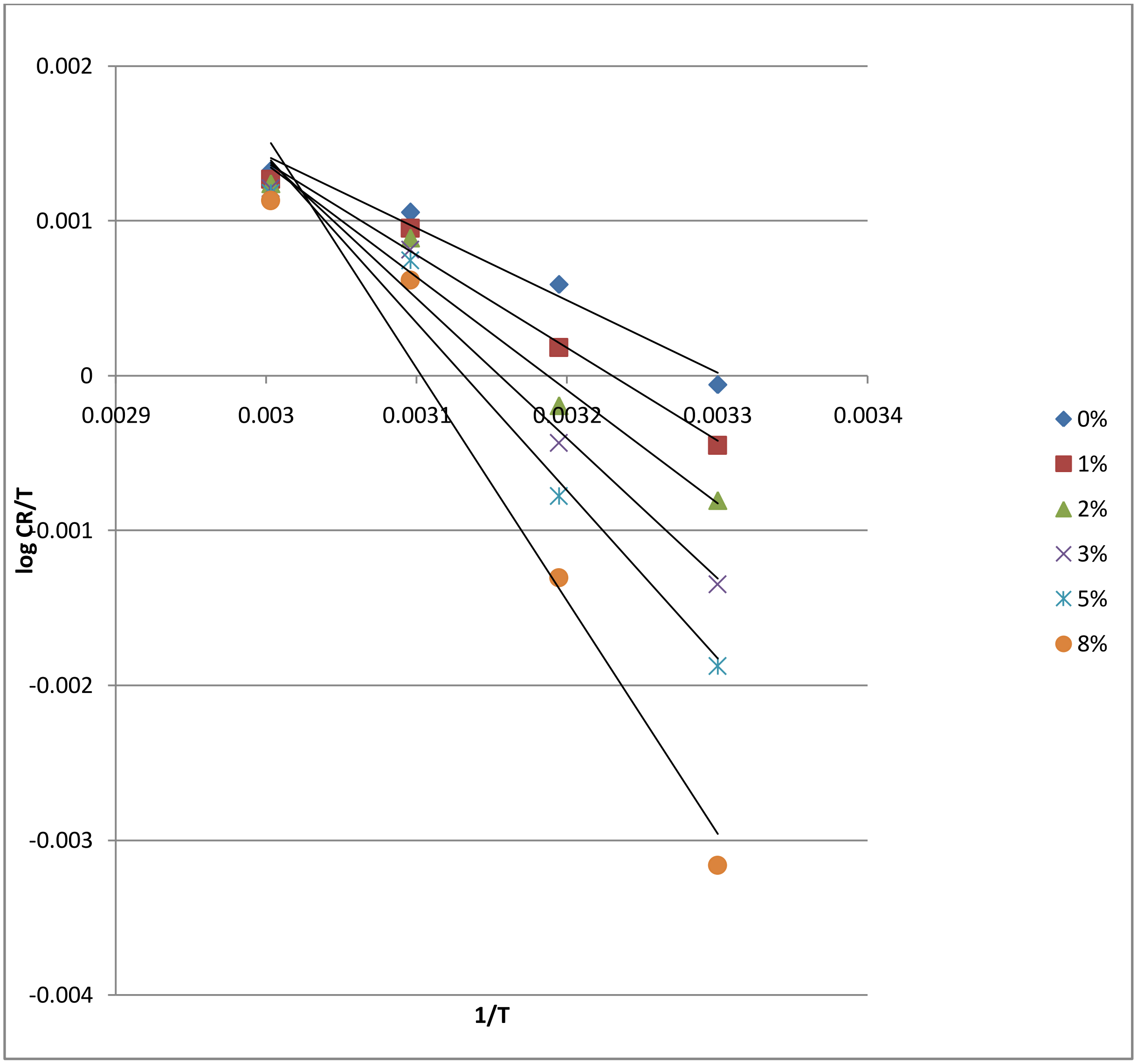

Figure25. Transition-state plots for mild steel corrosion in 1M HCl in absence and presence of various concentration of AEZJR

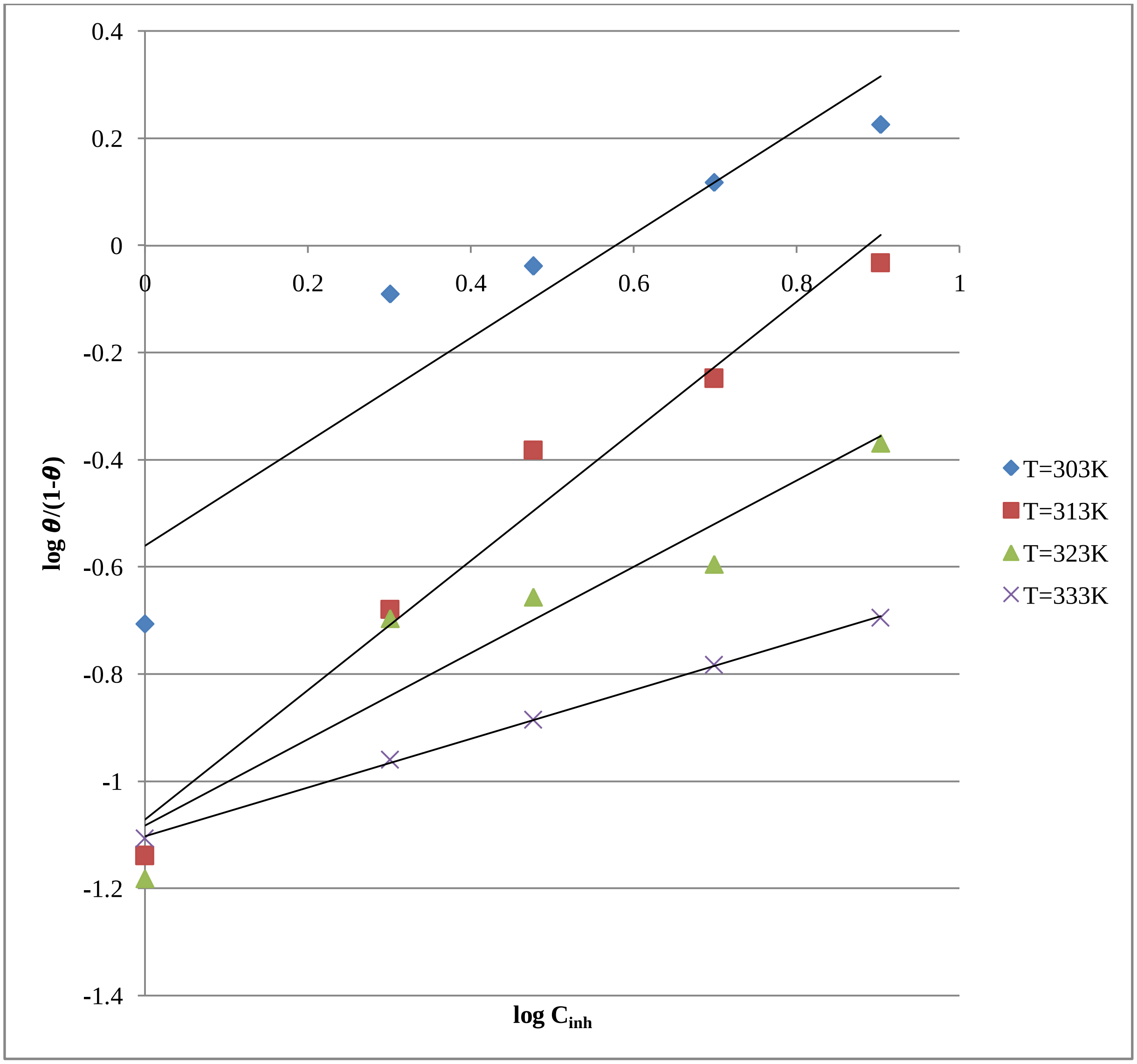

Figure26. Langmuir adsorption isotherms of AEZJR on mild steel surface in 1M HCl at different studied temperatures

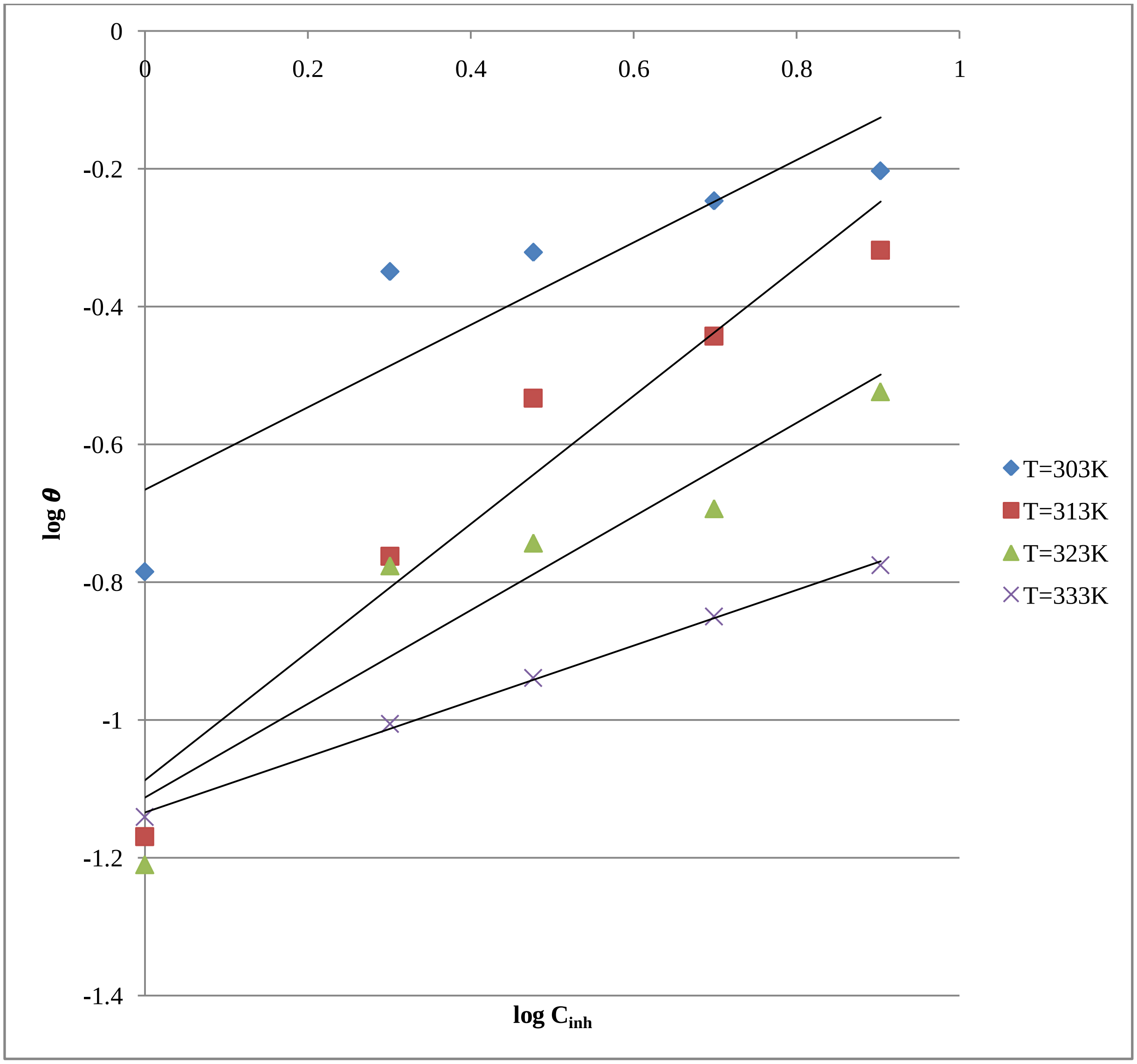

Figure27. Freundlich adsorption isotherms of AEZJR on mild steel surface in 1M HCl at different studied temperatures

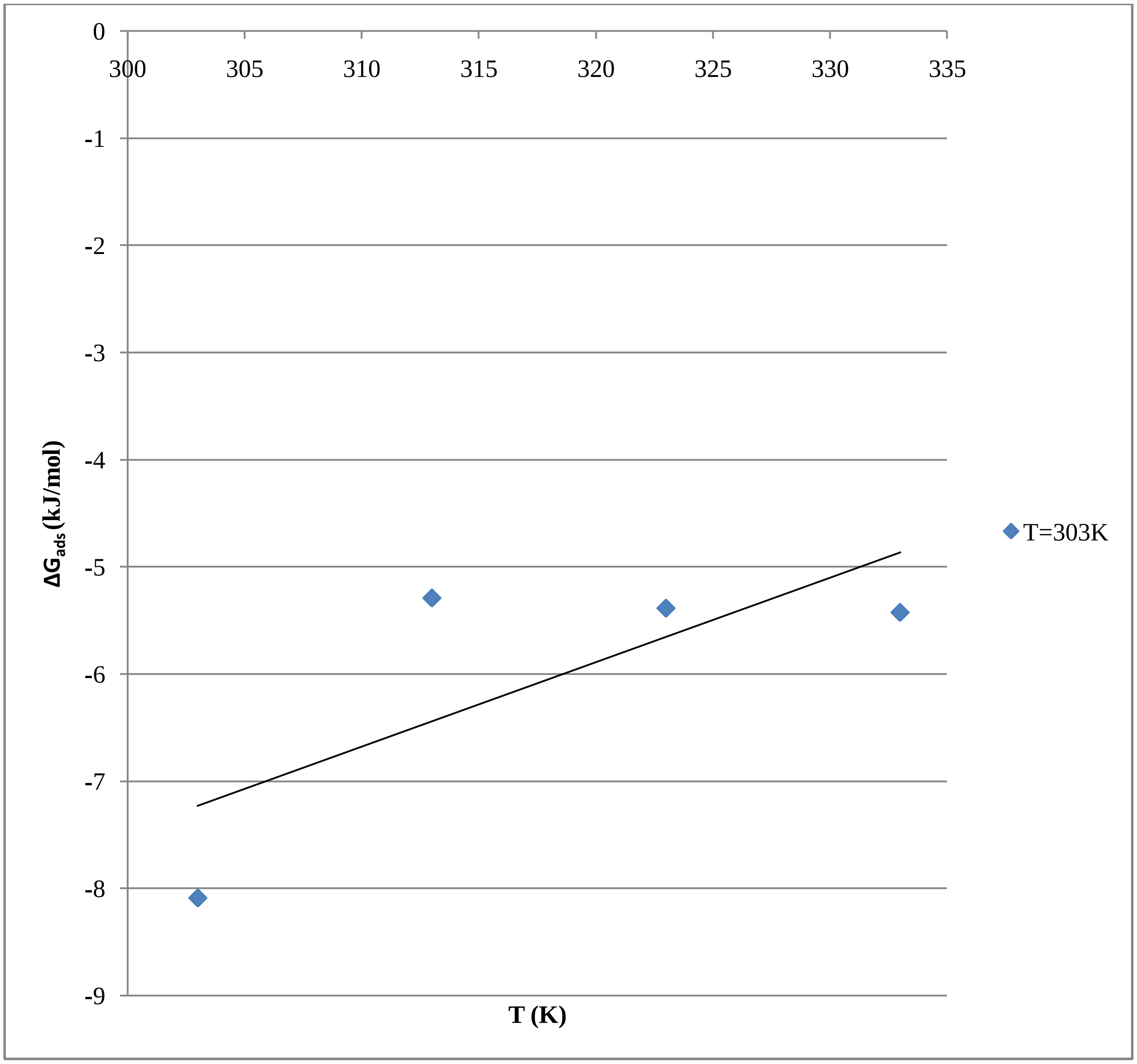

Figure28. The Variation of ΔG_{ads}(kJ/mol) with T (K) for mild steel corrosion in 1M HCl solution with AEZJR

CHAPTER – 4

DISCUSSION ON FINDINGS AND CONCLUSIONS

Findings of present study for corrosion inhibition with AEZJL, AEZJS, AEZJF and AEZJR at mild steel surfaces at different temperatures and conclusions drawn are discussed under following main headings.

CORROSION RATES:

Corrosion rates were calculated by Eq.(1) [139]. Table 1, 6, 11 and 16 shows that with increase in concentration of AEZJL, AEZJS, AEZJF and AEZJR as inhibitor in HCl at different temperatures, Corrosion rates of mild steel samples decrease this could be subjected to the adsorption of the phytoconstituents of inhibitor molecules with increase in concentration of inhibitor. The corrosion rate obeys Arrhenius type of reaction, as it increases with rise in temperature [139]. The minimum corrosion rate was observed .11 with 8% AEZJL inhibitor concentration while highest corrosion rate was observed 3.04 at 60^{o} C in absence of any of these choosen inhibitors.

INHIBITION EFFICIENCY:

From the obtained corrosion rates, inhibition efficiencies were calculated by using Eq.(2) [139,220]. Fig. 1, 8, 15 and 22 represents the variation of %IE with different concentrations of inhibitors AEZJL, AEZJS, AEZJF and AEZJR at different temperatures. Data in Table 2, 7, 12 and 17 show that % IE increase with increase in extract concentration, which is an indication of an increase in number of components of extract adsorbed on mild steel surface, which block the active sites of metal from acid attack and protect the metallic corrosion [141, 147]. Further the decrease in % IE with rise in temperature suggests electrostatic interaction (physical adsorption) of the extract molecules on mild steel surface [147]. This further indicates desorption of adsorbed inhibitor species at higher temperatures and occurance of metal dissolution [69]. Maximum % inhibition efficiency 88.54% is observed at 8% (v/v) concentration of inhibitor at AEZJL at 30^{o} C while minimum % inhibition efficiency was observed 2.76% at 1% (v/v) concentration of AEZJF at 50^{o} C.

KINETIC PARAMETERS:

Corrosion rates of steel specimens against concentration of inhibitor was calculated using kinetic relationship Eq.(3) [100, 140]. Fig 2, 9, 16 and 23 represents plot between log CR and log C_{inh} values for AEZJL, AEZJS, AEZJF and AEZJR respectively at different studied temperatures. B and K were calculated by slope and intercept of straight lines of the graph. The obtained results are summarized in Table 3, 8, 13 and 18 and can be discussed as follows [139].

- Negative values of B indicate that corrosion rate is inversely proportional to concentration of inhibitor. In other words the corrosion rates decrease with increase in concentration of inhibitor species.
- The high negative values of B reflect good inhibitive property of inhibitor. High negative value of B can be observed with steep mass of slope in graph (Fig. 2, 9, 16 and 23).
- Value of B is high at lower temperatures, indicates that inhibitive species is more effective comparatively at lower temperatures.
- The increase in K values with increase in temperature, indicating the increase in corrosion rates with temperature.

THERMODYNAMIC AND ACTIVATION PARAMETERS:

Thermodynamic and activation parameters like apparent activation energy E_{act}, enthalpy of activations ΔH^* and entropy of activation ΔS^* were calculated for steel dissolution process. Activation energies E_{act}, were calculated from the slopes of Arrhenius plots drawn between log CR and l/T as in Fig. 3, 10, 17 and 24 in accordance with the Arrhenius Eq.(4) [220,207]. Table 4, 9, 14 and 19 represents the calculated data of activation energies. The values of activation energies in presence of inhibitor were found higher than in uninhibited solution. This indicates the formation of higher energy barrier in corrosion reaction by inhibitor molecules. The increase in E_{act}, for corrosion process further interpreted as physical adsorption of inhibitor species on mild steel surface [119, 145, 159]. Besides this according to Damaskin the value of activation energy lesser than 80kJ/mol and even smaller than 5kJ/mol represents physical adsorption. This assertion supports the experimental results obtained in the present work. The values of enthalpies of activation ΔH^* and entropy of activation ΔS^* were calculated by transition state Eq.(5) [207, 220]. A plot of log (CR/T) versus l/T gave a straight line with slope of $(-\Delta H^*/2.303R)$ and intercept of $[(\log R/Nh) + (\Delta S^*/2.303\ R)]$ from which the values of ΔH^* and ΔS^* were calculated (Fig.4, 11, 18 and 25). These values are Tabulated in Table 4, 9, 14 and 19. Values ΔH^* were found positive. Positive values indicate endothermic nature of steel dissolution process [27, 134, 220]. Endothermic process further indicates that mild steel dissolution reduces at lower temperatures and increases with increase in temperature. Negative values of ΔS^* are indicative of formation of activated complex in rate determining step, which represents association rather than dissociation step, meaning the decrease in disorder takes place on going from reactants to activated complex [27, 72, 198]. It is also observed from data in Table 4, 9, 14 and 19 that E_{act}, and ΔH^* vary in the same manner. Values of both E_{act}, and ΔH^* increase with increase in concentration of inhibitor, suggesting that energy barrier increases with increase in inhibitor concentration. This means that corrosion reaction will further be pushed to surface sites that are characterized by progressively higher values of E_{act} as the concentration of inhibitor becomes greater [27, 196, 203]. The values of activation energy were found larger than a corresponding values of enthalpy of activation, indicate the involvement of a gaseous reaction, simply hydrogen evolution in corrosion process, associated with a decrease in total reaction volume [139].

ADSORPTION ISOTHERMS:

The nature of adsorption can be explained by understanding the process at metal/electrolyte interface. Further to understand the nature of adsorption, obtained surface coverage (θ) were fitted in different adsorption isotherms. Langmuir adsorption isotherm was drawn by using Eq. (8) [28, 69, 137, 165, 213] and Freundlich adsorption isotherm was drawn using the Eq.(10) [101] and straight lines were obtained. These isotherms are shown in Fig. 5, 12, 19 and 26 and Fig. 6, 13, 20 and 27 respectively.

ADSORPTION PARAMETERS:

[Gibbs Energy of Adsorption [ΔG_{ads}], Enthalpy of adsorption [ΔH_{ads}] and Entropy of Adsorption [ΔS_{ads}]

Values of K_{ads} were calculated by the intercept of Langmuir isotherm drawn according to the Eq.(8) between log (θ /1- θ) and log C_{inh} and by using this Gibbs energies were calculated by using Eq. (13) [99, 139]. The values of ΔG_{ads} were Tabulated in Table 5, 10, 15 and 20, ΔG_{ads} values have been found negative at all studied temperatures indicating spontaneous adsorption process of inhibitor molecule and strong interactions between inhibitor molecules and metal surface [1, 27, 38, 54, 189, 201, 202] Increase in ΔG_{ads}, values (becoming less negative) with the increase of temperature indicates the occurrence of exothermic process [139]. Table 5, 10, 15 and 20 show increase in ΔG_{ads} values with temperature indicate exothermic process of adsorption of inhibitor molecules, which is unfavourable at higher temperature due to desorption of inhibitor from metal Surface [139, 201]. Generally values of ΔG_{ads} upto -20 kJ/mol are consistent with electrostatic interactions (physical adsorption) between charged molecules and charged metal surface and values upto -40 kJ/mol or higher involve charge sharing or transfer from inhibitor molecules to metal surface to form coordinate type of bond (chemical adsorption) [27, 38, 77, 120, 143, 144, 210]. The values of ΔG_{ads} were found for inhibitors AEZJL from -8.06kJ/mol to -3.91 kJ/mol, for AEZJS from -8.53kJ/mol to -4.57kJ/mol, for AEZJF from -8.01kJ/mol to -4.23kJ/mol, for AEZJR from -8.08kJ/mol to -5.42kJ/mol, The obtained values G_{ads} were found less than -20kJ/mol indicated physical adsorption of inhibitor molecules. Further the value of ΔG_{ads} is more negative at lower temperatures indicating that corrosion inhibition process is more effective at lower temperatures. It has been observed that adsorption of negatively charged species is facilitated due to the positively charged metal. But positively charged species can also be adsorbed and protect the positively charged metal surface acting with a negatively charged intermediate such as acid anions, adsorbed on metal surface [27, 159, 210]. Obtained values of Gibbs energy were plotted against temperature (Fig. 7, 14, 21 and 28) according to the basic Eq. (14) [59, 139]. Intercept of graph between ΔG_{ads} versus T (Fig. 7, 14, 21 and 28) gives values of ΔH_{ads}, and by putting the values of intercept in Eq.(14) values of ΔS_{ads} were obtained. These obtained adsorption parameters Gibbs free energy of adsorption (ΔG_{ads}), enthalpy of adsorption (ΔH_{ads}), entropy of adsorption are listed in Table 5,10, 15 and 20. Values of ΔH_{ads} have been found negative indicating the exothermic adsorption process [72, 122, 119, 141], which further confirms lower %IE at higher temperatures, due to desorption of inhibitor molecules. The exothermic process is attributed to either physical or chemical adsorption or mixture of both [32]. In exothermic process, values of ΔH_{ads} predict physiorption or chemisorption. For physiorption values of ΔH_{ads} is lower than 40kJ/mol while for chemisorption it approaches to 100 kJ/mol [29,]. Values of ΔH_{ads} in Table 5, 10, 15 and 20 indicate physiorption. Negative values of ΔS_{ads} indicate decrease in entropy of adsorption process. This behavior can be explained as: Before the adsorption of inhibitor molecules onto mild steel surface, inhibitor molecules might freely move in bulk solution (inhibitor molecules were chaotic). But with the process of adsorption, inhibitor molecules were orderly adsorbed onto the steel surface as a result decrease in entropy is observed [120, 121].

A more interesting behavior is observed in Table 5,10, 15 and 20 that negative ΔS_{ads} value is accompanied with negative ΔH_{ads} value. This further agrees that when the adsorption is an exothermic process, it must be accompanied by a decrease in the entropy change and vice versa [139, 204).

CONCLUSIONS:

1. Results showed that AEZJL, AEZJS, AEZJF and AEZJR are observed good corrosion inhibitors for mild steel in 1M HCl solution under experimental conditions chosen. The comparative effectiveness of the four parts of the plant *Ziziphus jujuba* in corrosion inhibition is in order AEZJL, AEZJS, AEZJF and AEZJR.ie. AEZJL is observed most effective and AEZJR is observed least effective under experimental conditions chosen.

2. Corrosion rates increase with increase in temperature and decrease with increase in inhibitor concentration.

3. Inhibition efficiency increases at lower temperature this suggests the physiorption of inhibitor on mild steel surface.

4. Apparent activation energy increases with increase in inhibitor concentration, this also suggests physiorption.

5. Enthalpy of adsorption comes out negative which shows exothermic and physical adsorption process of inhibitors on mild steel surface.

6. The values of Gibbs free energies calculated were negative showing spontaneity of corrosion inhibition process of mild steel in 1M HCl in all inhibitors chosen viz AEZJL, AEZJS, AEZJF and AEZJR.

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SUMMARY

This thesis consists four different chapters.

Chapter 1: Introduction and Review of Literature

This chapter contains an introduction about corrosion phenomenon and corrosion of mild steel and its importance .It contains brief idea about natural corrosion inhibitor substances and corrosion inhibition of mild steel using natural plant products. It also contains a concise report of review of literature of subject along with the objective and significance of study.

Chapter 2: Materials, Methods And Methodology

This chapter consists description of four different parts of *Ziziphus Jujuba* selected plant for corrosion inhibition studies. Selected acid for preparation of different aggressive media viz. hydrochloric acid. It also includes detailed description of standard methods adopted for determination of weight loss, corrosion rates, inhibition efficiency, kinetic parameters, thermodynamic parameters, adsorption parameters and complete adopted methodology. Weight loss is determined gravimetrically, corrosion rates and inhibition efficiencies are calculated by using equation [1] and [2].Kinetic parameters , different thermodynamic parameters like activation energy (Eact),enthalpy of activation (ΔH^*) , entropy of activation (ΔS^*) and adsorption parameters like Gibbs energy of adsorption , enthalpy of adsorption , entropy of adsorption are calculated at four different temperatures with the help of corrosion rates using the equation [3] , [4] , [5] , [6] , [7] ,[13], [14] respectively. These all were studied at various concentrations of leaves,roots,stem,and fruits aqueous extract of selected plant materials in aggressive media.

Selection of plant as corrosion inhibitors

Four different parts of plant viz. *Ziziphus jujuba* was taken as natural green corrosion inhibitors for mild steel in aggressive media. Aqueous extract of *Ziziphus jujuba* leaves (AEZJL), aqueous extract of *Ziziphus jujuba* stem (AEZJS)), aqueous extract of *Ziziphus jujuba* roots (AEZJR) and aqueous extract of *Ziziphus Jujuba* fruits (AEZJF) were prepared for corrosion studies.

Acids selected for different aggressive media

Hydrochloric acid was selected for preparation of aggressive media. 1M solutions of acid were prepared for experimental studies.

Methods adopted for determination of weight loss , corrosion rates , inhibition efficiency , kinetic parameters , thermodynamic and activation parameters , Gibbs energy and adsorption parameters :

Determination of weight loss

Gravimetric technique was used for weight loss determination. Weight loss method described by Mettson was adopted for corrosion studies. For weight loss determination rectangular mild steel specimens (Thickness 0.03cm) of various dimensions (5.0 cm in length and 1.00 cm in width), (4.8 cm in length and 1.50 cm in width), (4.9 cm in length and 0.70 cm in width), (4.8 cm in length and 0.60 cm in width) were taken, abraded with different emery papers, degreased in acetone and washed with distilled water, dried and then the constant weight was recorded by electronic balance Citizen model CY204. Stock solutions of leaves extracts viz. AEZJL was prepared by heating 20 g of powdered leaves in 500 ml of distilled water for one hour, of AEZJS was prepared by 20 g of powdered stem in 500 ml of distilled water for one hour, of AEZJR was prepared by 20 g of powdered roots in 500 ml of distilled water for one hour ,of AEZJF was prepared by 20 g of powdered fruits in 500 ml of distilled water for one hour at 70°C-80°C in round bottom flasks respectively. These extracts were left overnight filtered and then made up to above-mentioned volume with distilled water. Aggressive media were prepared by 1M HCl in distilled water. The rectangular mild steel specimens were hanged by plastic thread and glass rod in 250 ml borosil glass beakers, each containing 100 ml of aggressive media for one hour at four different temperatures in presence and absence of different concentrations of extracts of four different parts of selected plant. After completion of immersion time, specimens were taken out washed with distilled water, dried and again abraded mildely with emery paper to remove the adhered material and weighed accurately by electronic balance and weight loss is calculated. The employed concentration range of palnt extracts were 1%-8%(v/v) for AEZJL, 1%-8%(v/v) for AEZJS, 1%-8%(v/v) for AEZJR, and 1%-8%(v/v) for AEZJF extract. The observations were taken at four different temperatures (303K, 313K, 323K and 333K).

Determination of Corrosion Rates (CR)

In 1M HCl corrosion rates of mild steel specimens at different temperatures were calculated by equation (1)

$$\mathrm{CR} = \left(\frac{\Delta \mathrm{W}}{\mathrm{At}}\right) \tag{1}$$

Where ΔW is the weight loss calculated of mild steel specimen before and after immersion in acidic media. A is the total surface area of different specimen and t is immersion time in minute.

Determination of Inhibition Efficiency (IE%)

By using corrosion rate data, inhibition efficiency was calculated by following equation (2).

$$\mathrm{IE}\ \% = \left(\frac{\mathrm{CR}_{\mathrm{blank}} - \mathrm{CR}_{\mathrm{inh}}}{\mathrm{CR}_{\mathrm{blank}}}\right) \times 100 \tag{2}$$

Where CR blank and CR inh are the corrosion rates of mild steel in the absence and presence of the specific concentration of inhibitor respectively.

Determination of Kinetic Parameters

Kinetic parameters B (reaction constant) and K (rate constant) were calculated by the equation (3).

$$\log CR = \log K + B \log C_{inh} \qquad (3)$$

where K is equal to CR at the inhibitor concentration of unity. B is the reaction constant which is the measure of inhibitor effectiveness and Cinh is the concentration in %(v/v) of inhibitor.

Determination of the thermodynamic and activation parameters

Thermodynamic and activation parameters like energy of activation (Eact), enthalpy of activation (ΔH^*) entropy of activation (ΔS^*) were calculated by equation (4) and (5).

$$\log CR = \log A - \left(\frac{Eact}{2.303 R\ T}\right) \qquad (4)$$

Where A is Arrhenius pre-exponential factor, CR is corrosion rate and T is temperature in Kelvin. For calculating Eact values, the graph was plotted between log CR values and (1/T) values.

$$\log\left(\frac{CR}{T}\right) = [(\log\left(\frac{R}{Nh}\right) + \left(\frac{\Delta S^*}{2.303 R}\right)] - [\left(\frac{\Delta H^*}{2.303 RT}\right)] \qquad (5)$$

Where N is Avogadro`s number, h is Planck’s constant. For calculating the values of (ΔS^*) and (ΔH^*), graph was plotted between log (CR/T) and (1/T) values.

Adsorption Isotherms

To study the adsorption process of inhibitor, different adsorption isotherms viz. Langmuir adsorption isotherm, Freundlich adsorption isotherm, Temkin adsorption isotherm were drawn by using the following equations (8), (10) and (11)

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \qquad (6)$$

Rearranging the above equation

$$\frac{\theta}{1-\theta} = K_{ads} \, . \, C_{inh} \qquad (7)$$

$$\log\left(\frac{\theta}{1-\theta}\right) = \log\left(K_{ads}\right) + \log\left(C_{inh}\right) \qquad (8)$$

Where θ is the degree of surface coverage and is equal to IE%/100, K_{ads} is the equilibrium constant of adsorption in (ml^{-1}L), (Cinh/ θ) is the inhibitor bulk concentration in (ml L^{-1}).

Freundlich isotherm is given by the following equations.

$$\theta = K_{ads} \, . \, C_{inh} \qquad (9)$$

$$\log \theta = 1\text{og}(K_{ads}) + \text{n} \log(C_{inh}) \qquad (10)$$

Where θ<n<1, θ and Kads is the equilibrium adsorption constant and Cinh is the inhibitor concentration in ml/L. Temkin adsorption is given by the following equation.

$$-2a\theta = 1\text{og}(K_{ads}) + \log(C_{inh}) \qquad (11)$$

Dtermination of Adsorption Parameters

Gibbs Energy ΔGads

Different adsorption parameters Gibbs energy of adsorption (ΔGads), enthalpy of adsorption (ΔHads), entropy of adsorption (ΔSads) were calculated by following equations (13), (14) and (15) respectively.

$$K_{ads} = \frac{1}{C} \exp\left(\Delta G_{ads}/RT\right) \qquad (12)$$

It can be written as

$$\Delta G_{ads} = -2.303RT \log (K_{ads}. C_{H_2O}) \tag{13}$$

Where Kads is the equilibrium adsorption constant calculated from Langmiur adsorption isotherm C_{H_2O} is the concentration of water in (1000 ml/L). ΔGads is Gibbs energy change in adsorption process. R is universal gas constant and T is the temperature in Kelvin.

Enthalpy of Adsorption(ΔHads) and Entropy of Adsorption (ΔSads)

Enthalpy and entropy of adsorption (ΔSads) are calculated by the following equation (14)

$$\Delta G_{ads} = \Delta H_{ads} - T\Delta S_{ads} \tag{14}$$

Where ΔHads is enthalpy of adsorption process, ΔSads is entropy of adsorption process and ΔGads is Gibbs energy of adsorption.

Chapter 3: Observations and Results

This chapter contains all observations and results in tabular and graphical forms for corrosion studies of mild steel in selected media. These tables show the data of calculated corrosion rates, inhibition efficiencies, kinetic parameters, thermodynamic activation parameters and adsorption parameters in absence and presence of corrosion inhibitors. The graphs include Arrhenius plots, various adsorption isotherms, transition state plots, plots between logarithm of corrosion rates and logarithm of concentrations of inhibitors etc. for various parts of plant extracts taken for study.

Chapter 4: Discussions on findings and conclusions

This chapter includes interpretation of findings. Obtained results revealed that corrosion rate generally increases with temperature and decreases with increase in concentration of inhibitor. Moreover inhibition efficiencies also increase with increase in inhibitor concentrations. Mechanisms of inhibition at mild steel surface are explained and discussed by various adsorption isotherms and Arrhenius plots.

1. Results showed that AEZJL, AEZJS, AEZJF and AEZJR are observed good corrosion inhibitors for mild steel in 1M HCl solution under experimental conditions chosen. The comparative effectiveness of the four parts of the plant *Ziziphus jujuba* in corrosion inhibition is in order AEZJL, AEZJS, AEZJF and AEZJR.ie. AEZJL is observed most effective and AEZJR is observed least effective under experimental conditions chosen.

2. Corrosion rates increase with increase in temperature and decrease with increase in inhibitor concentration.

3. Inhibition efficiency increases at lower temperature this suggests the physiorption of inhibitor on mild steel surface.

4. Apparent activation energy increases with increase in inhibitor concentration, this also suggests physiorption.

5. Enthalpy of adsorption comes out negative which shows exothermic and physical adsorption process of inhibitors on mild steel surface.

6. The values of Gibbs free energies calculated were negative showing spontaneity of corrosion inhibition process of mild steel in 1M HCl in all inhibitors chosen viz AEZJL, AEZJS, AEZJF and AEZJR.

Systematic alphabetically arranged bibliography is given at the end of thesis.

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CORROSION INHIBITION OF MILD STEEL WITH AQUEOUS EXTRACT OF ZIZIPHUS JUJUBA ROOTS IN 1M HCl SOLUTION

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ABSTRACT

The inhibition of mild steel (MS) in 1 M HCl solution with aqueous extract of Ziziphus Jujuba roots (AEZJR) was studied by weight loss method at 303-333K temperatures. It was found that inhibition efficiency increased with increase in concentration of extract and decreased with increase in temperature. Maximum 62.68% inhibition efficiency was observed at 303 K and at 8% (v/v) concentration of extract. Adsorption of extract at mild steel surface follows Langmuir adsorption isotherm. Physiorption is proposed by the values of Gibbs free energy, variation in inhibition energy with temperature and with activation energy values trend. Negative values of Gibbs energy reveals the spontaneity of inhibition process in extract at studied temperatures.

KEYWORDS: ***Ziziphus Jujuba*** roots, Corrosion, Langmuir adsorption isotherm, Mild steel, Weight loss method.

1. INTRODUCTION

Mild steel is generally used in structural industries. It is also used in transport and mechanical industries. Although it is common metal alloys to use in various industries but it have a major problem which is corrosion. Corrosion is the degradation of metal and their alloys by an electrochemical reaction and environment. The introduction of corrosion inhibitors is the best way to prevent metallic corrosion and save the great economic loss of country (48, 49)

Generally many chemical compounds is used for corrosion inhibitors but they are toxic and expansive. Green inhibitors are generally extracts of various part of plant. Which is eco friendly non toxic and low cost. They have great corrosion inhibitor property. So they are widely used as corrosion inhibitors for metal and it's alloys in acidic, basic and neutral medium.

Literature survey reveals various plant extracts that have been used as corrosion inhibitors for protection of different metals and their alloys. Extract of fenugreek seeds and roots[18],essential oils of *Menthaspicata, Lavandul amultifida, Pulicari amauritanica* [6,37,38] *Azadirachta indica*[24,27], extract of *Ananascomosus L.*[9], *Embilicaofficinalis*[26], *Garcinacola and Cola nitida*[8], *Nerium olender leaves* [48], *Calotropis procera* [49] etc. have been studied. In the continuity of above corrosion inhibition studies, the present work reveals the adsorption behavior and corrosion prevention properties of aqueous extract of roots of ***Ziziphus Jujuba*** for mild steel in 1 M HCl solution.

2. MATERIALS AND METHODS

Preparation of extract

The roots of *Ziziphus Jujuba* plant were taken, washed and air dried for 6-7 days, crushed and grind mechanically. 20 g of ground roots were heated in 200 ml distill water for one hour using air condenser at 70^{0}C - 80^{0}C. This extract was left overnight and then filtered and make up to 200 ml with distill water for the experiment.

Selection of steel specimens

Rectangular mild steel specimens of 5 cm length and 1 cm width were taken and abraded with a series of emery papers, degreased with acetone, washed with distill water, dried and constant weight was recorded by electronic balance.

Solution Preparation

1M HCl solution was prepared by 37% HCl (Merk Ltd.) using distill water. The employed concentration range of aqueous extract of *Ziziphus Jujuba* roots (AEZJR) was 1% to 8% (v/v).

Gravimetric Measurement

Gravimetric method is widely used method because of its reliability and simplicity in corrosion inhibition experiments. For each experiment 100 ml test solutions were taken in250 ml beaker and Rectangular specimen was immersed in it with plastic thread for one hour.

The experiments were carried out at different temperatures ranges from 303 K to 333K in thermostatic water bath. After one hour specimens were removed, washed with distill water, acetone dried and abraded with series of emery papers and then weighted accurately with electronic balance. It was noted that the surfaces of specimens became more rough in test solutions without the inhibitor than the surfaces of specimens which were immersed in test solutions containing different concentrations of inhibitor.

3. RESULT AND DISCUSSION

3.1 Corrosion rates

Corrosion rates were calculated by following equation (1).[**1, 34]**

$$C\,R\ (g\ cm^{-2} min^{-1}) = (W_1 - W_2/At) \qquad \textbf{(1)}$$

Where CR is corrosion rate, W1 is weight of mild steel specimen without inhibitor andW_2 is weight loss of mild steel specimen with inhibitor, A is area of MS specimen and t is immersion time. **Table1** shows that corrosion rates of mild steel decrease with increase in concentration of AEZJR inhibitor at all studied temperatures. This could be subjected to the adsorption of the phyto-constituents of inhibitor molecules with increase in concentration of inhibitor. The corrosion rate obeys Arrhenius type reaction, as it increases with rise in temperature.**[19]**

3.2 Inhibition efficiency

From the obtained corrosion rates, inhibition efficiencies were calculated by using following equation **(2).[1, 34]**

$$\mathbf{IE\% = \frac{CR_{blank} - CR_{inh}}{CR_{blank}} \times 100} \qquad (2)$$

Where CR_{blank} is the corrosion rate in absence of inhibitor and CR_{inh} is corrosion rate in presence of inhibitor. AEZJR are given in **Table 1.** Data in **Table1** show that %IE increase with increase in extract concentration, which is an indication of an increase in number of components of extract adsorbed on mild steel surface, which block the active sites of metal from acid attack and protect the metallic corrosion.**[20]** Further the decrease in % I.E. with rise in temperature suggests electrostatic interaction (physical adsorption) of the extract molecules on mild steel surface. This further indicates desorption of adsorbed inhibitor species at higher temperatures and metal dissolution takes place.**[35]** 62.68% inhibition efficiency is observed at 8% (v/v) concentration of inhibitor.

Table 1 Mild steel corrosion rates in 1 M HCl solution in absence and presence of different concentrations of AEZJR at different temperatures

C_{inh}in (v/v)%	CR x 10^{-3} (g cm^{-2} min^{-1})			
	303 K	313 K	323 K	333 K
0	0.67	1.33	2.27	3.04
1	0.56	1.24	2.13	2.82

2	**0.37**	**1.1**	**1.89**	**2.74**
3	**0.35**	**0.94**	**1.86**	**2.69**
5	**0.29**	**0.85**	**1.81**	**2.61**
8	**0.25**	**0.69**	**1.59**	**2.53**

Table 2 Inhibition efficiencies of AEZJR at different concentrations and temperatures in 1 M HCl solution

C_{inh}in (v/v)%	**I E (%)**			
	303 K	**313 K**	**323 K**	**333 K**
1	**16.42**	**6.77**	**6.17**	**7.24**
2	**44.78**	**17.29**	**16.74**	**9.87**
3	**47.76**	**29.32**	**18.06**	**11.51**
5	**56.72**	**36.09**	**20.26**	**14.14**
8	**62.69**	**48.12**	**29.96**	**16.78**

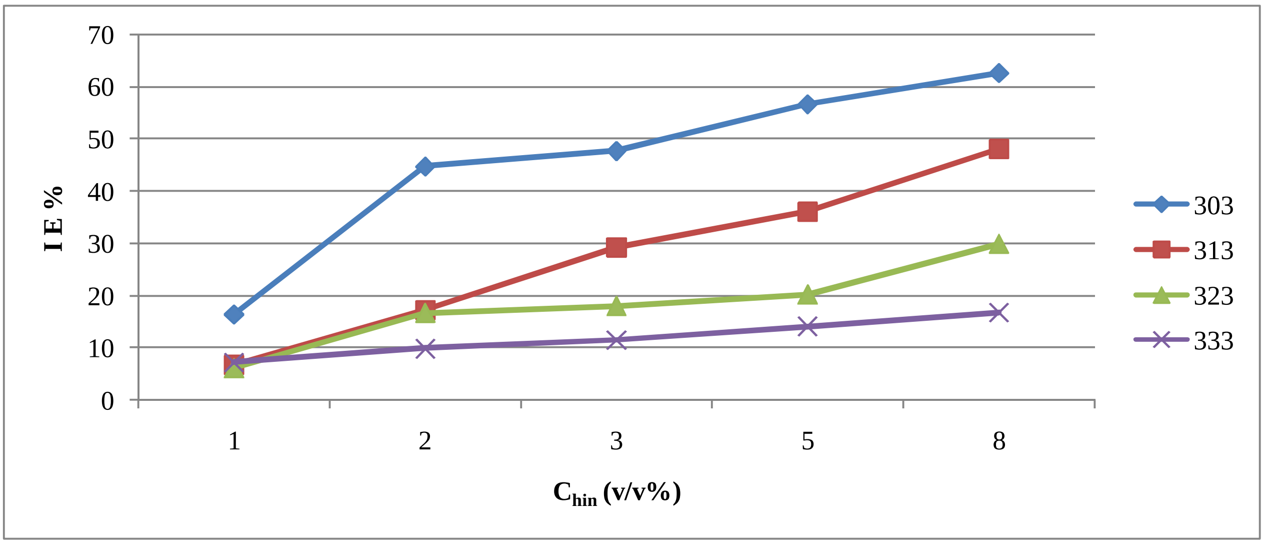

Figure1. Variation in I E % for mild steel corrosion in 1M HCl at different concentration of AEZJR at different studied temperatures

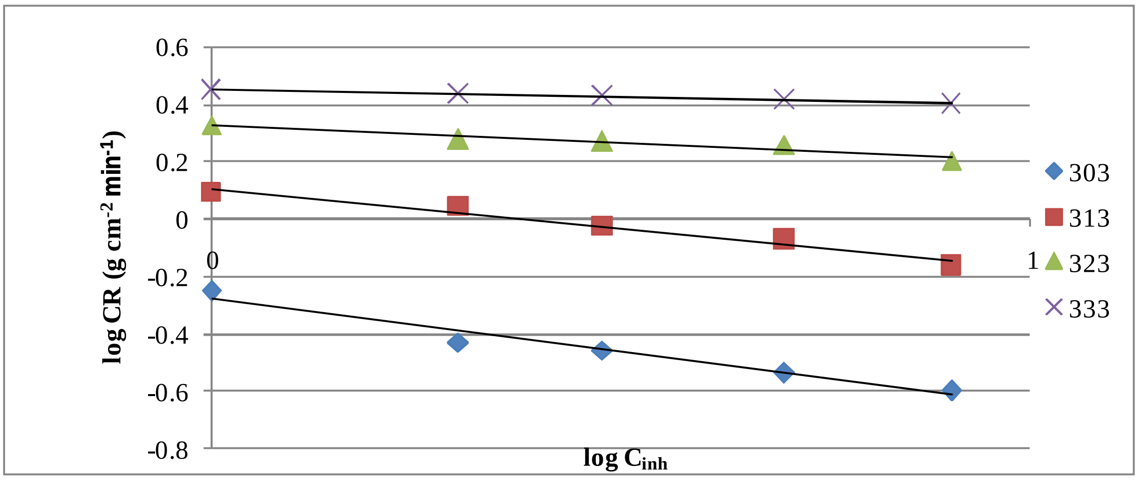

Figure2. Variation in log CR with log C_{inh} for mild steel corrosion in 1M HCl in presence of different concentration of AEZJR at various studied temperatures

3.3 KINETIC PARAMETERS

Assuming that corrosion rates of steel specimens against concentration of inhibitor obeys kinetic relationship as equation (3).**[19,38]**

$$\log CR = \log K + B \log C_{inh} \qquad (3)$$

Where K is rate constant and equal to CR when inhibitor concentration is unity. B is reaction constant which is measure of inhibitor effectiveness and C_{inh} is the concentration v/v %(ml/100ml) of AEZJR. Figure 2 represents plot between log CR and log C_{inh} values at various studied temperatures. B and K were calculated by slope and intercept of straight lines obtained in Figure 1. The obtained results are summarized in **Table 3** which can be discussed as follows**[19]** Negative values of B indicate that corrosion rate is inversely proportional to concentration of inhibitor. In other words the corrosion rates decrease with increase in concentration of inhibitor species. The high negative values of B reflects good inhibitive property of inhibitor High negative value of B can be observed as steep slope in graph (Fig.2).Value of B is high at lower temperatures, indicates that inhibitive species is more effective at comparatively lower temperatures. The increase in K values with increase in temperature, indicating the increase in corrosion rates with temperatures.

Table3. Kinetic parameters for mild steel corrosion in 1 M HCl solution with AEZJR

Temperature (K)	**Kinetic Parameters**	
	B	**K x 10^{-3} (g cm^{-2} min^{-1})**
303 K	**-0.372**	**0.52723**
313 K	**-0.278**	**1.279381**
323 K	**-0.124**	**2.118361**

333 K	-0.052	2.831392

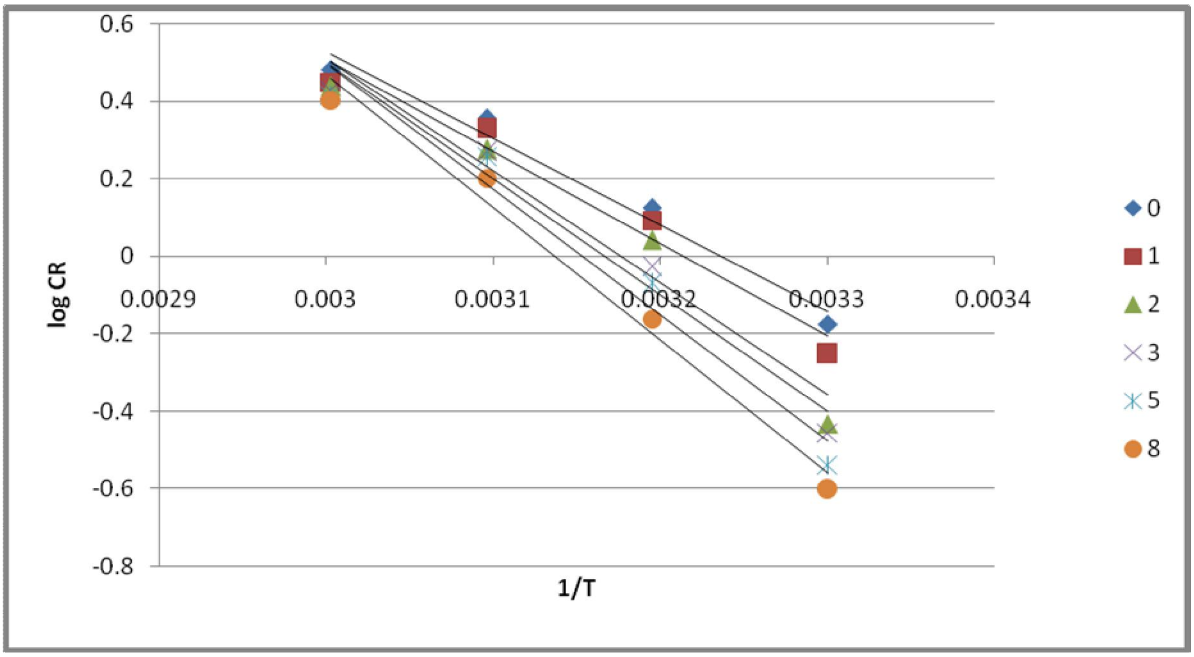

Figure3. Arrhenius plots for mild steel corrosion in 1M HCl in absence and presence of various concentration of AEZJR

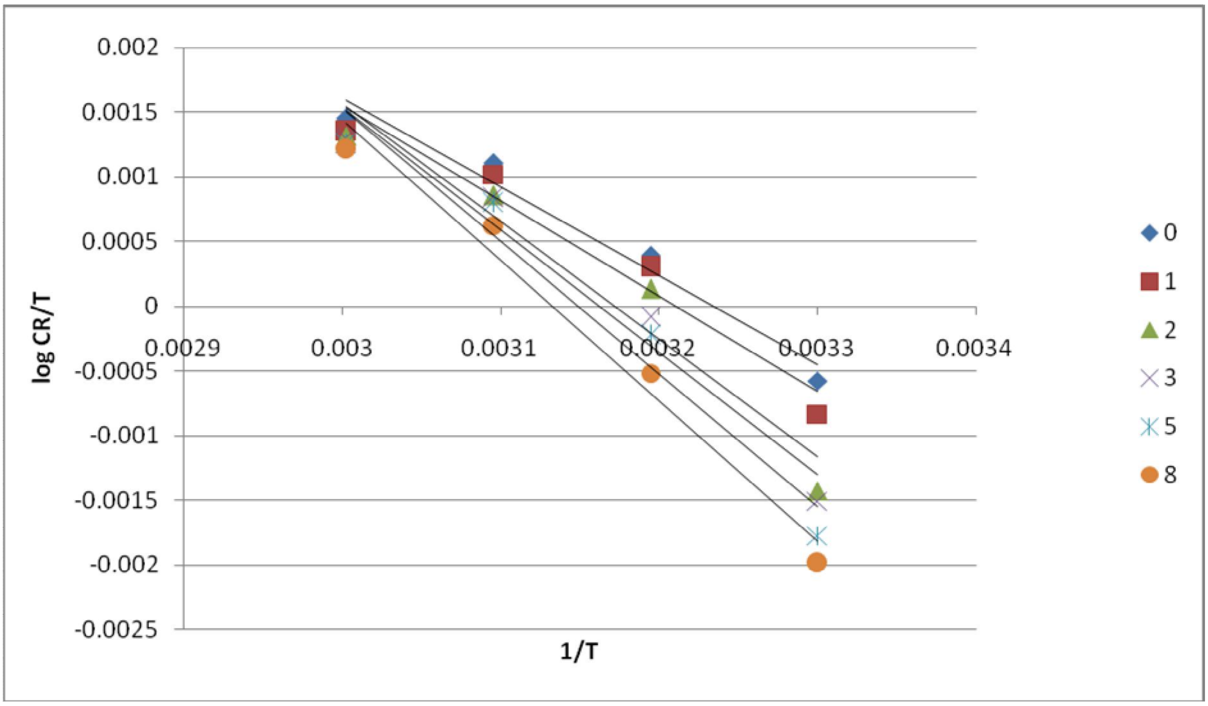

Figure4. Transition-state plots for mild steel corrosion in 1M HCl in absence and presence of various concentration of AEZJR

3.4 THERMODYNAMIC AND ACTIVATION PARAMETERS

Thermodynamic and activation parameters like apparent activation energy E_{act}, enthalpy of activation ΔH^*entropy of activation ΔS^* were calculated for steel dissolution process. Activation energy E_{act} were calculated by following Arrhenius equation (4)**[34,35]**

$$\log CR = \log A - \frac{E_{act}}{2.303RT}) \qquad (4)$$

Where A is Arrhenius pre-exponential factor, E_{act} is activation energy, R is universal gas constant, T is absolute temperature. The slope of log CR vs 1/T in Figure 3 gives the values of activation energies at studied concentrations. **Table 4** represents the calculated data of activation energies. The values of activation energies in presence of inhibitor were found higher than in uninhibited solution. This indicates the formation of higher energy barrier in corrosion reaction by inhibitor molecules. The increase in E_{act} for corrosion process in inhibitor solution further interpreted as physical adsorption of inhibitor species on mild steel surface.[16, **23, 25]** Besides this According to Damaskin[**47]**, the value of activation energy lesser than 80kJ/ mol and even smaller than 5kJ /mol represents physical adsorption. This assertion supports the experimental results obtained in the present study. The values of enthalpy of activation ΔH^* and entropy of activation ΔS^* were calculated by following transition state equation (5).[34,35]

$$\log_{(CR/T)} = [\log_{(R/Nh)} + [\Delta S^*/2.303RT - [\Delta H^*/2.303RT)]$$

Where h is planck's constant, N is Avogadro number R is the gas constant A plot of log(CR/T) vs 1/T gave a straight line with slope of $(-\Delta H^*/2.303R)$ and intercept of $[(\log R/Nh) + (\Delta S^*/2.303\ R)]$ from which the values of ΔH^* and ΔS^* were calculated (see Figure 4). These values are tabulated in **Table 4**. Values of ΔH^*were found positive. Positive values indicate endothermic nature of steel dissolution process.**[1, 17, 35]** Endothermic process further indicates that mild steel dissolution reduces at lower temperatures and increases with increase in temperatures. Negative values of ΔS^* are indicative of formation of activated complex in rate determining step, which represents association rather than dissociation step, meaning the decrease in disorder takes place on going from reactants to activated complex.[1**, 11, 30]**It is also observed from data in **Table 4** that E_{act} and ΔH^* vary in the same manner. Values of both E_{act} and ΔH^* increase with increase in concentration of inhibitor, suggesting that energy

barrier is increases with increase in inhibitor concentration. This means that corrosion reaction will further be pushed to surface sites that are characterized by progressively higher values of E_{act} as the concentration of inhibitor becomes greater.[1**, 29, 31]**The values of activation energy were found larger than corresponding values of enthalpy of activation, indicate the involvement of a gaseous reaction, simply hydrogen evolution in corrosion process, associated with a decrease in total reaction volume.[**19**]

Table 4. Activation and thermodynamic parameters for mild steel corrosion in 1 M HCL solution with AEZJR

C_{inh}in (v/v)%	**E_{act}(kJ/mol)**	**ΔH^* (kJ/mol)**	**ΔS^* (J/mol/K)**
0.0	**42.72**	**39.88**	**-177.64**
1.0	**45.46**	**42.80**	**-170.56**
2.0	**55.28**	**52.72**	**-143.63**
3.0	**57.35**	**54.80**	**-137.55**
5.0	**61.98**	**59.47**	**-130.48**
8.0	**65.50**	**63.03**	**-118.53**

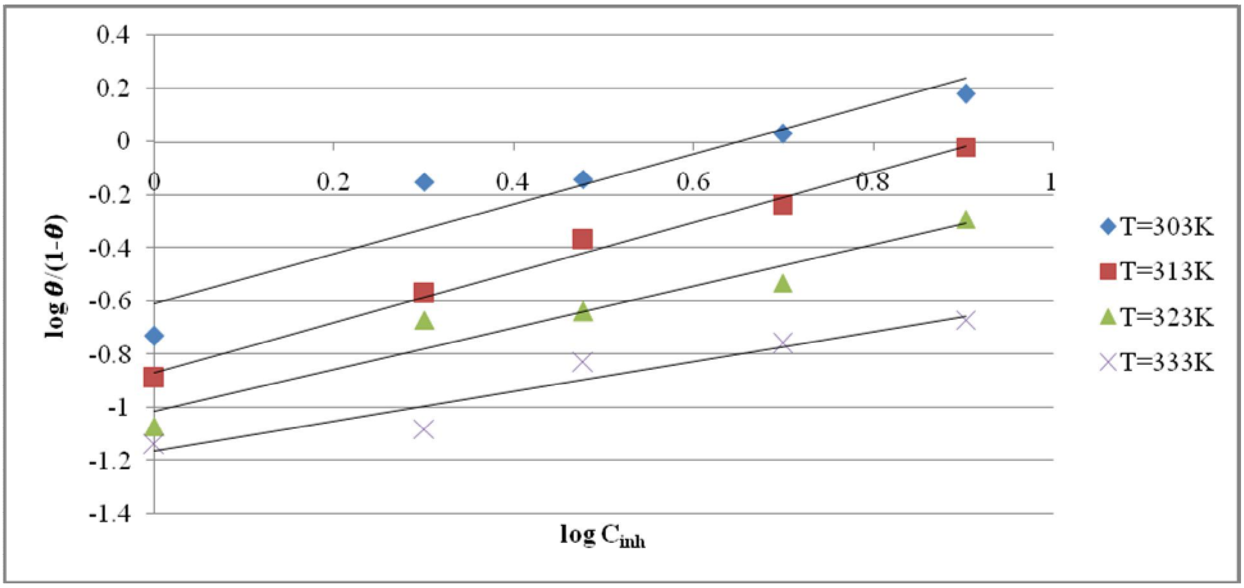

Figure5. Langmuir adsorption isotherms of AEZJR on mild steel surface in 1M HCl at different studied temperatures30°

3.5. ADSORPTION ISOTHERM AND GIBBS ENERGY

The nature of adsorption can be explained by understanding the process at metal/electrolyte interface. Further to understand the nature of adsorption, obtained surface coverage θ were fitted in different adsorption isotherms. Langmuir adsorption isotherm was the best fit. The mathematical expressions for Langmuir adsorption isotherm can be expressed by the
following equation.**[10,40,42- 44]**

$$\frac{C}{\theta} = \frac{1}{Kads} + \mathbf{C_{inh}} \qquad \textbf{(6)}$$

Rearranging the above equation (6) we get

$$\frac{\theta}{1-\theta} = \mathbf{K_{ads}C_{inh}} \qquad \textbf{(7)}$$

$$\mathbf{log\ (\frac{\theta}{1-\theta}) = logK_{ads} + logC_{inh}} \qquad \textbf{(8)}$$

Where K_{ads} is the equilibrium constant of adsorption, θ is the surface coverage, (1-θ) is the uncovered surface, C_{inh} is the concentration of inhibitor. Values of K_{ads} were calculated from the intercept of Langmuir adsorption isotherm drawn according to the equation (8) between log (θ /1- θ) and log C_{inh} (see Figure 5). The value of K_{ads} obtained from Langmuir adsorption isotherm is related to Gibbs energy according to the following equation (9)**[19, 38]**

$$\mathbf{K_{ads} = 1/C_{H2O}exp^{(-\Delta\ G/RT)}}$$

It can be written as:

$$\Delta\ G_{ads} = -\ 2.303\ RT\ \log\ (Kads.\ CH_2O) \qquad (10)$$

Where CH_2O is the concentration of water in (ml / L) at metal/ solution interface, R is universal gas constant and T is absolute temperature. The values of ΔG_{ads} were tabulated in **Table 5**. Obtained values of Gibbs energy were plotted against temperature in accordance with the following basic equation.[**19,39]**

$$\Delta G_{ads} = \Delta H_{ads} - T\Delta S_{ads} \qquad (11)$$

Intercept of graph between ΔG_{ads}vs T in Figure 7 gives value of ΔHads and by putting the value of intercept in equation (11) values of ΔS_{ads} were obtained. These obtained adsorption parameters Gibbs free energy of adsorption (ΔG_{ads}), enthalpy of adsorption (ΔH_{ads}) and entropy of adsorption (ΔS_{ads}) are listed in **Table 5.** ΔG_{ads} values has been found negative atall studied temperatures indicating spontaneous adsorption process of inhibitor molecules onmetal surface.[**1,4,5,7,19,28]** Generally values of ΔG_{ads} upto -20 KJ/mol are consistent with electrostatic interactions (physical adsorption) between charged molecules and charged metal surface and values upto -40 KJ/mol or higher involve charge sharing or transfer from inhibitor molecules to metal surface to form coordinate type of bond (chemical adsorption).[1,**4, 5, 12, 13, 21, 22, 33]** The obtained values of ΔG_{ads} were found less than -20kJ/mol indicated physical adsorption of inhibitor molecules. It has been observed that adsorption of negatively charged species is facilitated due to the positively charged metal. But positively charged species can also be adsorbed and protect the positively charged metal surface acting with a negatively charged intermediate such as acid anions, adsorbed on metal surface.[**1, 25, 33]**
Values of ΔH_{ads} has been found negative indicating the exothermic adsorption process[**11,14,16,20,34]** which further indicates lower %IE at higher temperatures, due to desorption of inhibitor molecules. The exothermic process is attributed to either physical or chemical adsorption or mixture of both.**[3]** In exothermic process, values of ΔH_{ads} predict physiorption or chemisorption. For physiorption values of ΔH_{ads} is lower than 40kJ/mol while for chemisorption it approaches to 100kJ/mol.[**36,2]** Values of ΔH_{ads} in **Table 5** indicate physiorption. Negative values of ΔS_{ads} indicate decrease in entropy of adsorption process. This behavior can be explained as follows: Before the adsorption of inhibitor molecules onto mild steel surface, they might freely move in bulk solution (inhibitor molecules were chaotic). But with the process of adsorption, inhibitor molecules were orderly adsorbed onto the steel surface as a result decrease in entropy is observed.[**13]** A more interesting behavior is observed in **Table 5** that negative ΔH_{ads} value is accompanied with negative ΔS_{ads} value. This further agrees that when the adsorption is an exothermic process, it must be accompanied by a decrease in the entropy change and vies versa.[**20,35]**The obtained positive values of ΔS_{ads} are the algebraic sum of the adsorption of organic molecules and the desorption of water molecules.[**15, 46]** Therefore the positive values of entropy of adsorption is the result of the substitution process, which can be attributed to the increase in the solvent entropy and more positive water desorption entropy.[**45]**

Table 5 Adsorption parameters for mild steel corrosion in 1 M HCl solution with AEZJR

Temperature (K)	**ΔG_{ads} (kJ/mol)**	**ΔH_{ads} (kJ/mol)**	**ΔS_{ads} (J/mol/K)**
303 K	**-7.84794**	**-35.08**	**-89.8748**
313 K	**-7.05217**		**-89.5458**
323 K	**-5.7499**		**-90.8053**
333 K	**-5.28394**		**-89.4777**

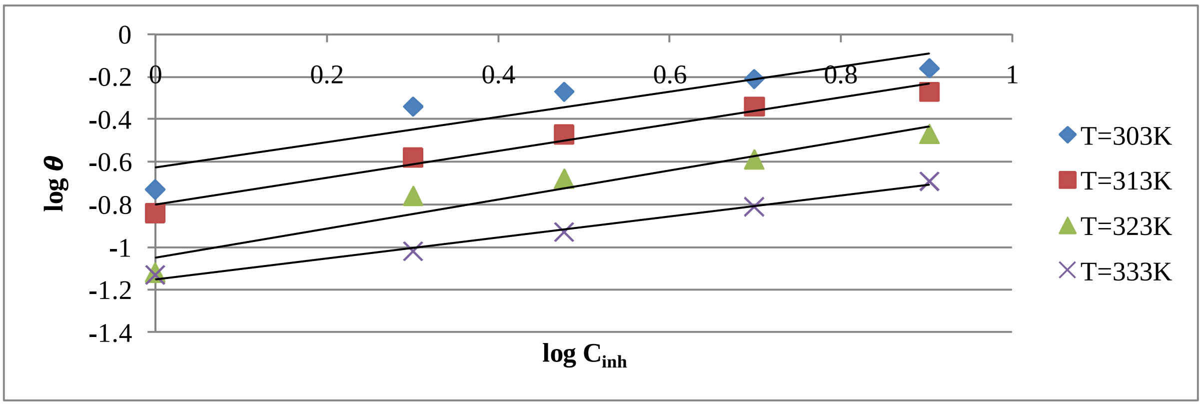

Figure6. Freundlich adsorption isotherms of AEZJR on mild steel surface in 1M HCl at different studied temperatures

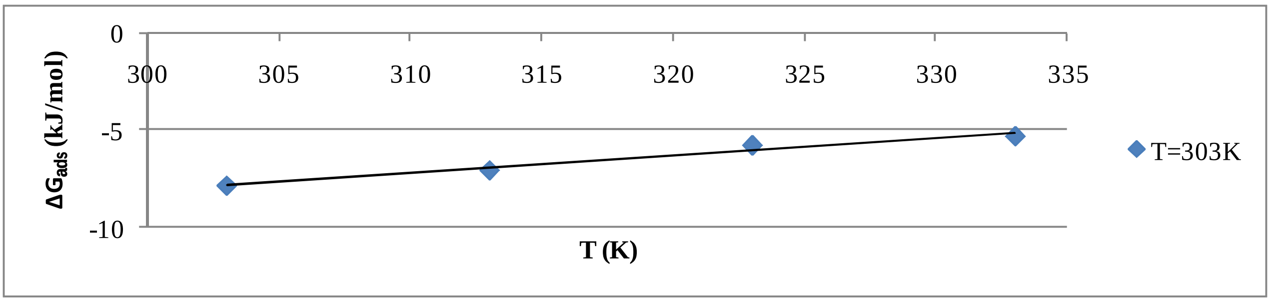

Figure7. The Variation of ΔG_{ads}(kJ/mol) with T (K) for mild steel corrosion in 1M HCl solution with AEZJR

4. CONCLUSIONS

1. Result showed that AEZJR is good corrosion inhibitor for mild steel in 1M HCl solution.
2. Corrosion rates increase with increase in temperature and decrease with increase in inhibitor concentration.
3. Inhibition efficiencies increases at lower temperature suggest the physiorption process of inhibitor on mild steel surface.
4. Apparent activation energy increases with increase in inhibitor concentrations also suggests pysiorption.
5. Enthalpy of adsorption comes out to be negative and lower than 40kJ/mol, which shows exothermic and physical adsorption process of inhibitor.
6. The values of Gibbs free energies calculated were negative shows spontaneity of corrosion inhibition process of mild steel in 1 M HCl in AEZJR.

5. ACKNOWLEDGEMENT

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Research Article

Thermodynamic Study of Green Corrosion Inhibitor on Mild Steel with Aqueous Extract of *Ziziphus Jujuba* Stem and Fruits in 1M HCl Solution

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Abstract

The Corrosion inhibition of mild steel in 1 M HCl solution with aqueous extract of *Ziziphus Jujuba stem* and *Ziziphus Jujuba fruits* is studied by weight loss method at 303-333K temperatures. It is found that inhibition efficiency rise with increase in concentration of extract and decreased with rise in temperature. Maximum 78.05% inhibition efficiency was observed at 303 K and 8% (v/v) concentration of *Ziziphus Jujuba stem*. While maximum 68.60% inhibition efficiency was observed at 303 K and 8% (v/v) concentration of *Ziziphus Jujuba fruits*. Value observed for Activation energy, Gibbs free energy and variation in I.E. with temp Suggest physisorption. Adsorption of extract at mild steel surface follows Langmuir adsorption isotherm. Negative values of Gibbs energy reveals the spontaneity of inhibition process in extracts at studied temperatures.

Keywords:*Ziziphus Jujuba* stem, *Ziziphus Jujuba fruits*, Corrosion, Langmuir adsorption isotherm, Mild steel, Weight loss method

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Introduction

Mild steel has widespread use in industries such as chemical processing, petroleum, constriction, pipelines, mining, marine applications and refining. Although it is one of the common metal alloys used in various industries but it suffers a major problem which is corrosion. Corrosion is the degradation of metal and their alloys by an electrochemical reaction with environment. Corrosion of metals and alloys is a well studied industrial problem hence found a fertile research field in green chemistry also. The introduction of corrosion inhibitors is the best way to prevent metallic corrosion and save the great economic loss of country [1].

Generally many chemical compounds is used as corrosion inhibitors but most of these are toxic and expensive. Green inhibitors are generally extracts of various parts of plants. Plant extracts are low cost and environmental safe. So the main advantage of using plant extracts as corrosion inhibitors are economic and environment safe. They have great corrosion inhibitor property. So they are widely used as corrosion inhibitors for metals and alloys in acidic, basic and neutral media.

Literature survey reveals various plant extracts that have been used as corrosion inhibitors for protection of different metals and their alloys. Extract of fenugreek seeds and roots[2], essential oils of *Menthaspicata*, *Lavandulamultifida*, *Pulicariamauritanica*[3,4] *Azadirachtaindica*[5,6], extract of *Ananascomosus L.*[7], *Embilicaofficinalis*[8], *Garcinacola and Cola nitida*[9], *Neriumolender leaves*, *Calotropisprocera* etc. have been studied. In the continuity of above corrosion inhibition studies to find out better corrosion inhibitor, the present work has been carried out which reveals the adsorption behaviour and corrosion prevention properties of aqueous extract of stem & fruits of *Ziziphus Jujuba* for mild steel in 1 M HCl solution.

Materials and Methods

Preparation of Ziziphus jujuba stem

The stem of *Ziziphus Jujuba* plant were taken, washed and air dried for 6-7 days, crushed and grind mechanically. 20 g of stem powder was heated in 200 mL distilled water for one hour using air condenser at 70^0C - 80^0C. This extract was left overnight and then filtered and make up to 500 mL with distilled water for the experiment.

Preparation of Ziziphus jujuba fruits

The fruits of *Ziziphus Jujuba* plant were taken, washed and air dried for 6-7 days, crushed and grind mechanically. 20 g of fruits powder was heated in 200 mL distilled water for one hour using air condenser at 70^0C - 80^0C. This extract was left overnight and then filtered and make up to 500 mL with distilled water for the experiment.

Selection of steel specimens

Rectangular mild steel (grade 220) specimens of 5 cm length and 1cm width and 0.03cm thickness were taken and abraded with a series of emery papers, degreased with acetone, washed with distilled water, dried and constant weight was recorded by electronic balance.

Solution Preparation

1M HCl solution was prepared by 37% HCl (Merck Ltd.) using distilled water. The employed concentration range of aqueous extract of *Ziziphus Jujuba stem* and *Ziziphus Jujuba fruits* was 1% to 8% (v/v).

Gravimetric Measurements

Gravimetric method is widely used method because of its reliability and simplicity in corrosion inhibition experiments. For each experiment 100 mL test solution was taken in250 mL beaker and Rectangular specimen was immersed in it with plastic thread for one hour.

The experiments were carried out at different temperatures from 303 K to 333K in thermostatic water bath. After one hour specimens were removed, washed with distilled water, acetone dried and abraded with series of emery papers and then weighted accurately with electronic balance. It was noted that the surfaces of specimens became rougher in test solutions without the inhibitor than the surfaces of specimens which were immersed in test solutions containing different concentrations of inhibitor.

Result and Discussion

Corrosion rates

Corrosion rates were calculated by following equation [10,11**]**

$$C\ R\ (g\ cm^{-2}min^{-1}) = (W_1\text{-}W_2/At) \qquad (1)$$

Where CR is corrosion rate, W_1 is weight of mild steel specimen without inhibitor andW_2 is weight of mild steel specimen with inhibitor, A is area of MS specimen and t is immersion time. **Tables 1** and **2** shows that corrosion rates of mild steel decrease with rise in concentration of *Ziziphus Jujuba* stem and *Ziziphus Jujuba fruits* inhibitor at all studied temperatures. This could be subjected to the adsorption of the phyto-constituents of inhibitor molecules with increase in concentration of inhibitor. The corrosion rate obeys Arrhenius type reaction, as it increases with rise in temperature [12].

Table 1 Mild steel corrosion rates in 1 M HCl solution in absence and presence of different concentrations of *Ziziphus jujuba* STEM at different temperatures

C_{inh}in (v/v)%	**CR x 10^{-3} (g cm^{-2} min^{-1})**			
	30^{o}C	**40^{o}C**	**50^{o}C**	**60^{o}C**
0	0.82	1.41	2.11	2.78
1	0.59	1.21	1.87	2.65
2	0.42	1.03	1.64	2.49
3	0.37	0.91	1.47	2.37
5	0.27	0.78	1.31	2.21
8	0.18	0.66	1.22	2.15

Inhibition efficiency

From the obtained corrosion rates, inhibition efficiencies were calculated by using following equation (2).

$$IE\% = \frac{CR_{blank} - CR_{inh}}{CR_{blank}} \times 100 \qquad (2)$$

Where CR_{blank} is the corrosion rate in absence of inhibitor and CR_{inh} is corrosion rate in presence of inhibitor. *Ziziphus jujuba* stem and *Ziziphus jujuba fruits* data are given in Table 1 and 2show that %IE increase with in extract concentrationand indication that increase in number of components of extract adsorbed on mild steel surface, which block the active sites of metal from acid attack and protect the metallic corrosion [13]. Further the decrease in % I.E. with rise in temperature suggests electrostatic interaction (physical adsorption) of the extract molecules on mild steel surface. This further indicates desorption of adsorbed inhibitor species at higher temperatures and metal dissolution takes place.[14] 78.05% inhibition efficiency is observed at 8% (v/v) concentration of inhibitor *Ziziphus jujuba* stem while 68.60% inhibition efficiency is observed at 8% (v/v) concentration of inhibitor *Ziziphus jujuba* fruits.

Table 2 Mild steel corrosion rates in 1 M HCl solution in absence and presence of different concentrations of Ziziphus jujuba fruits at different temperatures

C_{inh}in	**CR x 10^{-3} (g cm^{-2} min^{-1})**			
(v/v)%	**30^oC**	**40^oC**	**50^oC**	**60^oC**
0	0.86	1.46	2.17	2.89
1	0.64	1.31	2.11	2.76
2	0.57	1.17	2.03	2.67
3	0.47	1.12	1.87	2.61
5	0.39	1.01	1.78	2.54
8	0.27	0.73	1.63	2.47

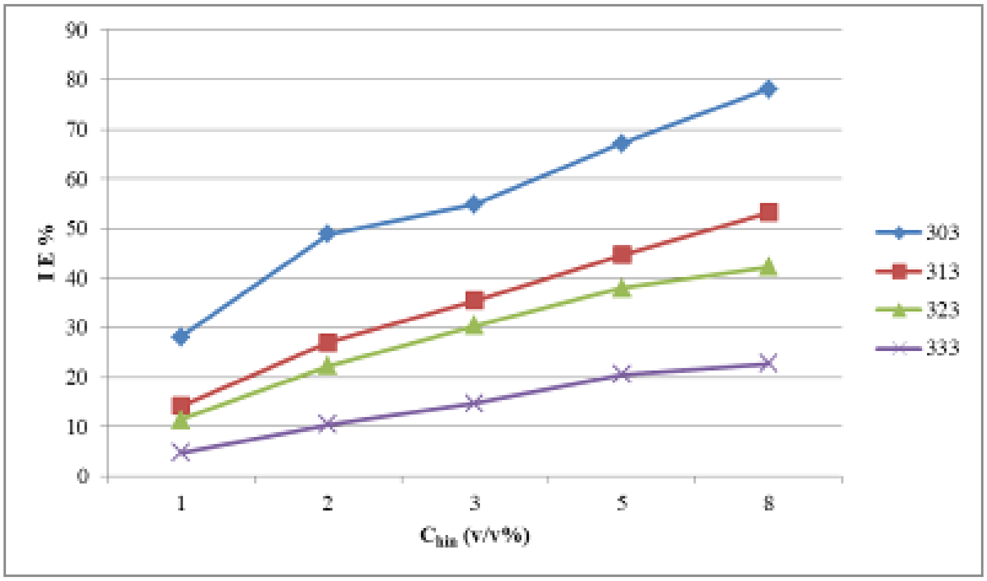

Figure 1 Variation in IE % for mild steel corrosion in 1M HCl at different concentrations of *Ziziphus jujuba* stem at different temperatures

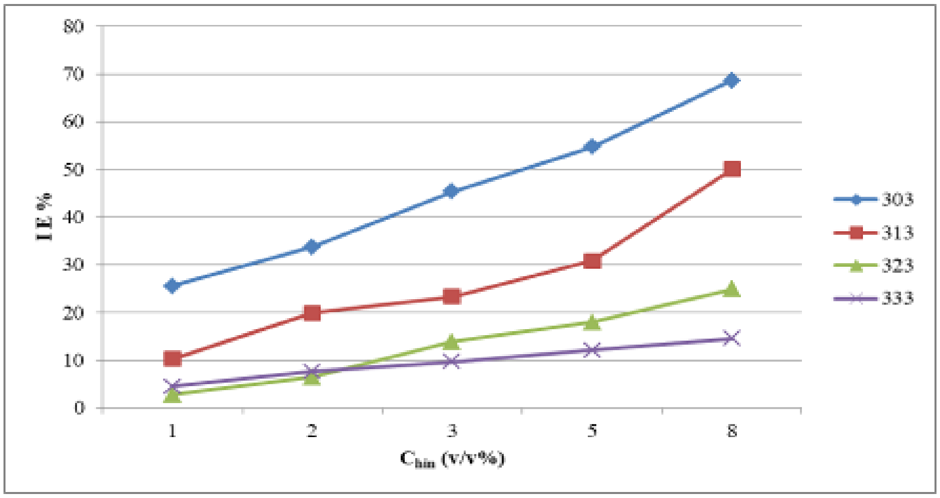

Figure 2 Variation in IE % for mild steel corrosion in 1M HCl at different concentrations of *Ziziphus jujuba* fruits at different temperatures

Table 3 Inhibition efficiencies of *Ziziphus jujuba* stem at different concentrations and temperatures in 1 M HCl solution

C_{inh}in (v/v)%	I E (%)			
	30°C	40°C	50°C	60°C
1	28.04	14.18	11.37	4.68
2	48.78	26.95	22.27	10.43
3	54.88	35.46	30.33	14.75
5	67.07	44.68	37.91	20.50
8	78.05	53.19	42.18	22.66

Table 4 Inhibition efficiencies of *Ziziphus jujuba* fruits at different concentrations and temperatures in 1 M HCl solution

C_{inh}in (v/v)%	I E (%)			
	30°C	40°C	50°C	60°C
1	25.58	10.27	2.764	4.49
2	33.72	19.86	6.45	7.61
3	45.34	23.28	13.82	9.68
5	54.65	30.82	17.97	12.11
8	68.60	50	24.88	14.53

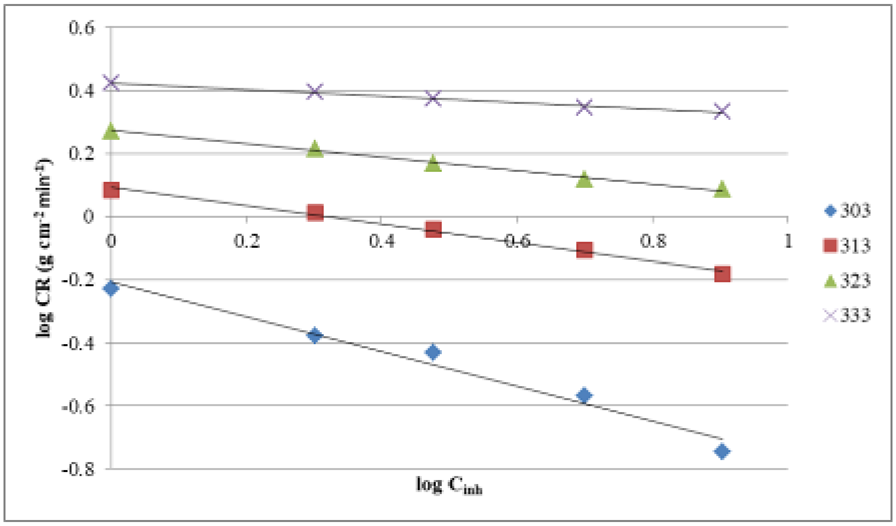

Figure 3 Variation in log CR with log C_{inh} for mild steel corrosion in 1M HCl in presence of different concentration of Ziziphus jujuba stem at various studied temperatures

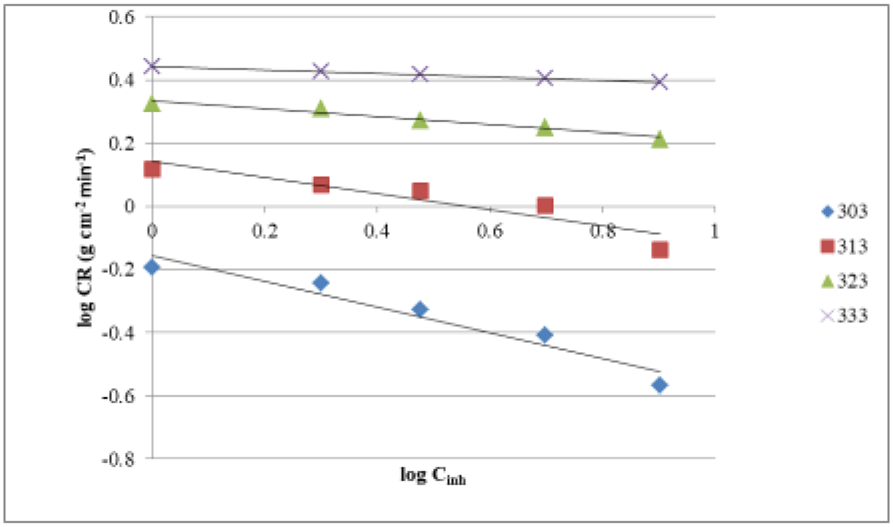

Figure4 Variation in log CR with log C_{inh} for mild steel corrosion in 1M HCl in presence of different concentration of *Ziziphus jujuba* fruits at various studied temperatures

Kinetic Parameters

Assuming that corrosion rates of steel specimens against concentration of inhibitor obeys kinetic relationship as equation (3)

$$\log CR = \log K + B \log C_{inh} \qquad (3)$$

Where K is rate constant and equal to CR when inhibitor concentration is unity. B is reaction constant which is measure of inhibitor effectiveness and C_{inh} is the concentration v/v% (mL/100mL) of *Ziziphus jujuba* stem and *Ziziphus jujuba* fruits. Figure 3 and 4are plots between log CR and log C_{inh} values at various studied temperatures. B and K were calculated by slope and intercept of straight lines obtained in **Figure 1** and **2**.The obtained results are summarized in **Table 3**and **4**which can be discussed as follows [24].Negative values of B indicate that corrosion rate is inversely proportional to concentration of inhibitor. In other words the corrosion rates decrease with rise in concentration of inhibitor species. The high negative values of B reflects good inhibitive property of inhibitor High negative value of B can be observed as steep slope in graph (**Figure 3** and **4**).Value of B is high at lower temperatures, indicates that inhibitive species is more effective at comparatively lower temperatures. The rise in K values with increase in temperature, indicating the rise in corrosion rates with temperatures.

Table 5 Kinetic parameters for mild steel corrosion in 1 M HCl solution with *Ziziphus jujuba* stem

Temperature (^{o}C)	**Kinetic Parameters**	
	B	**K x 10^{-3} (g cm^{-2} min^{-1})**
30^{o}C	-0.552	0.6209
40^{o}C	-0.291	1.2359
50^{o}C	-0.212	1.8707
60^{o}C	-0.105	2.6546

Table 6 Kinetic parameters for mild steel corrosion in 1 M HCl solution with *Ziziphus jujuba* fruits

Temperature (^{o}C)	**Kinetic Parameters**	
	B	**K x 10^{-3} (g cm^{-2} min^{-1})**
30^{o}C	-0.053	2.76058
40^{o}C	-0.125	2.15278
50^{o}C	-0.255	1.38676
60^{o}C	-0.407	0.70146

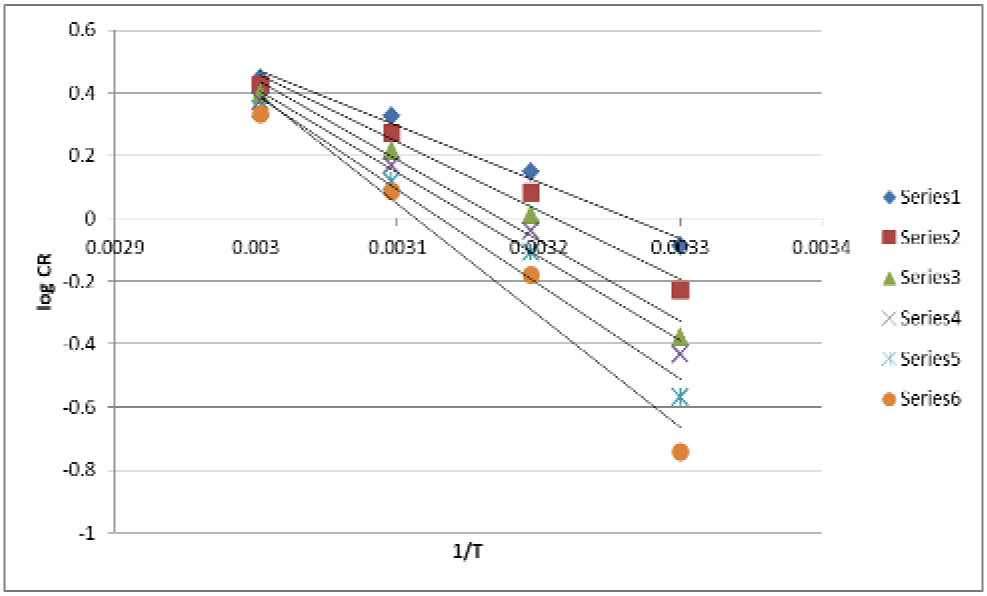

Figure 5 Arrhenius plots for mild steel corrosion in 1M HCl in absence and presence of various concentration of *Ziziphus jujuba* stem

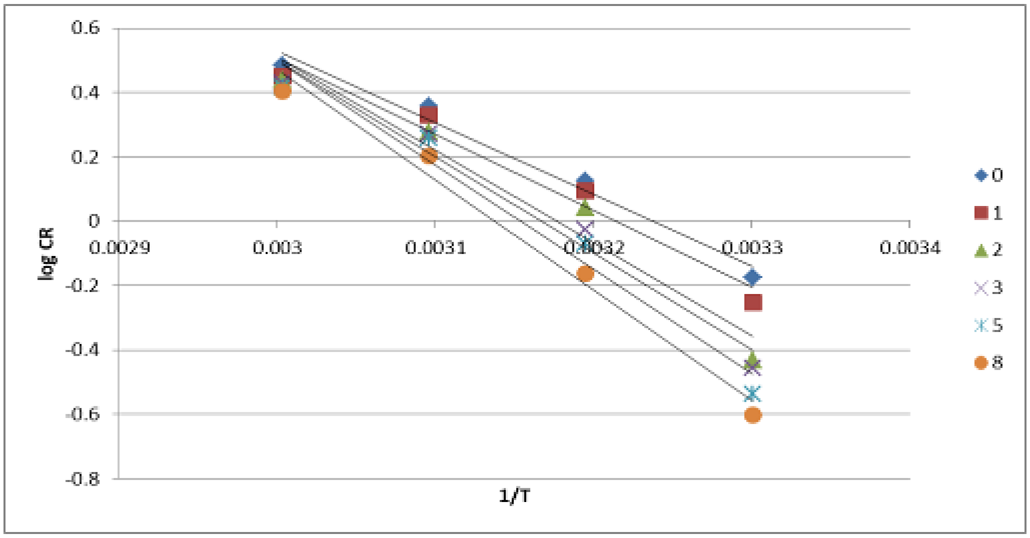

Figure6 Arrhenius plots for mild steel corrosion in 1M HCl in absence and presence of various concentration of *Ziziphus jujuba* fruits

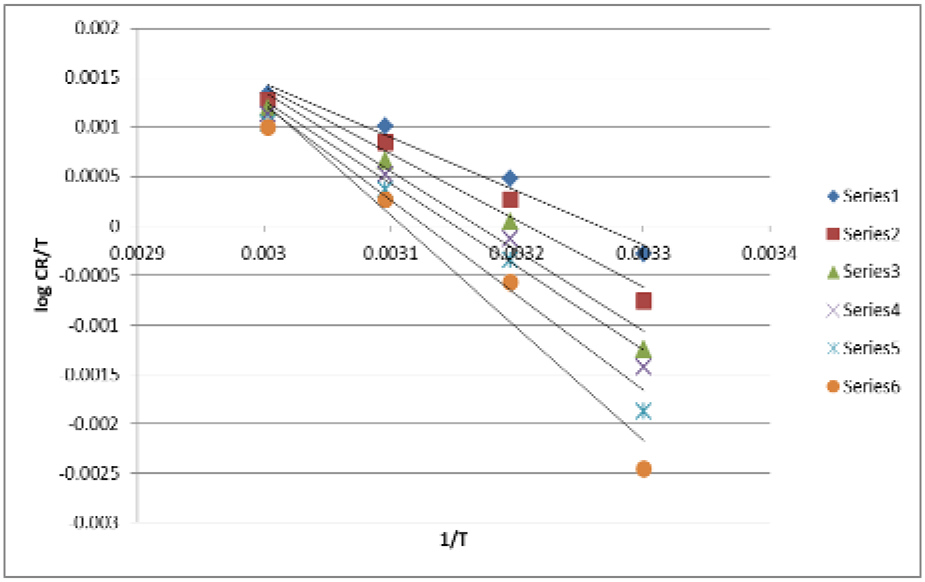

Figure 7 Transition-state plots for mild steel corrosion in 1M HCl in absence and presence of various concentrations of *Ziziphus jujuba* stem

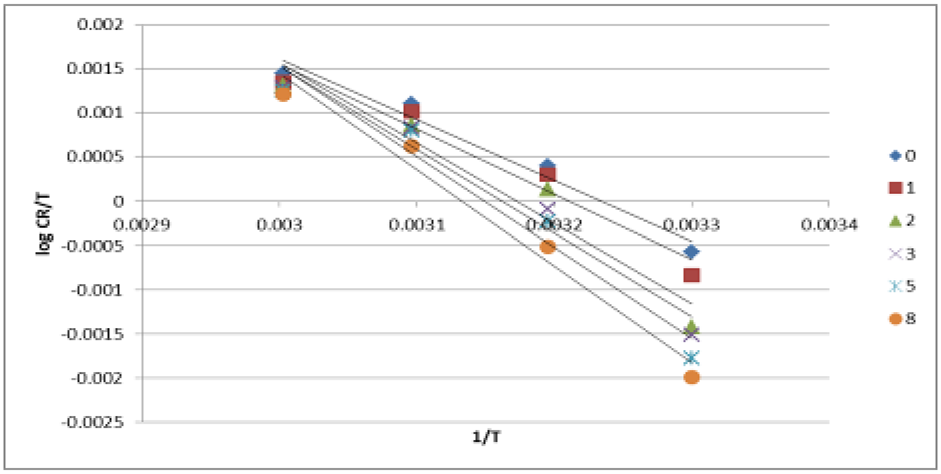

Figure 8 Transition-state plots for mild steel corrosion in 1M HCl in absence and presence of various concentrations of *Ziziphus jujuba* fruits

Thermodynamic and activation parameters

Thermodynamic and activation parameters like apparent activation energy E_{act}, enthalpy of activation Δ H*entropy of activation **Δ**S* can be calculated for steel dissolution process. Activation energies E_{act} were calculated by applying Arrhenius equation (4)

$$\log CR = \log A - \frac{Eact}{2.303RT} \qquad (4)$$

Where A is Arrhenius pre-exponential factor, E_{act} is activation energy, R is universal gas constant, T is absolute temperature. The slope of log CR vs 1/Tin **Figure 5** and **6** gives the values of activation energies at studied concentrations. **Table 7** and **8** contains the calculated data of activation energies. The values of activation energies in presence of inhibitor were found higher than in uninhibited solution. This indicates the formation of higher energy barrier in corrosion reaction by inhibitor molecules. The increase in E_{act} for corrosion process in inhibitor solution further interpreted as physical adsorption of inhibitor species on mild steel surface [15,16,17] Besides this According to Damaskin[18], the value of activation energy lesser than 80kJ/ mol and even smaller than 5kJ /mol represent physical adsorption. This assertion supports the experimental results obtained in the present study. The values of enthalpy of activation ΔH* and entropy of activation **Δ**S*can be calculated by following transition state equation (5).

$$\log(CR/T) = [\log(R/Nh) + [\Delta S^*/2.303R - [\Delta H^*/2.303RT\ )] \qquad (5)$$

Where h is plank's constant, N is Avogadro number R is the gas constant A plot of log(CR/T) vs 1/T gave a straight line with slope of (-ΔH*/2.303R) and intercept of [(log R/Nh) +(ΔS*/2.303 R)] from which the values of ΔH* and **Δ**S* can be calculated (**Figure 7** and **8**). These values are tabulated in Table 7 and 8. Values of ΔH*were found positive. Positive values indicate endothermic nature of steel dissolution process.[19] Endothermic process further indicates that mild steel dissolution reduces at lower temperatures and increases with in temperatures. Negative values of ΔS* are indicative of formation of activated complex in rate determining step, which further indicate association rather than dissociation step, meaning the decrease in disorder takes place on going from reactants to activated complex.[20,21]It is also observed from data in Table 7 and 8 that E_{act} and ΔH* vary in the same manner. Values of both E_{act} and ΔH* with in concentration of inhibitor, suggesting that energy barrier rise within inhibitor concentration .This means that corrosion reaction will further be pushed to surface sites that are characterized by progressively higher values of E_{act} as the concentration of inhibitor becomes higher [22,23]. The values of activation energy were found higher than corresponding values of enthalpy of activation, indicate the involvement of a gaseous reaction, simply hydrogen evolution in corrosion process, associated with a decrease in total reaction volume.

Table 7 Activation and thermodynamic parameters for mild steel corrosion in 1 M HCl solution with *Ziziphus jujuba* stem

C_{inh}in (v/v)%	**E_{act}(kJ/mol)**	**ΔH* (kJ/mol)**	**ΔS* (J/mol/K)**
0	34.22	31.64	-221.9
1	41.63	39.17	-182.12
2	48.92	46.64	-171.58
3	50.95	48.81	-138.46
5	57.52	55.54	-43.23
8	67.93	66.02	-43.23

Table 8 Activation and thermodynamic parameters for mild steel corrosion in 1 M HCl solution with *Ziziphus jujuba* fruits

C_{inh}in (v/v)%	**E_{act}(kJ/mol)**	**ΔH* (kJ/mol)**	**ΔS* (J/mol/K)**
0	33.93	31.25	-199.27
1	40.99	38.4	-186.02
2	43.69	41.17	-185.61
3	47.7	45.26	-144.85
5	52.2	49.81	-134.45
8	62.71	60.34	-126.74

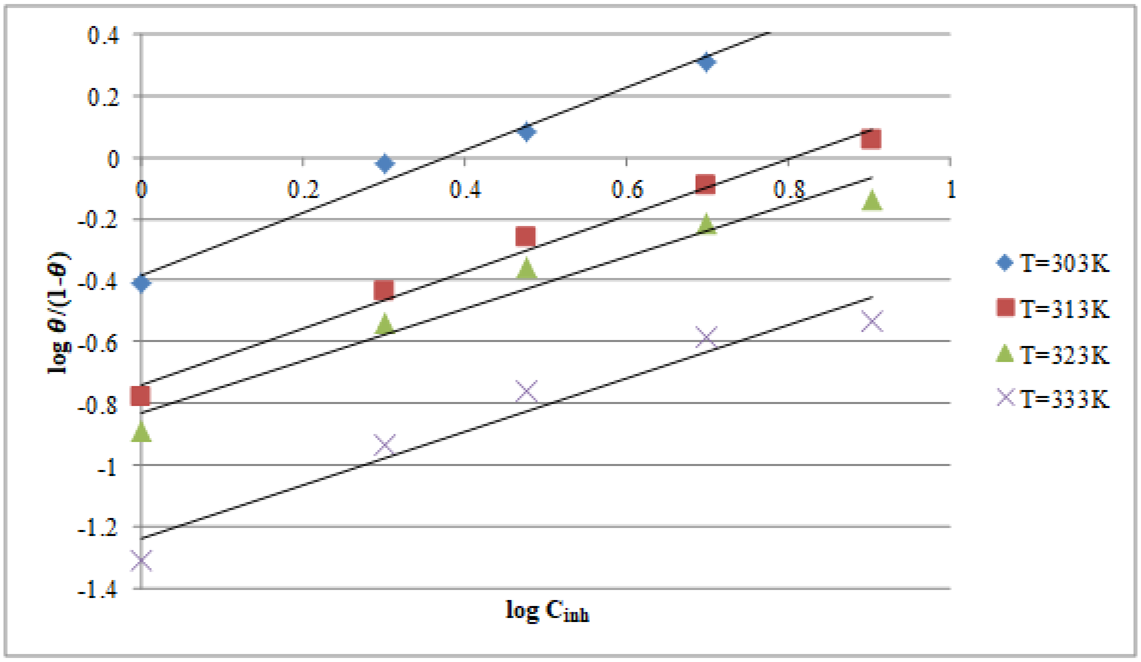

Figure 9 Langmuir adsorption isotherms of *Ziziphus jujuba* stem on mild steel surface in 1M HCl at different studied temperatures

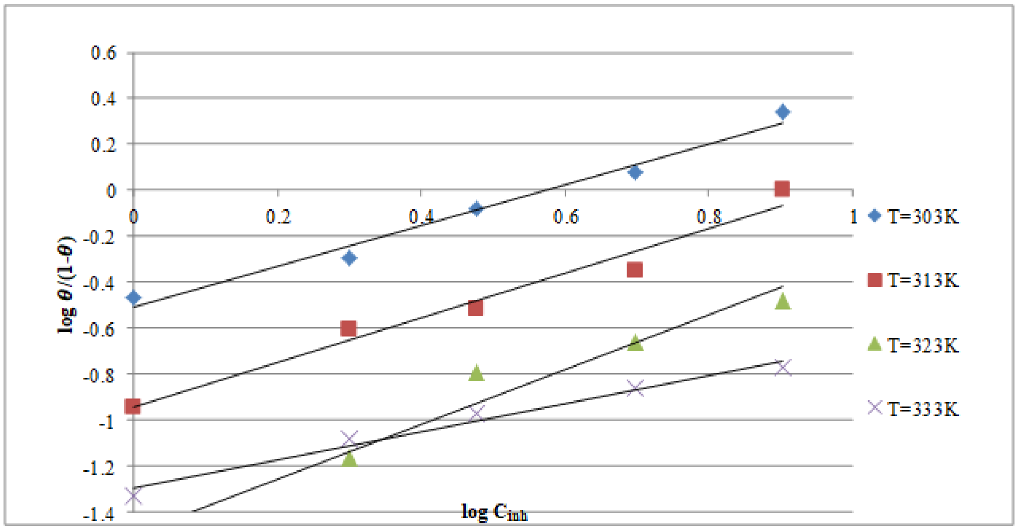

Figure 10 Langmuir adsorption isotherms of *Ziziphus jujuba* fruits on mild steel surface in 1M HCl at different studied temperatures

Adsorption isotherm and Gibbs energy

The nature of adsorption can be explained by the process at metal/electrolyte interface. Further to understand the nature of adsorption, obtained surface coverage θ were fitted in different adsorption isotherms. Langmuir adsorption isotherm was the best fit. The mathematical expressions for Langmuir adsorption isotherm can be expressed by the following equation [24-28].

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C_{inh} \qquad (6)$$

Rearranging the above equation (6) we get

$$\frac{\theta}{1-\theta} = K_{ads}C_{inh} \qquad (7)$$

$$\log\left(\frac{\theta}{1-\theta}\right) = \log K_{ads} + \log C_{inh} \qquad (8)$$

Where K_{ads} is the equilibrium constant of adsorption, θ is the surface coverage, (1-θ) is the uncovered surface, C_{inh} is the concentration of inhibitor. Values of K_{ads} were calculated from the intercept of Langmuir adsorption isotherm drawn according to the equation (8) between log (θ /1- θ) and log C_{inh} (**Figure 9** and **10**). The value of K_{ads} obtained from Langmuir adsorption isotherm is related to Gibbs energy according to the following equation (9).

$$K_{ads} = 1/C_{H2O} \exp^{(-\Delta G/RT)} \qquad (9)$$

It can be written as:

$$\Delta G_{ads} = -2.303\ RT \log (K_{ads} . C_{H2O}) \qquad (10)$$

Where CH_2O is the concentration of water in (mL / L) at metal/solution interface, R is universal gas constant and T is absolute temperature. The values of ΔG_{ads} were tabulated in **Table 5**. Obtained values of Gibbs energy were plotted against temperature in accordance with the following basic equation [29].

$$\Delta G_{ads} = \Delta H_{ads} - T\Delta S_{ads} \qquad (11)$$

Intercept of graph between ΔG_{ads} vs T in **Figure 13** and **14** gives value of ΔH_{ads} and by putting the value of intercept in equation (11) values of ΔS_{ads} were obtained. These obtained adsorption parameters Gibbs free energy of adsorption (ΔG_{ads}), enthalpy of adsorption (ΔH_{ads}) and entropy of adsorption (ΔS_{ads}) are in **Table 9** and **10**. ΔG_{ads} values have been found negative at all studied temperatures indicating spontaneous adsorption process of inhibitor molecules on metal surface [30-33]. Generally values of ΔG_{ads} upto -20 KJ/mol are consistent with electrostatic interactions (physical adsorption) between charged molecules and charged metal surface and values upto -40 KJ/mol or higher involve charge sharing or transfer from inhibitor molecules to metal surface to form coordinate type of bond (chemical adsorption) [34-38]. The obtained values of ΔG_{ads} were found less than -20kJ/mol indicated physical adsorption of inhibitor molecules. It has been observed that adsorption of negatively charged species is facilitated due to the positively charged metal. But positively charged species can also be adsorbed and protect the positively charged metal surface acting with a negatively charged intermediate such as acid anions, adsorbed on metal surface.

Values of ΔH_{ads} have been found negative indicating the exothermic adsorption process [39], which further indicates lower %IE at higher temperatures, due to desorption of inhibitor molecules. The exothermic process is attributed to either physical or chemical adsorption or mixture of both [40]. In exothermic process, values of ΔH_{ads} predict physisorption or chemisorptions in exothermic process. For physisorption values of ΔH_{ads} is lower than 40kJ/mol while for chemisorption it reaches to 100kJ/mol [41,42]. Values of ΔH_{ads} in Table 9 and 10 indicate physisorption. Negative values of ΔS_{ads} indicate decrease of entropy of adsorption process. This behaviour can be explained as that before the adsorption of inhibitor molecules onto mild steel surface, they might freely move in bulk solution (inhibitor molecules were chaotic), but with the process of adsorption, inhibitor molecules became orderly and adsorbed onto the steel surface as a result decrease in entropy is observed. A more interesting behaviour is observed from Table 9 and 10 that negative ΔH_{ads} value is accompanied with negative ΔS_{ads} value. This further agrees that when the adsorption is an exothermic process, it must be accompanied by a decrease in the entropy change and vies versa.The obtained positive values of ΔS_{ads} are the algebraic sum of the adsorption of organic molecules and the desorption of water molecules [43]. Therefore the positive values of entropy of adsorption may result due to substitution process, which can be attributed to the solvent entropy and more positive water desorption entropy [44].

Table 9 Adsorption parameters for mild steel corrosion in 1 M HCl solution with *Ziziphus jujuba* stem

Temperature(^oC)	**ΔG_{ads}(kJ/mol)**	**ΔH_{ads}(kJ/mol)**	**ΔS_{ads}(J/mol/K)**
30^{o}C	-8.5325	-45.43	-121.774
40^{o}C	-7.0761		-122.536
50^{o}C	-6.7765		-119.67
60^{o}C	-4.5762		-122.684

Table 10 Adsorption parameters for mild steel corrosion in 1 M HCl solution with *Ziziphus jujuba* fruits

Temperature(^{o}C)	ΔG_{ads}(kJ/mol)	ΔH_{ads}(kJ/mol)	ΔS_{ads}(J/mol/K)
30^{o}C	-7.9698	-50.55	-140.53
40^{o}C	-6.7525		-139.93
50^{o}C	-3.4369		-145.86
60^{o}C	-4.3658		-138.69

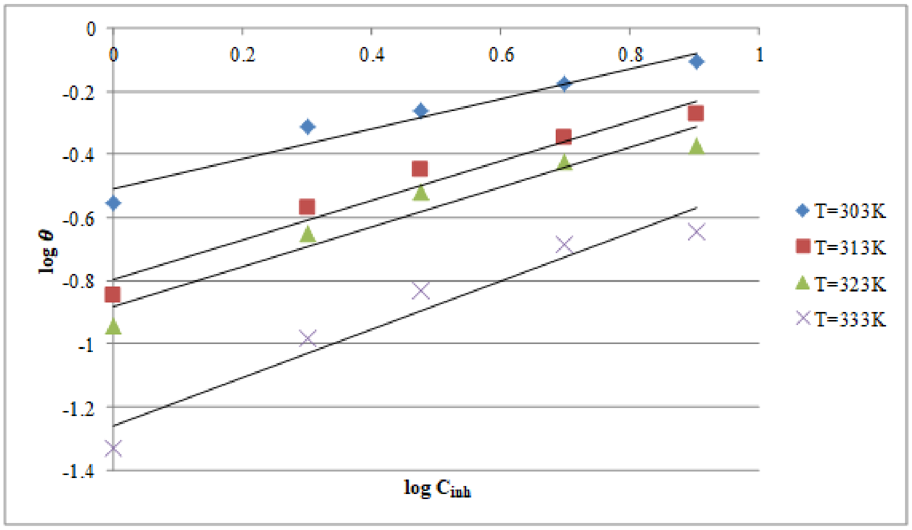

Figure 11. Freundlich adsorption isotherms of *Ziziphus jujuba* stem on mild steel surface in 1M HCl at different studied temperatures

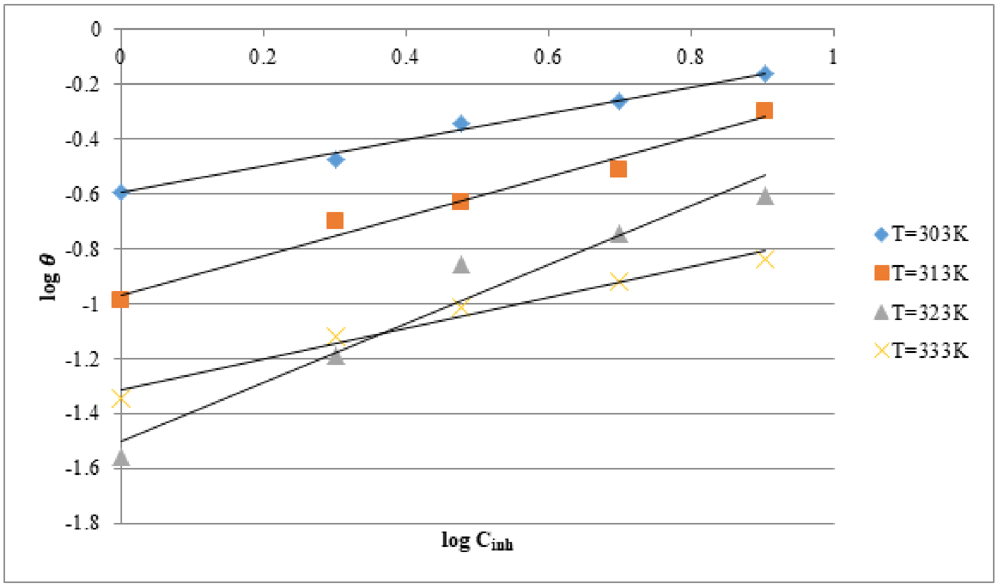

Figure 12 Freundlich adsorption isotherms of *Ziziphus jujuba* fruits on mild steel surface in 1M HCl at different studied temperatures

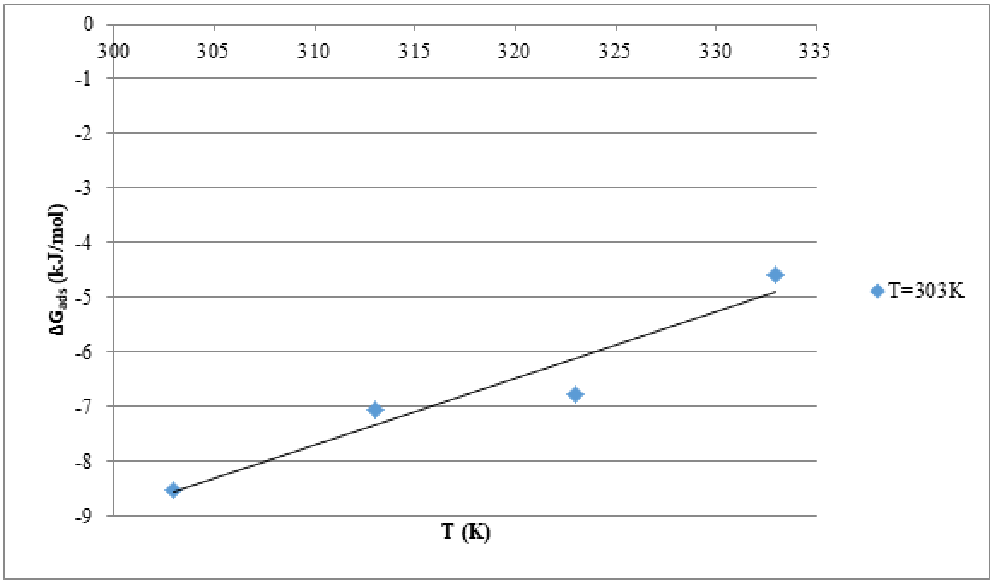

Figure 13 The Variation of ΔG_{ads}(kJ/mol) with T (K) for mild steel corrosion in 1M HCl solution with *Ziziphus jujuba* stem

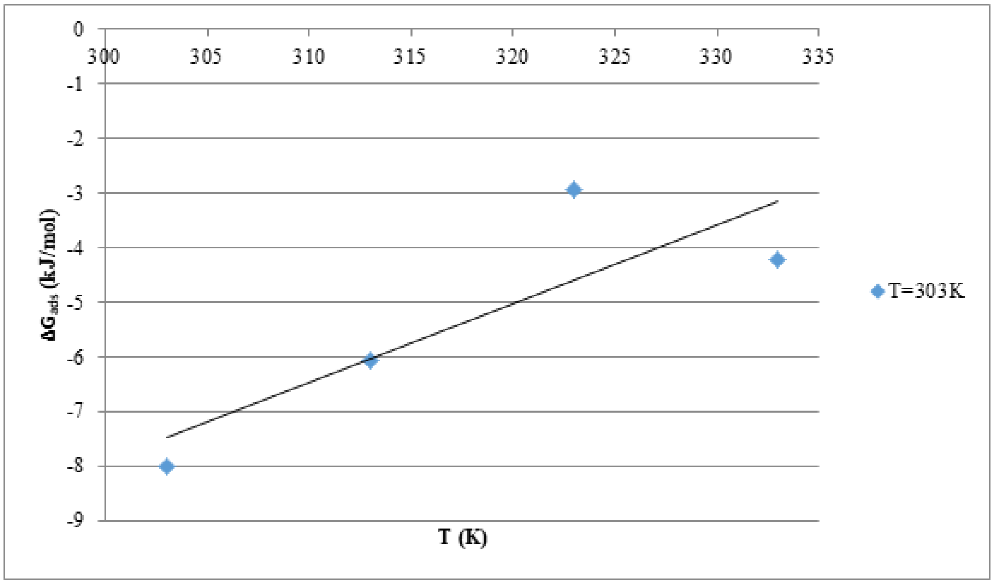

Figure 14 The Variation of ΔG_{ads}(kJ/mol) with T (K) for mild steel corrosion in 1M HCl solution with *Ziziphus jujuba* fruits

Conclusions

Result showed that ZIZIPHUS JUJUBA STEM and ZIZIPHUS JUJUBA FRUITS are good corrosion inhibitors for mild steel in 1M HCl solution. Corrosion rates with in temperature and decrease with in inhibitor concentration. Inhibition efficiencies at lower temperature suggests the physisorption process of inhibitor on mild steel surface. Apparent activation energy with in inhibitor concentration also suggests physisorption. Enthalpy of adsorption show exothermic and physical adsorption process of inhibitor. Nagative values of Gibbs free energies shows spontaneity of corrosion inhibition process of mild steel in 1 M HCl in Ziziphus jujuba stem and fruits.

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To,

Rakesh Kumar Dubey, Nitin Gupta, S.M. Nafees, Kalpana S.
Govt. College, Gangapur city, Sawai Madhopur
Rajasthan-322201

Dear Sir/Madam

We are happy to inform you that your paper entitled **"Inhibition of mild steel corrosion in HCL solution by leaves of *ziziphus jujuba*"** has been accepted for publication in the scientific research journal Nature Environment and Pollution Technology (p-ISSN 0972-6268; e-ISSN 2395-3454). The paper is likely to come in Vol. 19, No. 2 (June), Year 2020.

Thanking you,

Yours sincerely,

P. K. Goel
Editor