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Corrosion Inhibitors used in Pipelines Carrying Simulated Oil Well Water – An Overview and Inhibition of Corrosion of Mild Steel in Simulated Oil Well Water by Aqueous Extract of *Chrysanthemum Indicum* Flower- Case Study

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Abstract

Simulated oil well water (SOWW) is conceded out by pipelines made of several alloys for instance mild steel & L80. These alloys may undergo corrosion owing to presence of various aggressive ions present in SOWW. To prevent this several inhibitors have been used. Several methods have been used to estimate inhibition efficiency of extract. Weight loss study, electrochemical study like potentiodynamic polarization study & electrochemical impedance spectroscopy study, Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), nuclear magnetic resonance spectroscopy (NMR), atomic force microscopy (AFM) and TEM have been employed in these studies. Recent developments in this field of research is presented in detail briefly. As a study Inhibition of corrosion of mild steel in simulated oil well water by aqueous extract of *Chrysanthemum indicum* flower is also discussed.

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Keywords

Adsorption Isotherm; Contact Angle; Chrysanthemum Indicum Flower; Inhibition Efficiency; Simulated Oil Well Water.

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Introduction

Simulated Oil Well Water

Simulated oil well water (SOWW) is carried out by pipelines made of several alloys. These alloys undergo corrosion owing to presence of various aggressive ions present in SOWW. To prevent this several inhibitors have been used. Many researches have been carried out in this regard.[1-10]

Metals

Some inhibitors have been used to thwart corrosion of many metals like N80 carbon steel alloys,[1] API 5LX carbon steel,[2] X80 pipeline steel,[3] X-65 type carbon steel,[4] mild steel,[5-7] metallic S90 steel[8] and carbon steel.[9, 10]

Medium

Inhibition efficiency of extracts in scheming corrosion of metals in various environments has been investigated. The medium includes HCl,[1] oil well produced water,[2] oil field waters,[3] oil well formation water,[4] simulated oil well water,[5-7] oil fields,[8] produced water in acidizing oil wells[9] and 15 % HCl.[10]

Methods

Several methods have been used to estimate the inhibition efficiency of extracts.[1-10] Weight loss study ,[1, 2, 5-7, 9, 10] electrochemical techniques,[1-10] Langmuir adsorption isotherm,[1] Fourier transform infrared spectroscopy,[2, 4, 6-10] SEM,[2, 6, 7, 9, 10] nuclear magnetic resonance spectroscopy,[4, 8] atomic force microscopy[4, 6-8] and TEM[10] have been employed in these studies.

Inhibitors

Inhibitors such as *Glycyrrhiza glabra*,[2] thiourea base imidazoline quaternary ammonium salt,[3] *Allium sativum* (Garlic),[5] *Chrysanthemum indicum* flower,[6] *Andrographis paniculata*[7] and *Aliphatic tricationic surfactants*[8] have been used in these studies.

Results are abridged in Table 1.

Table 1: Summary of results

S. No.	Metal	Medium	Inhibitor	Method	Findings	Reference
1	N80 carbon steel alloys	HCl	(E)-N-(benzo[d]thia -zol-2-yl)-1-pheny -lmethanimine (H-BTPM), (E)-N-(6-methylbenzo[d] thiazol-2-yl)-1-ph-enylmethanimine (Me-BTPM), and (E)-2-(benzylideneamino) benzo[d]thiazole-6-thiol (SH-BTPM)	gravimetric and electrochemical techniques, Langmuir adsorption isotherm	BTPM series acted as anticorrosive property and act as potential biocides	1
2	API 5LX carbon steel `	oil well generated water environment	*Glycyrrhiza glabra*	weight loss method & potentiodyna -mic polarization study & electro-chemical imped-ance spectros-copy study, Fourier transform infrared spectro-scopy & SEM analysis	both abiotic & biotic systems are pretentious by unadorned pitting type of corrosion reaction & suppressed corrosion issues by forming shielding layer over carbon steel surfaces	2
3	X80 pipe line steel	Simulated oil-field	thiourea base imidazoline qua	polarization curve measure	Corrosion inhibitor is much appropriate	3

		waters	-ternary ammo -nium salt	-ment, EIS method and scanning vibrating electrode technique	for usage in neutral waters & it has decent corrosion inhibition effect in temperature range of 40~60 °C	
4	X-65 type carbon steel	oil well formation water under H_2S environ -mnet	cationic surfactants like 1-ethyl-4H-ben zo[d][1,3]thiazin-1 -ium bromide (BTB) & N-ethyl-N,N-dioc -tyloctan-1-aminium bromide (DAB)	Electrochemical studies such potentiodynamic polarization studies & EIS measurements. FTIR & NMR techniques and atomic force microscopy	inhibit both cathodic & anodic type of adsorption on metal surface, inhibition efficiency obtained 93 % for compound BTB & 84% for compound DAB	4
5	mild steel (MS)	simulated oil well water (SOWW)	*Allium sativum* (Garlic)	weight loss study & electrochemical studies	Charge transfer resistance (R_t) value upsurges, electrochemical impedance value upsurges, whereas double layer capa-citance (C_{dl}) drops, good inhibitor for corrosion of MS in SOWW	5
6	mild steel	simulated oil well water	*Chrysanthemum indicum* flower	weight loss method and by electrochemical measurements, FTIR spectros-copy, SEM & AFM	To study mechanistic aspects of corrosion inhibition, maximum IE obtained at 93%	6
7	mild steel	simulated oil well water	*Andrographis paniculata*	Weight loss study, potentiodynamic polarization study & electrochemical impedance spectroscopy, FTIR, SEM and AFM	94% inhibition efficiency, controls the cathodic reac-tion predominantly, protective film formed on mild steel surface is confirmed by electrochemical impedance spectro -scopy, potential application in petroleum industry obeys Langmuir adsorption isotherm, potential application in petroleum industry	7

8	metallic S90 steel	oil fields	Aliphatic trica-tionic surfactants	Elemental analysis FTIR spectroscopy and Nuclear magnetic reson-ance spectros-copy, electro-chemical studies & Atomic force microscopy	Obtained 93 % inhibition efficiency tricationic amph-iphiles performed as both cathodic and anodic type inhibitors, followed Langmuir isotherm	8
9	carbon steel	generated water in acidizing oil wells	2-(2-(3,4-bis(2-methoxyethoxy) tetrahydrofuran-2-yl)-2-(2-meth-oxyethoxy)ethoxy) ethyl stearate, Tween-60	FTIR and TGA techniques, UV-Visible spectroscopy, weight loss method, elect-rochemical studies & SEM	escalation in tempe-rature results to partial desorption of inhibitor molecules at metal surface, which make corrosion rate increase, positive sign of activation enthalpy (ΔHa) imitates endo-thermic nature of carbon steel dissolution process	9
10	carbon steel	15% HCl	Bis(2-aminoethyl) amine-modified graphene oxide	weight loss methods, electrochemical studies, FTIR, SEM and TEM	synergistic action and IE was obtained at 96.77%	10

Case Study

Inhibition of Corrosion of Mild Steel in Simulated Oil Well Water by Aqueous Extract of *Chrysanthemum Indicum* Flower

Experimental

Preparation of Inhibitor

12 g of shade dried *Chrysanthemum indicum* flower (CIF) was boiled with DD water. Extract was filtered and made upto 100 ml. This solution was used as corrosion inhibitor.

Preparation of Simulated Oil Well Water (SOWW)

In 100 mL of doubly distilled water, sodium chloride (3.5 g), calcium chloride (0.305 g) and magnesium chloride (0.186 g) are added. Just before experiment, add 0.067 g sodium sulfide and 0.4 mL of concentrated hydrochloric acid to generate hydrogen sulfide gas to form a simulated oil well water encompassing 100 ppm of H_2S.[11]

Preparation of Mild Steel (MS)

Mild steel specimens (0.0267 % S, 0.06 % P, 0.4 % Mn, 0.1 % C & rest iron) of dimensions 1.0 cm x 4.0 cm x 0.2 cm were polished to a mirror finish & degreased with acetone.

Weight Loss Scheme

Mild steel specimens in triplicate were engrossed in 100 ml of simulated oil well water encompassing numerous concentrations of inhibitor (aqueous extract of *Chrysanthemum indicum* flower) for a period of one day. Weight of specimens formerly & subsequently entanglement was indomitable using Shimadzu balance, model AY62. Corrosion products were eviscerated with Clarke's solution.[12] Variance between preliminary weight prior to deployment & final weight was castoff for deviousness of corrosion rate by using following formula.[13]

Corrosion rate, mdd = W/AT ...(1)

Where, mdd is corrosion rate articulated in terms of metal loss (mg) per decimeter square area per day, W is loss in weight (mg), A is area of panels (dm^2) & T is exposure time (days).

Inhibition efficiency was premeditated using relation.

Inhibition efficiency = $[(CR_1-CR_2)/CR_1] \times 100$ % ...(1)

Where,

CR_1 = corrosion rate in nonexistence of inhibitor
CR^2 = corrosion rate in existence of inhibitor.

The surface coverage was premeditated using relation.[14]

Surface coverage, θ = %IE/100 ...(3)

Contact Angle

Contact angle measurements on the surface were executed on VCA Optima instrument fortified with CCD camera for imaging. Deionized water under static conditions with drop volume of 5 ml was engaged to conclude contact angle. VCA Optima XC software providing with instruments was castoff for fitting drop shapes to determine contact angle of water on surface. This measurement was reiterated three times for each sample, average values with standard deviations ±2 are testified.[15]

Results & Discussion

A green corrosion of an aqueous extract of *Chrysanthemum indicum* flower (CIF) has been applied to regulate corrosion of mild steel in existence of simulated oil well water (SOWW). Findings will be expedient in petroleum technology. These inhibitors may be included to oil well water conceded by pipelines made of mild steel.

Weight Loss Method

Inhibition efficiency (IE %), corrosion rate (CR) & surface coverage (θ) values was premeditated from weight loss method[16] for mild steel with nonexistence & existence of various concentrations of (CIF) at room temperature are abridged in Table 2. From Table 2, it is obvious that as concentrations of inhibitor upsurges, inhibition efficiency upsurges, corrosion rate drops & surface coverage upsurges. Maximum inhibition efficiency of 93 % was reached for mild steel when immersed in 10 ml of extract concentration. That is oxidation of mild steel is lessened by coverage of active molecules from inhibitor on metal surface.[6]

Table 2: Corrosion rate & inhibition efficiency of MS in SOWW medium in different concentrations of inhibitor (CIF)

Volume of inhibitor (CIF)ml	Corrosion rate (CR)mdd	IE %	θ Surface coverage
0	14.55	-	-
2	3.64	75	0.75
4	3.26	78	0.78
6	2.76	81	0.81
8	1.75	88	0.88
10	1.02	93	0.93

Adsorption Isotherm

An adsorption isotherm provides direct relationship between corrosion efficiency with degree of surface coverage at room temperature for various concentrations of inhibitor solutions. Adsorption isotherm provides basic evidence about nature of interaction between mild steel surface & inhibitor molecular constituents.[17] Adsorption of corrosion inhibitor molecules occurs on mild steel surface by displacement of molecule of water adsorbed on metal surface. Also, adsorption depends on temperature, chemical composition & concentration of inhibitor & electrochemical potential at metal-solution interface.[18]

There are several isotherms proposed to account for adsorption of corrosion inhibitor molecules on surface of metal. From isotherm, linear relationship between θ and concentration of inhibitor can be found. In this study, the changes in the θ and thereby the change in the efficiency of inhibitor is determined by using different isotherm model.

Langmuir Adsorption Isotherm

Degree of surface coverage (θ) for innumerable concentrations of inhibitor (2, 4, 6, 8, 10 ml) at room temperature was found from the weight loss method. According to Langmuir isotherm, the following equation relates the surface coverage (θ) and inhibitor concentration, C.

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \quad ...(4)$$

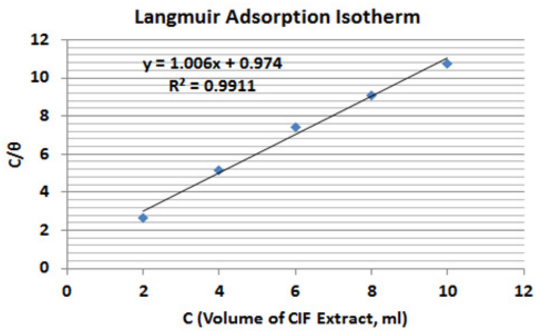

Fig. 1: Langmuir Adsorption isotherm on mild steel engrossed in SOWW in occurrence of inhibitor (CIF)

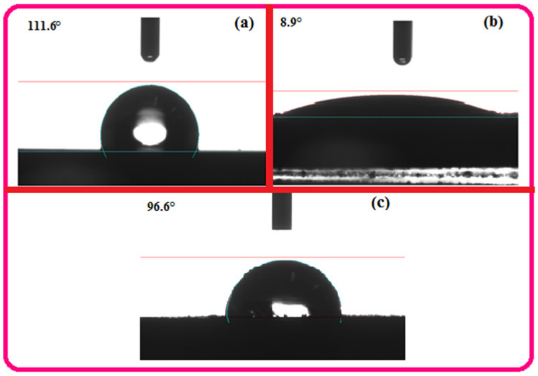

Fig. 2: The contact angle images of (a) polished MS, (b) MS engrossed in corrosive environment (SOWW) (c) MS immersed in corrosive environment containing the inhibitor (CIF)

The plot of Langmuir adsorption isotherm, C/θ vs C shown in Figure 1. Values of adsorption parameters obtained from Langmuir adsorption isotherm including ΔG^0_{ads}, R^2, slope and intercept of inhibitor on mild steel surface are listed in Table 3. Negative sign of ΔG^0_{ads} make sure extemporaneity of adsorption process & constancy of adsorbed layer on steel surface. ΔG^0_{ads} is premeditated from equation.

$$\Delta G^0_{ads} = -2.303\ RT \log (K_{ads} \times 55.55) \quad ...(5)$$

Table 3: Adsorption factors acquired from Langmuir adsorption isotherm for corrosion inhibitive effect of aqueous extract of CIF on corrosion of mild steel in SOWW

R^2	Slope	Intercept	K_{ads}	ΔG^0_{ads} kJ/mol
0.9911	1.006	0.974	1.0267	-10.188

Table 4: Contact angle analysis of different environment

System	Contact angle (°)
Polished MS	111.6
MS immersed in corrosive environment	8.9
MS immersed in corrosive environment encompassing inhibitor (CIF) system	96.6

The R^2 value was very high 0.9911. The negative value of Gibb's free energy approves that adsorption of inhibitor on metal is spontaneous. These interpretations indicates that adsorption of inhibitor molecules on metal surface comply with the Langmuir adsorption isotherm.[19, 20]

Analysis of Contact Angle Measurement

Contact angle measurement is modest technique for characterization of surfaces. It is useful in explaining the data such as information between a hydrophobic and hydrophilic surface of the metal and surface of the protective film formed.[21] When contact angle increases, hydrophobicity also increases. Because of this, when water repellent nature of surface upsurges & corrosion inhibition efficiency also increases. The contact angle images are shown in Figure 2. Contact angle values of polished metal, metal immersed in corrosive environment (SOWW)

& metal engrossed in inhibitor (CIF) system are given in Table 4.

It is pragmatic from Table 4, that contact angle for polished metal is precise high (111.6°). For polished metal engrossed in SOWW, the contact angle is precise small (8.9°). For polished metal engrossed in inhibitor system the contact angle is in between that of the above two systems (96.6°). The contact angle measurement study is expedient in explaining hydrophobicity of metal surface & corrosion inhibition efficiency upsurges of inhibitor system.[22-24]

Conclusions

- In this study, anti-corrosive property of aqueous extract of CIF has been tested against the mild steel in SOWW medium.
- Diminution in corrosion rate & escalation in inhibition efficiency of mild steel in SOWW media was observed with upsurge in concentration of CIF. Maximum inhibition efficiency of 93 % was accomplished for 10 ml of CIF.
- Adsorption process tracked Langmuir isotherm model. Negative value of $\Delta G0ads$ achieves that adsorption process was extemporaneous.
- Contact angle measurement studies reveal that the inhibitors form protective layer on mild steel surface in SOWW environment.

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Conflict of Interest
The authors do not have any conflict of interest.

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