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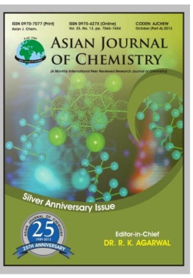

Synergistic Effect of Halides Ions on the Corrosion Inhibition of *Abelmoschus esculentus* Seed Extract on Mild Steel in H_2SO_4

V.S. PRIYA[1], A. ALI FATHIMA SABIRNEEZA[2,*] and S. SUBHASHINI[2]

[1]Department of Chemistry, Government College of Technology, Coimbatore-641 013, India
[2]Department of Chemistry, Avinashilingam Institute for Home Science and Higher Education for Women, Coimbatore-641 043, India

*Corresponding author: E-mail: fathima.rahiman@gmail.com

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The inhibitive effect of *Abelmoschus esculentus* seed extract on the corrosion of mild steel in sulphuric acid was investigated using gravimetric, potentiodynamic and electrochemical impedance spectroscopy (EIS) techniques. The results obtained showed that *Abelmoschus esculentus* seed extract could serve as an effective inhibitor for the corrosion of mild steel in sulphuric acid. The percentage inhibition increased with increasing concentration of the extract at room temperature. Maximum inhibition efficiency of 90 % was obtained with 0.5 % v/v concentration. The inhibition efficiencies obtained from impedance and polarization measurements were in good agreement. Poteniodynamic polarization studies clearly revealed that the extract behave as mixed type inhibitor. The inhibition efficiency was significantly affected by the temperature of the medium. The synergism parameters (S) obtained was found to be greater than unity which indicates that the enhanced inhibition efficiency caused by the addition of halides is only due to synergism.

Key Words: *Abelmoschus esculentus*, Mild steel, Corrosion inhibitor, Electrochemical impedance spectroscopy, Synergism.

INTRODUCTION

The corrosion of metallic materials in acidic solution causes considerable loss. In order to reduce the corrosion of metals several techniques have been adopted. The use of inhibitors during acid pickling procedure is one of the most practical methods for protection against corrosion in acidic media. Currently there is public criticism of the synthetic inhibitors for their hazardous effect. Plants are rich resources of naturally synthesized chemicals. Plant extracts contains several organic compounds which have corrosion inhibiting abilities. The extracts from the leaves, seeds, bark of plants have been reported to inhibit metallic corrosion in acidic medium. A summary of plants extracts used as corrosion inhibitors have been recently given by Okafor *et al.*[1] and Raja and Sethuraman[2].

The present work was designed to investigate the corrosion inhibition of mild steel in acid medium by *Abelmoschus esculentus* seed extract and the influence of different halides on the inhibitive action of the extract.

EXPERIMENTAL

Mild steel of 2 mm thickness with a composition of Mn-0.271, C-0.143, Si-0.041, P-0.035, S-0.030, Mo-0.018, Ni-0.006, Cr-0.002 and Fe-99.454 % was obtained from local market. The sheet was press-cut into 1 cm × 5 cm coupons. The coupons were degreased with ethanol, polished with water paper, dried and stored in moisture free desiccators prior to use. 1 M H_2SO_4 solution prepared from reagent grade H_2SO_4 was employed as the corrodent for the study.

Abelmoschus esculentus seeds were collected from a local farm and dried. 5 % stock solution of the seed extract of *Abelmoschus esculentus* was prepared as reported by Abiola *et al.*[3]. 5 g of powdered seed was refluxed with 100 mL of 1 M H_2SO_4 for 3 h. The solution was allowed to stand for 8 h, filtered and stored. The filtrate was diluted with appropriate quantity of 1 M H_2SO_4 to obtain inhibitor test solution of 0.05-0.5 % v/v concentrations.

Gravimetric measurements: The gravimetric measurements were carried out as per described ASTM standard procedure[4]. Pre weighed mild steel coupons were immersed in triplicate in test solutions with and without varying concentrations of the *Abelmoschus esculentus* extract using glass hooks. They were removed after a particular period (1, 3, 6, 12 and 24 h) of immersion, washed with alkali, followed by distilled water, dried and reweighed. Experiments were also conducted at 30, 40, 50, 60 and 70 ºC by immersing the coupons for 0.5 h. From the weight loss data the corrosion rates (CR) and inhibition efficiencies were calculated using equations mentioned elsewhere[5].

Electrochemical techniques: For electrochemical measurements, the mild steel coupon coated with commercially available lacquer with an exposed area of 1 cm^2 were used and the experiments were carried out in a conventional three electrode cell assembly consisting of a mild steel coupon as a working electrode. All electrochemical measurements were carried out using potentiostat/Galvanostat (Solatron 1280 B). The polarization studies were carried out in the potential range -0.1 mV to -1 mV against the corrosion potential at a sweep rate of 2 mV/s to study the effect of corrosion inhibition of mild steel by *Abelmoschus esculentus* seed extract. The linear Tafel segments of anodic and cathodic curves were extrapolated to corrosion potential to obtain the corrosion current densities, I_{corr}. The linear polarization studies were carried out from cathodic potential of - 0.02 V *versus* corrosion potential to an anodic potential of +0.02 V corrosion potential at a sweep rate 0.125 mV/s to study polarization resistance (R_p).

Electrochemical impedance measurements were performed using AC voltage of 10 mV amplitude in the frequency range of 0.1 Hz to 20 kHz. The values of charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) were obtained using Nyquist and Bode plots.

RESULTS AND DISCUSSION

Effect of immersion time: The corrosion of mild steel in different concentrations of *Abelmoschus esculentus* seed extract in molar sulphuric acid at 30 ºC was investigated. Fig. 1 shows the variation of inhibition efficiency against inhibitor concentration. The results revealed that the extract actually inhibited the sulphuric acid induced corrosion to an appreciable extent. Inhibition efficiency increased with increase in inhibitor concentration. It is obvious that the inhibition efficiency varied linearly with immersion period in plain acid and inhibited acid, showing the absence of insoluble product on steel surface[6]. Also inhibition efficiency increased with increase in immersion time. The increase of IE with immersion time may be due to the increase in adsorption of the inhibitor as time passes on. The maximum inhibition efficiency was observed for 12 h of immersion.

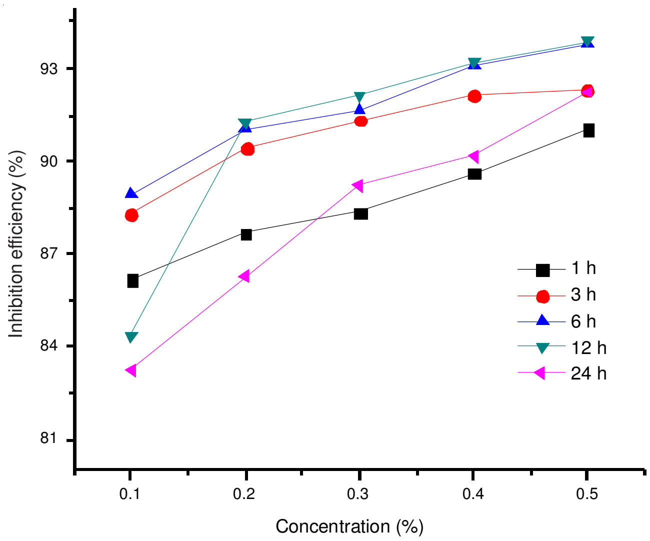

Fig. 1. Variation of inhibition efficiency with concentration for different immersion time

Adsorption studies: The mechanism of the corrosion inhibition of mild steel with the *Abelmoschus esculentus* seed extracts proceeds by the simple adsorption mode[7]. To describe adsorption process a number of mathematical relations have been suggested some being empirical and other theoretical. The simplest theoretical equation is that due to Langmuir and given by the equation[8].

$$\theta = \frac{bC}{1 + bC}$$

The plots of log (θ/1-θ) *versus* log C yields straight line (Fig. 2), where θ is the surface coverage (θ = IE/100) and C is the inhibitor concentration. The correlation coefficient is close to unity, confirming that the present system obeys Langmuir isotherm model suggesting monolayer adsorption on the energetically uniform heterogeneous metal surface with interactions in the adsorbed layer[9].

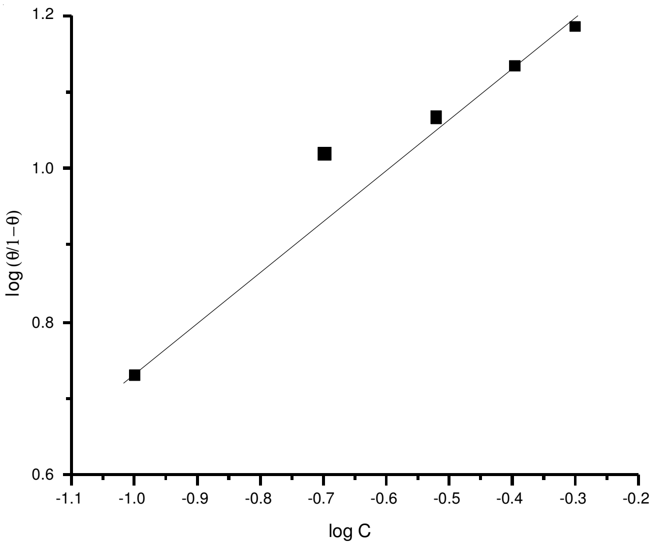

Fig. 2. Langmuir adsorption isotherm *Abelmoschus esculentus* seed extract on mild steel after 12 h of immersion

Effect of temperature: Effect of temperature on the corrosion behaviour of mild steel was studied by immersing the coupons for 0.5 h in the stagnant solution with and without inhibitor. Fig. 3 shows the variation of inhibition efficiency with immersion temperature of the system. Fig. 3 revealed that the inhibition efficiency increased with increase in concentration of the inhibitor at all the studied temperatures (30-70 ºC). Also inhibition efficiency decreased with increasing temperature of the system. A decrease in inhibition efficiency with increasing temperature suggests physical adsorption mechanism. The decrease may be due to the fact that most effects at elevated temperatures are adverse to corrosion inhibition by increasing the corrosion rate and decreasing the tendency of the inhibitor to be adsorbed on the metal surface[6].

Kinetic and thermodynamic factors: The log of corrosion rate is a linear function with 1/T (Arrhenius equation)[10,11]:

$$\log CR = -\frac{E_a}{2.303RT} + \lambda$$

where E_a is the apparent effective activation energy, R the general gas constant expressed in J/Kmol and λ is the Arrhenius

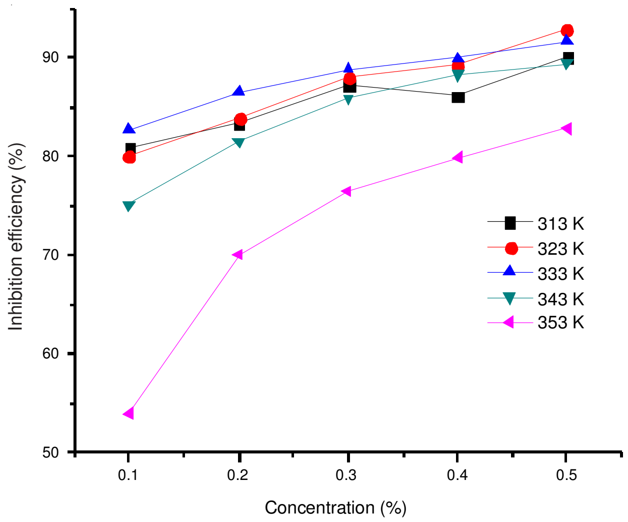

Fig. 3. Variation of inhibition efficiency with temperature of different concentrations of *Abelmoschus esculentus* seed extract

pre-exponential factor. A plot of log of corrosion rate obtained by weight loss measurement *versus* 1/T gave a straight line as shown in Fig. 4 with a slope of -Ea/2.303R. The values of activation energy are listed in Table-1.

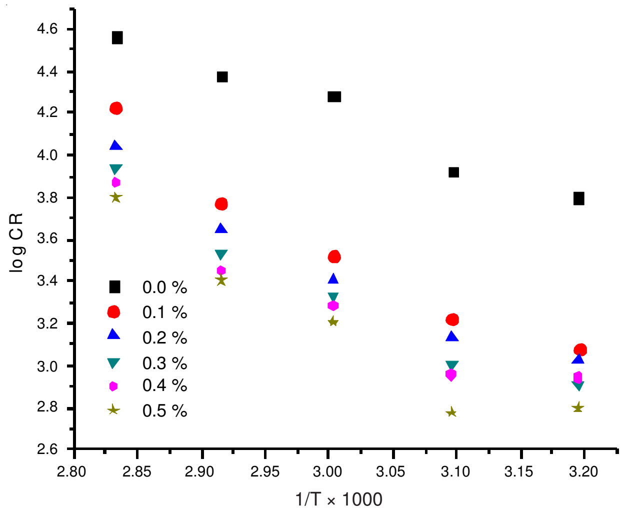

Fig. 4. Arrhenious plots for mild steel corrosion in presence of *Abelmoschus esculentus* seed extract

The free energy of adsorption (ΔG_{ads}) at different temperatures was calculated using the following equation[12] and presented in Table-1.

$$\Delta G_{ads} = -RT\ln(55.5K); \qquad K = \frac{\theta}{C}(1-\theta) \qquad (4)$$

where θ is degree of coverage on the metal surface, C is the concentration of the inhibitor and K is equilibrium constant. The negative values of free energy of adsorption indicate spontaneous adsorption of inhibitor molecules on the mild steel surface. The value of $-\Delta G_{ads}$ for inhibited system is less than 40 kJ mol^{-1} indicates that the inhibitor molecules are physically adsorbed on the surface of mild steel[13]. The ΔG_{ads} values are used to calculate enthalpy and entropy of adsorption process by using the thermodynamic relation, $\Delta G_{ads} = \Delta H_{ads} - T\Delta S_{ads}$. The obtained values of ΔH_{ads} and ΔS_{ads} are also presented in Table-1. The negative ΔH_{ads} values indicate that the adsorption of inhibitor molecules is an exothermic process. The negative ΔS_{ads} values are attributed to the adsorption process which is accompanied by an increase in order of the system resulting from the associated complex of inhibitor and mild steel[14].

Potentiodynamic polarization: Electrochemical measurements were carried out using the electrochemical analyzer Solartron 1280 B. Electrochemical techniques such as linear polarization, Tafel intercept method and electrochemical impedance spectroscopy were carried out. The values of Tafel constants ba and bc, corrosion current density (I_{corr}) and corrosion potential (E_{corr}) and IE are given in Table-2. The potentiodynamic polarization curves are depicted in Fig. 5. It is inferred that I_{corr} decreases with increase in concentration of *Abelmoschus esculentus* seed extract in acid medium. The result confirms the inhibitive action of *Abelmoschus esculentus* seed extract in 1 M H_2SO_4. Inhibition efficiency calculated using I_{corr} was found to be maximum at 0.5 % concentration. The values of Tafel constants ba and bc with respect to the blank, indicate that the inhibitor under study behave like a mixed type inhibitor[15]. Linear polarization resistance (LPR) in the presence and absence of *Abelmoschus esculentus* seed extract was calculated using Stern-Geary theory and are presented in the Table-2. It is clear that the values of R_p increases with increase in concentration of the *Abelmoschus esculentus* seed extract. Results of Tafel polarization and linear polarization resistance infer the effectiveness of extract on corrosion inhibition of mild steel in sulphuric acid medium.

Electrochemical impedance spectroscopy: The corrosion behavior of mild steel in 1 M H_2SO_4 in the absence and presence of various concentrations of *Abelmoschus esculentus* seed extract was investigated by electrochemical impedance technique at room temperature. Impedance diagrams shown in Fig. 6 have a semicircular appearance and it indicates that the corrosion of mild steel is controlled by charge transfer process. It was clear that *Abelmoschus esculentus* seed extract is acting profoundly as an excellent inhibitor to reduce acid corrosion of mild steel. The values of charge transfer resistance

TABLE-1
KINETIC AND THERMODYNAMIC FACTORS FOR MILD STEEL CORROSION IN PRESENCE OF *Abelmoschus esculentus* SEED EXTRACT

Conc. of AE seed extract (%)	Activation energy E_a (kJ/mol)	Free energy of adsorption ΔG_{ads} (kJ/mol)					ΔH_{ads} (kJ/mol)	ΔS_{ads} (kJ/Kmol)
		30 ºC	40 ºC	50 ºC	60 ºC	70 ºC		
Blank	**42.02**	–	–	–	–	–	–	–
0.1	59.69	-20.16	-20.68	-21.96	-21.14	-18.99	-26.93	-0.0190
0.2	53.70	-18.80	-19.52	-20.70	-20.24	-18.97	-16.20	-0.0103
0.3	54.14	-18.54	-19.33	-20.17	-20.01	-18.75	-15.73	-0.0109
0.4	52.96	-17.55	-18.88	-19.68	-19.79	-18.48	-11.10	-0.0176
0.5	55.28	-17.95	-19.48	-19.64	-19.45	-18.40	-16.12	-0.0086

TABLE-2
ELECTROCHEMICAL PARAMETERS FOR MILD STEEL CORROSION IN PRESENCE OF *Abelmoschus esculentus* SEED EXTRACT

Conc. of AE seed extract (%)	LPR method		TEM method					EIS method	
	R_p (Ω)	IE (%)	b_a (mV/dec)	b_c (mV/dec)	E_{corr} (mV *vs.* SCE)	I_{corr} (mA/cm^2)	IE (%)	R_{ct} (Ω)	IE (%)
Blank	4.88	–	236	167	475.3	6.84	–	5.17	–
0.1	14.55	66.46	160	111	469.8	2.03	70.27	10.97	52.92
0.2	15.11	67.70	157	103	460.7	1.89	72.24	28.90	82.08
0.3	19.55	75.03	167	90	464.8	1.31	80.70	46.61	88.89
0.4	20.39	76.06	168	92	459.3	1.23	81.98	83.25	93.78
0.5	20.40	76.07	170	89	470.6	1.06	84.49	83.62	93.80

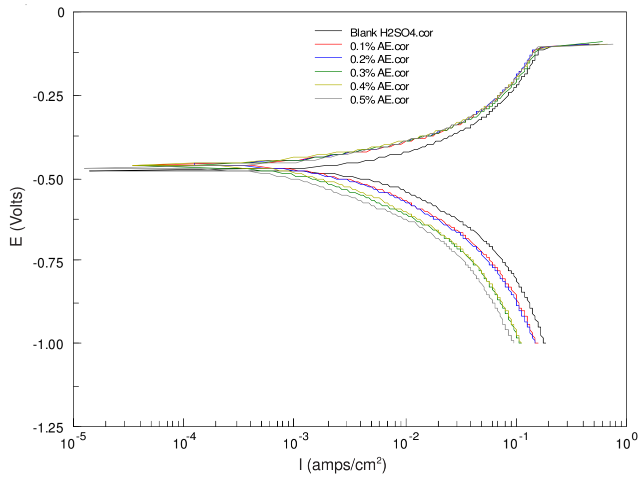

Fig. 5. Potentiodynamic polarization plots for mild steel in 1 M H_2SO_4 containing various concentrations of *Abelmoschus esculentus* extract

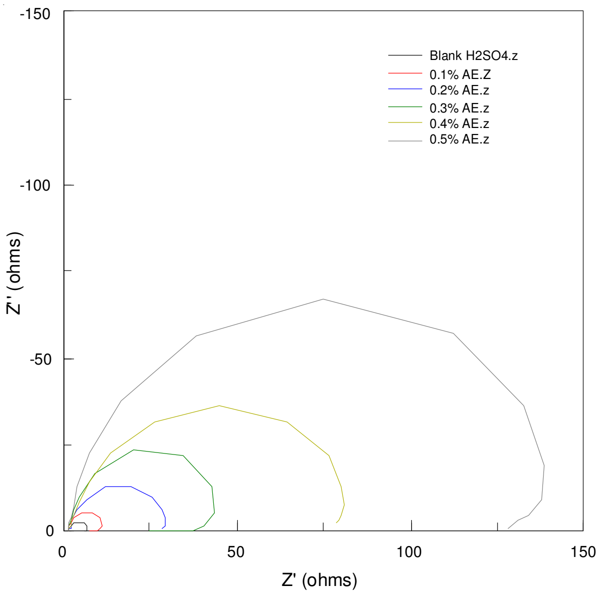

Fig. 6. Nyquist representations for mild steel corrosion in 1 M H_2SO_4 containing various concentrations of *Abelmoschus esculentus* seed extract

(R_{ct}), double layer capacitance (C_{dl}) and IE are also represented in Table-2. With increase in concentration of *Abelmoschus esculentus* seed extract the charge transfer resistance value increased. The maximum IE was found to be 93.80 % at 0.5 % concentration in the presence of the extract. The decrease in C_{dl} with increase in concentration of *Abelmoschus esculentus* seed extract indicates the adsorption of the compounds on the metal surface.

Synergistic effect of halides: Improved performance of the inhibitor in the presence of halide ions have been observed by several investigators[16-18] and were ascribed to synergistic effect. Synergism is a combined action of compounds greater in total effect than the sum of individual effects. The performance of *Abelmoschus esculentus* seed extract was evaluated in presence of chloride, bromide and iodide ions by weight loss measurements at higher temperatures to increase the inhibition efficiency and tabulated in Table-3. It is clear from the results that iodide ions have better synergism than bromide and chloride ions. The synergism parameter 'S' was calculated using the relation initially given by Aramaki and Hackermann and reported elsewhere[17-20].

$$S = \frac{1 - I_{1+2}}{1 - I'_{1+2}}$$

where I_{1+2} indicates the sum of individual inhibition efficiencies of halide ion and inhibitor, I'_{1+2} denotes the combined inhibition efficiency. The calculated synergism parameter was recorded in Table-3.

The high synergism parameter of iodide ion is due to its low electro negativity and high ionic size. The ionic radius of I^- (1.33 Å) is higher than that of Br^- (1.14 Å) which in turn higher than the Cl^- (0.99 Å) ion. The IE increases in the order $Cl^- < Br^- < I^-$ which indicates the role of the size of the halide ions in the combined inhibition process. It was already reported that strong chemisorption of iodide ions on the metal is responsible for this trend[18] which in turn facilitates the adsorption of inhibitor through columbic attraction.

TABLE-3
EFFECT OF HALIDE IONS ON THE CORROSION INHIBITION OF *Abelmoschus esculentus* EXTRACT AND THE CALCULATED SYNERGISM PARAMETER

Parameter	System	KCl			KBr			KI		
		313 K	343 K	353 K	313 K	343 K	353 K	313 K	343 K	353 K
IE (%)	Blank + 10^{-3} KX	33.4	31.3	29.0	42.3	34.2	37.0	49.3	35.0	38.0
	0.05 % + 10^{-3} KX	85.0	79.6	76.1	90.6	88.3	81.7	99.0	99.1	99.0
	0.10 % + 10^{-3} KX	85.9	86.2	80.6	91.5	91.1	85.1	99.2	99.2	99.1
Synergism parameter (S)	0.05 % + 10^{-3} KX	1.847	1.226	0.713	1.876	1.252	0.887	1.879	1.672	1.362
	0.10 % + 10^{-3} KX	1.849	1.236	0.426	1.888	1.313	1.071	1.894	1.762	1.549

Conclusion

Abelmoschus esculentus seed extract has shown a remarkable performance as an inhibitor for mild steel in H_2SO_4 solution. The inhibitor used in the present study followed Langmuir adsorption isotherm which indicated the monolayer formation. Thermodynamic parameters confirm the strong interaction between the compounds present in the extract and the mild steel surface. The free energy values indicate spontaneity and the physical nature of the adsorption process. Strong adsorption of the inhibitor on the active sites of the metal surface suppresses the dissolution process and leads to the formation of a protective film. Polarization curves obtained in the presence of the extract indicate that it controls both anodic and cathodic reactions and behave as a mixed type inhibitor. Electrochemical impedance spectroscopy studies also revealed that the corrosion of the mild steel in H_2SO_4 is controlled by charge transfer process. The synergistic effect reported to increase in the order of $Cl^- < Br^- < I^-$. The high synergistic effect of the iodide ion over the others is attributed to its large ionic radius, high hydrophobicity and low electronegativity.

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