



# CORROSION INHIBITOR ALOE VERA – NICKEL SYSTEM CONTROLLING THE CORROSION OF CARBON STEEL IN RAIN WATER

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The corrosion inhibition efficiency of an aqueous extract of Aloe Vera (AV) in controlling the corrosion of carbon steel rain water in absence and presence of with  $\text{Ni}^{2+}$  has been studied by weight loss method. Weight loss study reveals that the formulation consisting of 5 ml of AV and 50 ppm of  $\text{Ni}^{2+}$  has 98% inhibition efficiency. The results of polarisation study show that the formulation function controls the cathodic reaction predominantly. The AC impedance spectra reveal that a protective film formed on the metal surface. The UV – visible absorption spectra indicates the possibility of formation of  $\text{Fe}^{2+}$ -AV complex and also  $\text{Ni}^{2+}$ -AV complex in the solution. FTIR spectrum reveal that the protective film consists of  $\text{Fe}^{2+}$ -AV complex and  $\text{Ni}(\text{OH})_2$ .

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several plant extracts<sup>12-16</sup> and eco-friendly inhibitors<sup>17,18</sup> attracted the researchers. Investigation of natural inhibitors is particularly interesting because they are non-expensive, ecologically friendly/acceptable and possess no threat to the environment. The present work is undertaken:

1. to evaluate the inhibition efficiency (*IE*) of an aqueous extract of Aloe Vera (AV) in controlling the corrosion of carbon steel in Rain water, in the absence and presence of  $\text{Ni}^{2+}$ ,

2. to understand the mechanistic aspects of corrosion inhibition by potentiodynamic polarization studies and AC impedance analysis,

3. to analyse the protective film formed on the carbon steel by FTIR spectra and fluorescence spectra, and

4. to propose a suitable mechanism for corrosion inhibition.

## Introduction

Natural products are nontoxic, biodegradable and readily available. The recent trend in research on environmental friendly corrosion inhibitors is taking us back to exploring the use of natural products as possible sources of cheap, nontoxic, and eco-friendly corrosion inhibitors. These natural products are either synthesized or extracted from aromatic herbs, spices, and medicinal plants. Of increasing interest is the use of medicinal plant extracts as corrosion inhibitors for metals in acid solutions. This is because these plants serve as incredibly rich sources of naturally synthesized chemical compounds that are environmentally acceptable, inexpensive, readily available, and renewable sources of materials.<sup>1,2</sup> These chemicals include alkaloids, flavonoids, terpenoids, glycosides, tannins, saponins, fats and oils, and carbohydrates, and so forth.<sup>3-11</sup>

## Methods and Materials

### Preparation of Plant extract

An aqueous extract of Aloe Vera was prepared by grinding 50 g of Aloe Vera with double distilled water, filtering and suspending impurities, and making up to 500 ml. The extract was used as corrosion inhibitor in the present study.

### Preparation of specimens

Carbon steel specimens (0.0267% S, 0.06% P, 0.4% Mn, 0.1% C and the rust iron) with dimensions of 1.0 cm x 4.0 cm x 0.2 cm were polished to a mirror finish and degreased with trichloroethylene.

### Weight-loss method

Relevant data on the rain water used in this study are given in Table 1. Carbon steel specimens in triplicate were immersed in 100 ml of the solutions containing various concentrations of the inhibitor in the presence and absence of Ni<sup>2+</sup> for one day. The weight of the specimens before and after immersion determined using Shimadzu balance, model AY62. The corrosion products were cleansed with Clarke's solution.<sup>19</sup> The inhibition efficiency (*IE*) was then calculated using the equation

$$IE = 100 [1 - (W_2 / W_1)] \%$$

where  $W_1$  and  $W_2$  are the corrosion rates in the absence and presence of the inhibitor, respectively.

**Table 1.** Parameters of rain water

Parameter	Value
pH	6.82
Conductivity	115 $\mu$ mhos $cm^{-1}$
TDS	24 ppm
Chloride	12 ppm
Sulphate	3 ppm
Total hardness	20 ppm

### Potentiodynamic polarization study

Polarization studies were carried out in an H & CH electrochemical work station impedance analyzer model CHI660A. A three electrode cell assembly was used. The working electrode was carbon steel. A saturated calomel electrode (SCE) was used as the reference electrode and a rectangular platinum foil was used as the counter electrode.

### AC impedance measurements

The instrument used for polarization was also used for AC impedance study. The cell set up was the same as that used for polarization measurements. The real part and imaginary part of the cell impedance were measured in ohms at various frequencies. The values of charge transfer resistance ( $R_t$ ) and the double layer capacitance ( $C_{dl}$ ) were calculated.

### Surface Examination

The carbon steel specimens were immersed in various test solutions for a period of one day, taken out and dried. The nature of the film formed on the surface of metal specimens was analysed by FTIR spectroscopic study.

### Fluorescence spectra

These spectra were recorded in a Hitachi F-4500 fluorescence spectrophotometer.

### FTIR Spectra

FTIR spectra were recorded in a Perkin – Elmer 1600 spectrophotometer. The film was carefully removed, mixed thoroughly with KBr made in to pellets and FTIR spectra were recorded.

## Results and Discussion

### Analysis of result of weight – loss method

The corrosion rate (*CR*) of carbon steel immersed in rain water (shown in Table 1) in the absence and presence of inhibitor systems are given in Tables 2-4. The inhibition efficiency (*IE*) are also given in these Tables. It is seen from Table 2 that the aqueous extract of Aloe Vera (AV) alone is not a good inhibitor. But in presence of Ni<sup>2+</sup>, it shows excellent inhibition efficiency. As the concentration of Ni<sup>2+</sup> increases, the inhibition efficiency (Table 3) also increases. For example, 5 ml AV shows 5% *IE*. 50 ppm of Ni<sup>2+</sup> shows 44% *IE*. But it is interesting to note that the formation consisting of 5 ml AV and 50 ppm Ni<sup>2+</sup> shows 98% *IE*. This suggests that a synergistic effect exist between Ni<sup>2+</sup> and AV solution. That is mixed inhibitors shows better inhibition efficiency than individual inhibitors. This is accounts for very high *IE* offered by AV- Ni<sup>2+</sup> system. As the immersion period increases, *IE* decreases (Table 4-6). This is due to that Ni<sup>2+</sup>-AV complexes are not much transported towards the metal surface. Hence inhibition efficiency decreases.

**Table 2.** Corrosion rates (*CR*) of carbon steel in aqueous solution in the presence of inhibitor and the inhibition efficiency obtained by weight loss method (inhibitor system: AV alone; immersion period: one day).

S.No.	AV ml	Ni <sup>2+</sup> ppm	IE %	CR mdd
1	0	0	-	41.00
2	1	0	-20	49.20
3	2	0	-15	47.15
4	3	0	-3	42.23
5	4	0	-2	40.18
6	5	0	5	38.95

**Table 3.** Corrosion rates (*CR*) of carbon steel in aqueous solution in the presence of inhibitor and the inhibition efficiency obtained by weight loss method (inhibitor system: Ni<sup>2+</sup> alone; immersion period: one day).

S.No.	AV ml	Ni <sup>2+</sup> ppm	IE %	CR mdd
1	0	0	-	41.00
2	0	10	12	36.08
3	0	20	12	36.08
4	0	30	22	31.98
5	0	40	34	27.06
6	0	50	44	22.96

**Table 4.** Corrosion rates (*CR*) of carbon steel in aqueous solution in the presence of inhibitor and the inhibition efficiency obtained by weight loss method (inhibitor system: AV + Ni<sup>2+</sup> system; immersion period: one day).

S.No.	AV ml	Ni <sup>2+</sup> ppm	IE %	CR mdd
1	0	0	-	41.00
2	1	50	44	22.96
3	2	50	51	20.09
4	3	50	56	18.04
5	4	50	66	13.94
6	5	50	98	0.82

**Table 5.** Corrosion rates (CR) of carbon steel in aqueous solution in the presence of inhibitor and the inhibition efficiency obtained by weight loss method (inhibitor system: AV + Ni<sup>2+</sup> system; immersion period: two days).

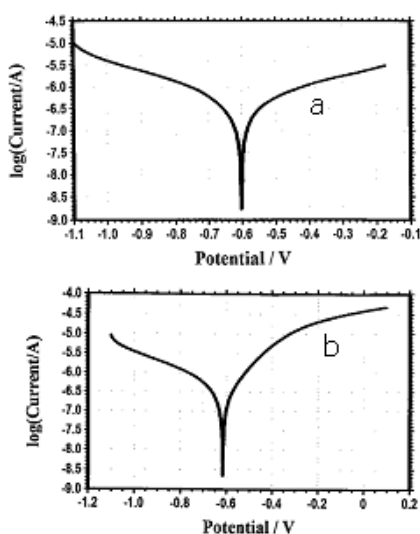
S.No.	AV ml	Ni <sup>2+</sup> ppm	IE %	CR mdd
1	0	0	-	12.00
2	1	50	4	11.50
3	2	50	8	11.04
4	3	50	17	9.96
5	4	50	33	8.04
6	5	50	66	4.10

**Table 6.** Corrosion rates (CR) of Carbon steel in aqueous solution in the presence of inhibitor and the inhibition efficiency obtained by weight loss method (inhibitor system: AV + Ni<sup>2+</sup> system; immersion period: three days).

S.No.	AV ml	Ni <sup>2+</sup> ppm	IE %	CR mdd
1	0	0	-	5.00
2	1	50	17	4.15
3	2	50	20	4.00
4	3	50	21	3.96
5	4	50	30	3.50
6	5	50	37	3.16

#### Analysis of results of polarisation study

The polarization curves of carbon steel immersed in rain water in the presence and absence of inhibitors are shown in Figure 1. The corrosion parameters are given in Table 7. When carbon steel is immersed in rain water environment, the corrosion potential is -602 mV vs saturated calomel electrode (SCE). When 5 ml of AV and 50 ppm of Ni<sup>2+</sup> are added to the rain water, the corrosion potential shifts to the cathodic side (-616 mV vs SCE). This suggests that this formulation controls the cathodic reaction predominantly. The Tafel slopes  $b_a$  and  $b_c$  for this system are not shifted equally (203 mV decade<sup>-1</sup> and 130 mV decade<sup>-1</sup>).



**Figure 1.** Polarization spectra. a: rain water, b: rain water containing 5 ml AV + 50 ppm of Ni<sup>2+</sup>.

**Table 7.** Corrosion parameters of carbon steel immersed in various test solutions obtained by polarization method. (inhibitor system: AV + Ni<sup>2+</sup> system).

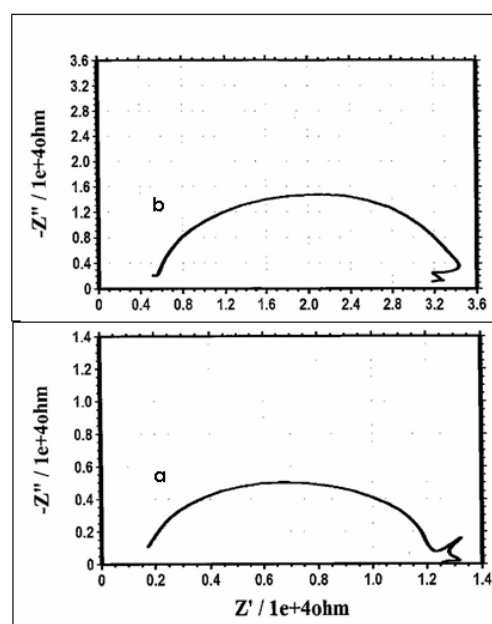
System	$E_{corr}$ , mV vs SCE	$b_c$ , mV decade <sup>-1</sup>	$b_a$ , mV decade <sup>-1</sup>	LPR $\Omega$ cm <sup>2</sup>	$I_{corr}$ A cm <sup>-2</sup>
Rain water	-602	184	235	144795	$2.647 \cdot 10^{-7}$
Rain water + 5 ml of AV + 50 ppm of Ni <sup>2+</sup>	-616	203	130	169700	$2.385 \cdot 10^{-7}$

When carbon steel immersed in rain water, the corrosion current,  $I_{corr}$  is  $2.647 \cdot 10^{-7}$  A cm<sup>-2</sup>. When 5 ml of AV and 50 ppm of Ni<sup>2+</sup> is added to rain water, the Corrosion Current decreases from  $2.647 \cdot 10^{-7}$  to  $2.385 \cdot 10^{-7}$  A cm<sup>-2</sup>. Linear polarization resistance (LPR) value increases from 144795  $\Omega$  cm<sup>2</sup> to 169700  $\Omega$  cm<sup>2</sup>. This indicates that protective film formed on the metal surface.<sup>20-26</sup>

#### Analysis of the results of AC impedance studies

The AC impedance spectra of carbon steel immersed in rain water, in the presence and absence of inhibitors, are shown in Figure 2. The AC impedance parameters namely charge transfer resistance ( $R_t$ ) and the double layer capacitance ( $C_{dl}$ ) are given in Table 8. When the carbon steel immersed in rain water, the  $R_t$  value is 1299  $\Omega$  cm<sup>2</sup> and the  $C_{dl}$  value is  $4.4 \cdot 10^{-10}$  F cm<sup>-2</sup>. When 5 ml of AV and 50 ppm of Ni<sup>2+</sup> are added to the rain water, the  $R_t$  value is increased from 1299 to 1336  $\Omega$  cm<sup>2</sup> and the  $C_{dl}$  value has decreased from  $4.4 \cdot 10^{-10}$  to  $1.9 \cdot 10^{-10}$  F cm<sup>-2</sup>.

The increase in  $R_t$  values and decrease in  $C_{dl}$  values confirms that a protective film is formed on metal surface. This decreases corrosion rate of carbon steel and increases the inhibition efficiency.



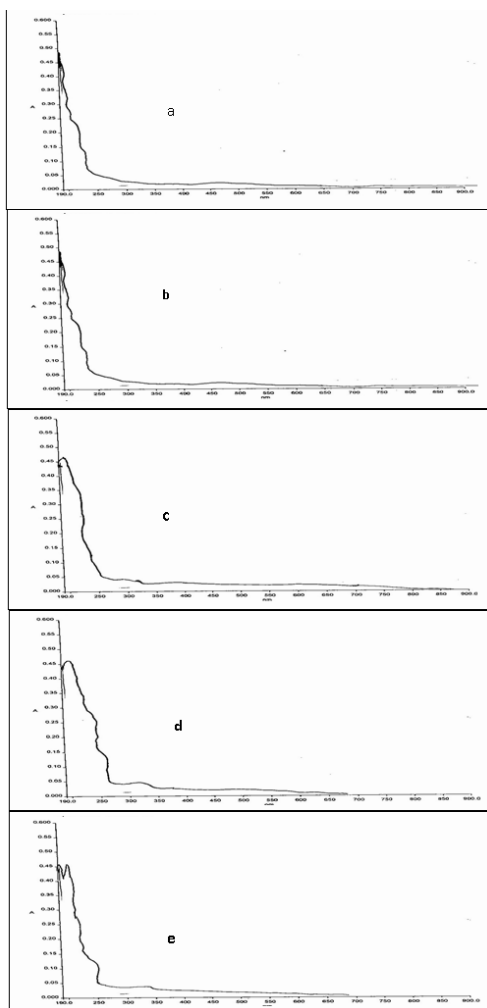
**Figure 2.** Polarization spectra. a: rain water, b: rain water containing 5 ml AV + 50 ppm of Ni<sup>2+</sup>.

**Table 8.** Corrosion parameters of carbon steel immersed in various test solution obtained by AC impedance spectra.

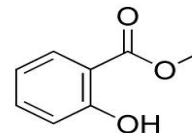
System	$R_t$ $\Omega \text{ cm}^2$	$C_{dl}$ $\text{F cm}^{-2}$
Rain water	1299	$4.4 \cdot 10^{-10}$
Rain water + 5 ml of AV + 50 ppm of $\text{Ni}^{2+}$	1336	$1.9 \cdot 10^{-10}$

**UV-Visible spectral study**

The UV fluorescence spectra are given in Figure 3. It is observed from Figure 3c that AV has maximum absorbance of 197.73 at 1.483 nm and the absorbance fall sharply and reaches 0.0015 at 378 nm. The Figure 3d reveals that AV- $\text{Ni}^{2+}$  gives a maximum absorbance of 1.1483 at 197.73 nm and decreases sharply with increase in wavelength and reaches 0.0015 at 383 nm. The increase in the absorbance value on the addition of  $\text{Ni}^{2+}$  clearly indicates the occurrence of interaction between  $\text{Ni}^{2+}$  and AV. When  $\text{Fe}^{2+}$  added to AV (Figure 3e), two small peaks have appeared at 211.7 nm (abs 0.4170) and at 197 (abs 0.2710). The appearance of these two peaks is a clear proof for the formation of complex between  $\text{Fe}^{2+}$  and AV. The UV-visible absorption spectra indicate the possibility of the formation of  $\text{Fe}^{2+}$ -AV complex and also  $\text{Ni}^{2+}$ -AV complex in the solution.

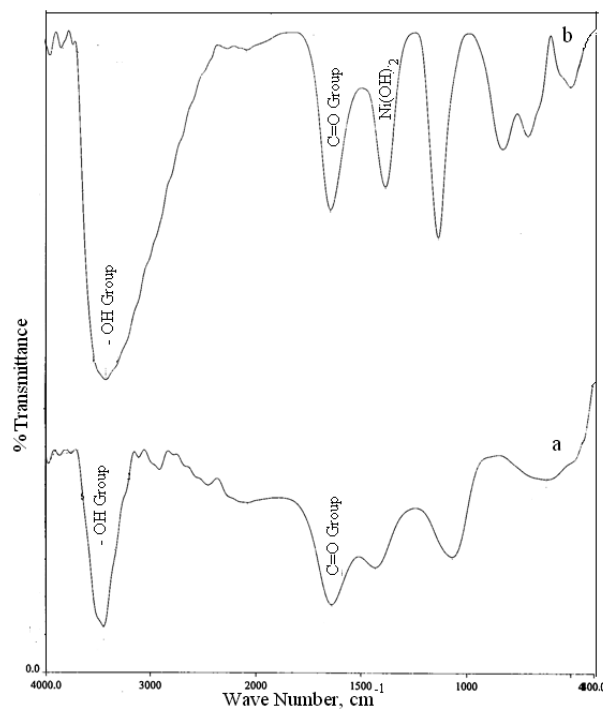
**Figure 3.** UV fluorescence spectra. a:  $\text{Ni}^{2+}$ , b:  $\text{Fe}^{2+}$ , c: AV, d: AV +  $\text{Ni}^{2+}$ , e: AV +  $\text{Fe}^{2+}$ .**FTIR spectra**

The FTIR spectra are given in Figure 4. The active principle in an aqueous extract of Aloe Vera is shown in Scheme 1. It contains phenolic -OH group and carboxyl (C=O) group.



Scheme 1

A few drops of an aqueous extract of aloe vera (AV) was dried on a glass plate. A solid mass was obtained. Its spectrum is shown in Figure 4a. The hydroxyl (-OH) group appears at  $3431 \text{ cm}^{-1}$  and carboxyl group (C=O) appears at  $1631 \text{ cm}^{-1}$ . The FTIR spectrum of the protective film formed on the metal surface after immersion in the solution containing 5 ml of AV, 50 ppm of  $\text{Ni}^{2+}$  is shown in the Figure 4b. The phenolic -OH stretch shifted from  $3431 \text{ cm}^{-1}$  to  $3408 \text{ cm}^{-1}$ . The C=O stretching shifted from  $1631 \text{ cm}^{-1}$  to  $1629 \text{ cm}^{-1}$ . These shifts confirm the formation of  $\text{Fe}^{2+}$ -Aloe Vera complex on the anodic sites of the metal surface.<sup>26,27</sup> The peak at  $1367 \text{ cm}^{-1}$  is due to  $\text{Ni}(\text{OH})_2$  formed on the cathodic sites of the metal surface. Thus the FTIR spectrum studies leads to the conclusion that the protective film  $\text{Fe}^{2+}$ -Aloe Vera complex formed on the anodic sites of metal surface and  $\text{Ni}(\text{OH})_2$  formed on the cathode sites of metal surface.

**Figure 4.** FTIR spectra. a: pure Aloe Vera extract, b: film formed on carbon steel after immersion in rain water containing 5 ml of AV and 50 ppm of  $\text{Ni}^{2+}$ .

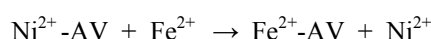
### Mechanism of corrosion inhibition

Weight loss study reveals that the formulations consisting of 5 ml of AV and 50 ppm of Ni<sup>2+</sup> has 98% inhibition efficiency. FTIR spectrum reveals that the protective film consist of Fe<sup>2+</sup>-AV complex and Ni(OH)<sub>2</sub>. In order to explain the above observation the following mechanism of corrosion inhibition is proposed.<sup>28-30</sup>

1. When the environment consisting of 5 ml of AV and 50 ppm of Ni<sup>2+</sup> is prepared, there is formation of Ni<sup>2+</sup>-AV complex.

2. When carbon steel is introduced in this solution, there is diffusion of nickel complexes towards the metal surface.

3. On the metal surface, nickel complex are converted into iron complexes on the anodic sites.



4. The released Ni<sup>2+</sup> combines with OH<sup>-</sup> to form Ni(OH)<sub>2</sub> on the cathodic sites.



5. Thus the protective film consist of Fe<sup>2+</sup>-AV complex and Ni(OH)<sub>2</sub>.

### Conclusion

Weight Loss study reveals that the formulation consisting of 5ml of AV and 50 ppm of Ni<sup>2+</sup> has 98% inhibition efficiency.

The results of polarisation study show that the formulation function controls the cathodic reaction predominantly.

The AC impedance spectra reveal that a protective film formed on the metal surface.

The UV–visible absorption spectra indicate the possibility of formation of Fe<sup>2+</sup>-AV complex and also Ni<sup>2+</sup>-AV complex in the solution.

FTIR spectrum reveal that the protective film consists of Fe<sup>2+</sup>-AV complex and Ni(OH)<sub>2</sub>.

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