



Chrysanthemum Flower Extract as a Green Inhibitor for Aluminium Corrosion in Alkaline Medium

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Abstract : The inhibition efficiency of the aqueous extracts of the *Chrysanthemum* flower as an inhibitor for the Aluminium metal in the alkaline medium was tested using weight loss, potentiodynamic polarisation and AC impedance method. The results obtained showed that the flower extract acts as efficient inhibitor for the system. The inhibition efficiency increases with the increase in the concentration of the inhibitor. Potentiodynamic polarization study reveals that the system controls the cathodic reaction predominantly. The straight line obtained as a result of Langmuir and Temkin adsorption isotherm physical adsorption of the inhibitor on the metal surface. The nature of the film formed on the metal surface was analysed using Scanning Electron Microscope (SEM).

Keywords : Inhibitor, Adsorption isotherm, SEM, Aluminium.

Introduction

Corrosion results in destroying the lusture and beauty of the objects. By using suitable inhibitors it can be controlled. Corrosion inhibitors are those compounds when added to the corroding environment delays the phenomenon of corrosion [1]. The inhibitors contain a number of heteroatoms like oxygen, sulphur, nitrogen etc. in their structure. The inhibitors control corrosion by simply blocking the active sites of the metal surface [2]. The aim of using the inhibitor is to reduce the corrosion rate [3]. Aluminium, the lightest of the known metals has been used extensively to make machinery and aircraft parts. Aluminium gets corroded very easily in the alkaline medium when compared with the other media with profuse hydrogen evolution [4].

The present study is to find out a cheap, non-toxic and eco-friendly inhibitor. In this study *Chrysanthemum* flower extract (PE) had been used to control corrosion of Aluminium in alkaline medium. The inhibitive effect of the flower extract was determined using weight loss, potentiodynamic polarization and AC impedance method. The surface analysis of the protective film was done using Scanning Electron Microscope.

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Experimental method

Preparation of the specimen

Aluminium metals of dimensions 1.0 cm x 4.0 cm x 0.1 cm containing 1.5% Pb, 0.1% Ga, 1% In and the remainder Al were mechanically polished to a mirror finish and degreased with acetone. They were used for the weight loss method and surface examination studies.

Preparation of the flower extract (PE)

Chrysanthemum flowers were collected and dried under shade and an aqueous extract of it was prepared by refluxing 5 g of it with double distilled water for 3 hours, cooled, filtering the suspended impurities and making up to 200ml. The extract was used as corrosion inhibitor in the present study.

Weight-loss method

The weight loss technique is the conventional and simplest of all corrosion techniques. Aluminium metals were completely immersed in 100 ml of the test solution (0.5 N, 0.3 N and 0.1 N HCl) containing various concentrations of the inhibitor (PE) for a period of 3 hours. The weights of the specimen before and after immersion were determined using a digital balance. The corrosion inhibition efficiency (IE) was then calculated using the equation

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

W_1 and W_2 are the corrosion rate in the absence and in the presence of the inhibitor.

Corrosion rate is calculated assuming uniform corrosion over the entire surface of the coupon. Corrosion rates (CR) are calculated from weight loss method using the formula

$$CR = 534 W / DAT \text{ Mils per year (mpy)}$$

where, W = weight loss in milligrams, D = density of specimen g/cm^3 , A = area of specimen in square inches, T = exposure in hours.

Potentiodynamic Polarization

Polarization studies were carried out in a CHI electrochemical work station with impedance model 608 E. A three – electrode cell assembly was used. The working electrode was Aluminium metal. A SCE was the reference electrode. Platinum as the counter electrode. Both cathodic and anodic polarization curves were recorded in the absence and presence of the flower extract. From polarization studies, corrosion parameters such as corrosion potential (E_{corr}), corrosion current (I_{corr}), Tafel slopes anodic (β_a) and cathodic (β_c) were calculated and a linear polarization study was done. The scan rate (V/S) was 0.01. Hold time at E_r (s) was zero and quiet time (s) was two.

AC Impedance Spectra

The same instrument used for polarization study was used to record AC impedance spectra also. The real part (Z') and imaginary part (Z'') of the cell impedance were measured in ohms at various frequencies. Values of charge transfer resistance (R_t) and the double layer capacitance (C_{dl}) were calculated.

Scanning Electron Microscope

The nature of the film formed on the exterior of the Aluminium metal surface was analysed using SEM. The surface analysis of the polished Aluminium metal and the same in inhibited and uninhibited environment was investigated. Aluminium specimens were immersed in blank and in the inhibitor solutions for a period of 3 hours. The specimens were taken out rinsed with double distilled water, dried and witnessed under scanning electron microscopy to observe the surface morphology.

Results and Discussion

Weight loss method:

The weight loss study was carried out without and with the inhibitor. The concentration of the inhibitor was varied from 2 ml to 10 ml. Their corresponding IE and CR are tabulated in Table 1. It was observed that 8 ml of PE showed 97 % IE in 0.5N NaOH when compared with other systems. Hence this system was chosen as the best system for further studies. The results also indicates that as the IE increases the CR decreases. Hence it shows that the PE acts as a potent inhibitor for the corrosion of Aluminium in various alkaline solution [5].

Table 1The corrosion IE and the corresponding CR in mills per year (mpy) of PE in controlling the corrosion if Aluminium in various alkaline solution

PE in ml	0.5N NaOH		0.3N NaOH		0.1N NaOH	
	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)
0	0	2503	0	1298.15	0	775
2	64	1256.76	58	545.22	24	589
4	71	1019.64	66	441.371	36	496
6	88	421.92	76	311.556	43	441.75
8	97	105.48	86	181.741	57	333.25
10	67	1160.28	48	675.038	32	527

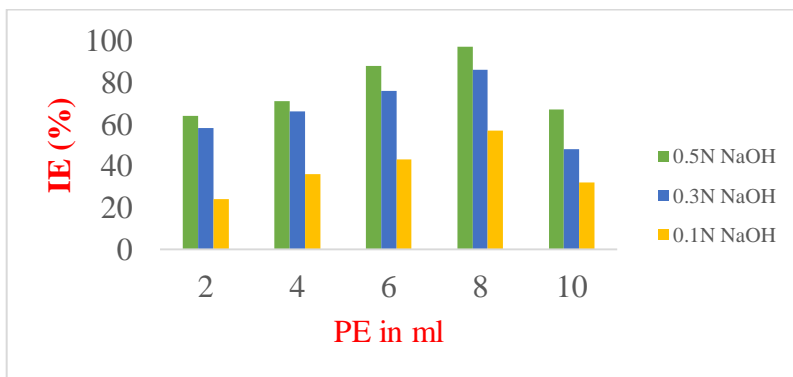


Figure 1 Graph of inhibition efficiency (IE) of PE in controlling the corrosion of Aluminium in various concentrations of NaOH solution

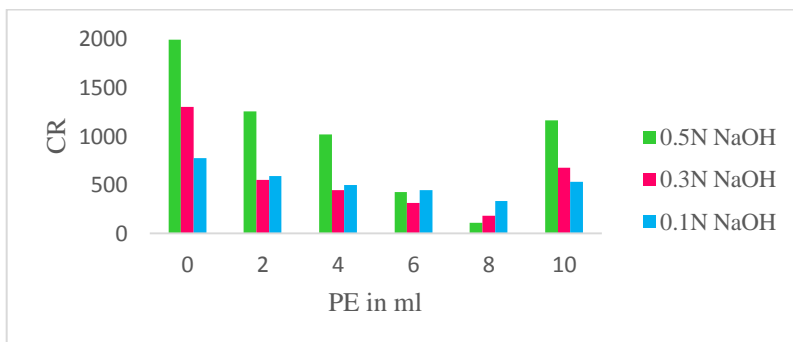


Figure 2 Graph of corrosion rate of PE in controlling the corrosion of Aluminium in various concentrations of NaOH

Effect of Temperature

The table 2 represents effect of temperature on the IE of Aluminium in alkaline and in the presence of different concentration of the inhibitors at various temperatures ranging from 303 K to 323 K for an immersion period of 3 hours. The value of IE, CR and the surface coverage (θ) are tabulated in. It was observed that the rate of corrosion increases with rise in temperature. However the CR is much decreased for the inhibited solution than the uninhibited solution. The decrease in the CR is due to the mitigating effect of the PE on the metal specimens [6].The IE was found to decrease as the temperature was increased from 303 K to 323 K. This shows that the adsorption of PE on the metal surface may be due to physical adsorption [7]. The high surface coverage data also implies that the adsorption of PE at the Aluminium interface may be due to the electrostatic force between the atoms on the metal surface and the adsorbate (inhibitor molecules) [8]. By plotting the values of θ versus $\log C$ and C/θ values versus C , straight line graphs were obtained (Figure 3 and 4), which showed that Temkin and Langmuir adsorption isotherms are obeyed.

Table 2 Effect of Temperature on the IE of the PE

PE in ml	303 K			313 K			323 K		
	IE (%)	θ	CR (mpy)	IE (%)	θ	CR (mpy)	IE (%)	θ	CR (mpy)
0	65	0.65	1233.7	69	0.69	1280.38	63	0.63	1353.5
2	79	0.79	259.07	74	0.74	332.89	69	0.69	419.58
4	85	0.85	185.05	80	0.80	256.07	78	0.78	297.77
6	90	0.90	123.37	86	0.86	179.25	82	0.82	243.63
8	96	0.96	49.34	93	0.93	89.6	91	0.91	121.81

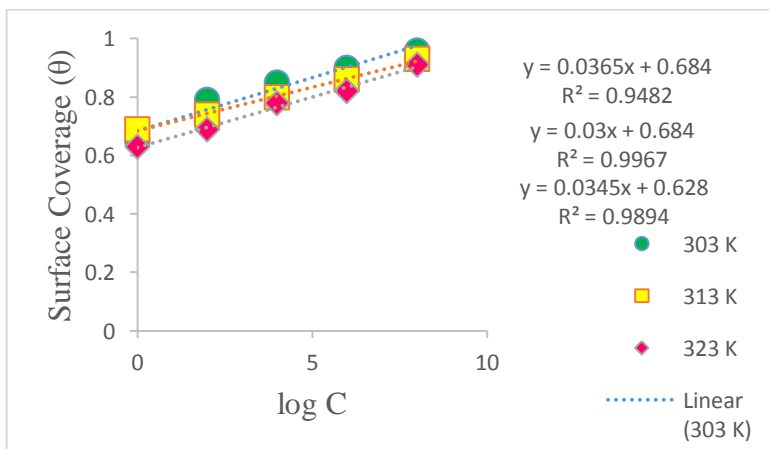


Figure 3 Temkin adsorption isotherm

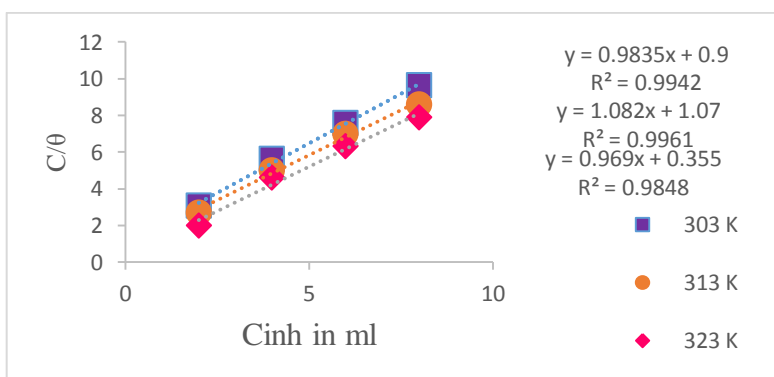


Figure 4 Langmuir adsorption isotherm

Analysis of Polarisation curves

Figure 5 shows the anodic and cathodic polarisation curves for Aluminium in 0.5N NaOH with and without various concentrations of PE. The numerical value of the potentiodynamic parameters such as corrosion potential (E_{corr}), corrosion current (I_{corr}), Tafel slopes (β_a and β_c) and linear polarisation resistance (LPR) are given in table 3. The I_{corr} value and the LPR value for 0.5N NaOH are 7.002×10^{-7} A/cm² and 54×10^3 ohm cm². For 8 ml PE the corrosion current value was decreased to 1.29×10^{-7} A/cm² and the LPR value was increased to 14×10^5 ohm cm². Table 3 indicates that as the concentration of the PE increases up to 8 ml, I_{corr} value decreases and the LPR value increases which confirm that, the degree of inhibition depends upon the inhibitor concentration till 8 ml and it can be mentioned here that the optimum concentration of the PE extract is 8 ml. When the Tafel slopes (β_a and β_c) are compared the shift in the cathodic slope (5.412 to 14.613 V/dec) is found to be greater than the shift in the anodic slope (5.924 to 10.926 V/dec) suggesting that the cathodic reaction is predominantly controlled by the system [9]. No definite trend was observed in the shift of E_{corr} value [10].

Table 3 Corrosion parameters for Aluminium in 0.5N NaOH solution

PE in ml	E_{corr} V VS SCE	I_{corr} A/cm ²	β_a (v/dec ⁻¹)	β_c (v/dec ⁻¹)	LPR ohm cm ²
0	-1.369	7.002×10^{-7}	5.924	5.412	54×10^3
2	-1.452	6.067×10^{-7}	4.456	5.911	69×10^3
4	-1.358	4.927×10^{-7}	4.900	6.430	77×10^3
6	-1.372	3.234×10^{-7}	6.437	7.436	96×10^3
8	-1.355	1.29×10^{-7}	9.708	12.040	14×10^5
10	-1.413	1.42×10^{-7}	10.536	14.613	13×10^4

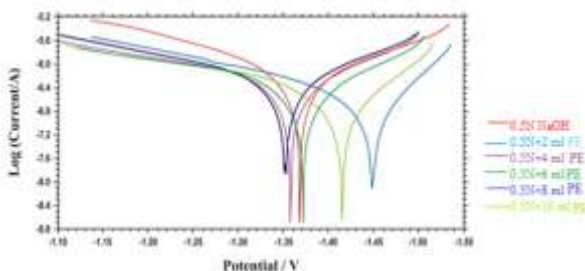


Figure 5 Polarization curves for Aluminium in 0.5N NaOH solution

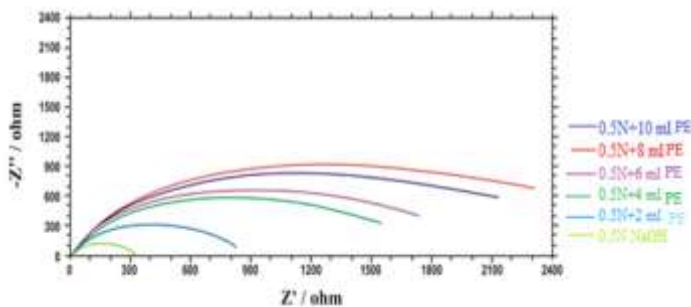
Analysis of AC impedance spectra

The formation of protective film on the metal surface can be detected using AC impedance spectra. The Nyquist representation for Aluminium in 0.5N NaOH in the absence and presence of various concentrations of PE is exposed in figure 6 and their corresponding impedance parameters such as R_t and C_{dl} are represented in the table 4. It was observed that the Nyquist plots are approximately semicircular in nature. The charge transfer process is responsible for the semicircular nature of the spectra, which mainly controls the corrosion of Aluminium. The increase in size and shape of the loop with the increase in concentration of the inhibitor may be attributed to the formation of protective layer on the metal surface and this further controls corrosion [11].

The impedance parameters such as charge transfer resistance (R_t) and double layer capacitance (C_{dl}) are given in table 4. When Aluminium metal was immersed in 0.5N NaOH the R_t value was 310 ohm cm². Addition of PE shifts the R_t value and reaches a maximum of 2320 ohm cm² at 8 ml. Correspondingly their C_{dl} value decreases from 2.9185×10^{-8} F/cm² to 3.899×10^{-9} F/cm². This decrease in C_{dl} value with the increase in R_t value suggests the formation of protective film on the surface of the Aluminium metal [12].

Table 4 Impedance parameters of Aluminium in 0.5N NaOH solution

System	Nyquist plot	
	R_t ohm cm^2	C_{dl} F/ cm^2
Blank	310	2.9185×10^{-8}
2 ml P.E	830	1.1150×10^{-8}
4 ml P.E	1570	5.7627×10^{-9}
6 ml P.E	1730	5.229×10^{-9}
8 ml P.E	2320	3.899×10^{-9}
10 ml P.E	2150	4.20813×10^{-9}

**Figure 6 AC impedance spectra of Aluminium immersed in 0.5N NaOH and various concentrations of the inhibitor**

Thermodynamic parameters

The calculated values like apparent activation energy (E_a), heat of adsorption (Q_{ads}), and free energy adsorption (ΔG_{ads}) for different concentrations of the PE are shown in table 5. The results showed that E_a increases as inhibitor concentration increases. E_a of PE varies between 78.6 and 110.5 KJ/mol. Corrosion primarily occurs at surface sites free of adsorbed inhibitor, the higher E_a values in inhibited solutions imply that extracts mechanically screen the active sites of Aluminium surface thereby decreasing the surface area available for corrosion.

The heat of adsorption, Q_{ads} were all negative and ranged from -14.28 to -46.63 KJ/mol for PE. The negative Q_{ads} value indicate adsorption and hence inhibition efficiency decreases as temperature increases, supporting the earlier proposed physisorption mechanism.

The free energy adsorption ΔG_{ads} , were all negative in the temperatures under study. This indicates the adsorption of inhibitor on the surface of Aluminium, and it was proposed that it may be physical adsorption ($\Delta G_{ads} < 40$ KJ/mol) [13]. Generally, the values of ΔG_{ads} around -20 KJ/mol or less negative are consistent with physisorption while those around -40 KJ/mol or more negative values involve chemisorptions [14].

Table 5 Thermodynamic parameters for the corrosion of Aluminium in 0.5N NaOH at different temperatures

PE in ml	Activation energy, E_a (KJ/mol)	Heat of adsorption Q_{ads} (KJ/mol)	Free energy change ΔG_{ads} (KJ/mol) of adsorption at 303 K	Free energy change ΔG_{ads} (KJ/mol) of adsorption at 313 K
0	78.6	-14.28	-11.67	-11.67
2	82.6	-21.99	-13.45	-12.75
4	85.8	-27.46	-14.49	-13.61
6	92.6	-30.12	-15.65	-14.69
8	110.5	-46.63	-18.12	-16.63

Surface Analysis

Scanning Electron Microscope (SEM) was used to examine the surface of the Aluminium species. The Aluminium species before and after immersion in the absence and presence of the inhibitor for a period of 3 hours were taken out, washed carefully with distilled water, dried and kept in desiccator. The SEM micrographs of the examined surfaces are shown in figure 7 (a,b,c). The SEM micrograph of the polished Aluminium metal surface was smooth in the absence of any corrosion products and was heavily damaged when immersed in 0.5N NaOH. It occurred as a result of the attack of the corrosive solution in the absence of the inhibitor. On addition of the inhibitor there was an improvement in the metal surface. This improvement in surface morphology was due to the formation of a good protective film which was responsible for the inhibition of corrosion [15].

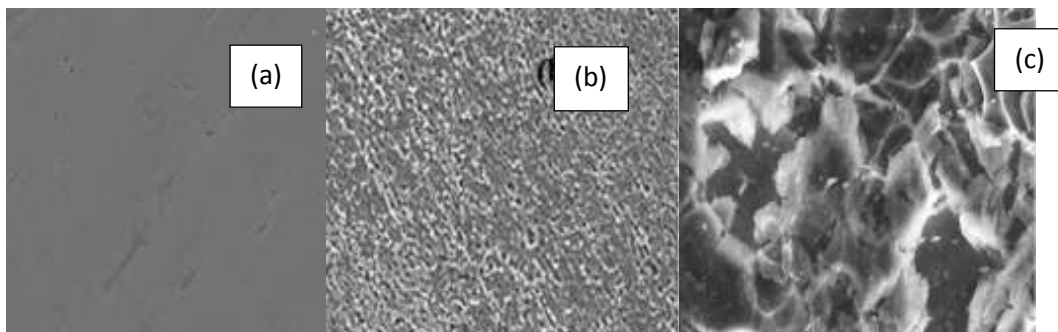


Figure 7 SEM micrographs of a) Polished Aluminium metal (control), b) Aluminium metal immersed in 0.5N NaOH, c) Aluminium metal immersed in 0.5N NaOH containing 8 ml of PE

Conclusion

It was found that the *Chrysanthemum* flower extract acts as a potent inhibitor for the corrosion of Aluminium in 0.5N NaOH solution. The inhibition efficiency is found to increase with the increases in the concentration of the inhibitor. IE of 97% was observed on addition of 8 ml of PE. Potentiodynamic polarisation curves prove that the inhibitor predominantly controls the cathodic reaction. The adsorption of inhibitor on the metal surface was best explained by Langmuir and Temkin adsorption isotherms. The SEM analysis proves the formation of protective film on the metal surface.

References

1. Riggs O L, Corrosion inhibitors, NACE, Houston, TX, 1973, pp. 11.
2. Makanjuola Oki, Kayode Oki, John Otaigbe and Samuel Otokor, Corrosion Inhibition of Aluminium in HCl by Amine Modified Epoxy Resin, J Materials, 2013;2013: 1-5.
3. Obot I B, Obi-Egbedi N O and Umoren S A, Adsorption Characteristics and Corrosion inhibitive properties of Clotrimazole for Aluminium Corrosion in hydrochloric acid, Int J Electroche Sci., 2009; 4: 863-877.
4. Fouda A S, Aggour Y, Bekhit G and Ismaili M A, Moringa Oleifera leaves extract as green corrosion inhibitor for Zinc in polluted sodium chloride solution, Int J Advanced Research, 2014; 2: 1158-1170.
5. Joseph Rathish R, Rajendran S, Lydia Christy J, Corrosion behaviour of metals in artificial sweat, The Open Corrosion Journal, 2010; 3: 38.
6. Sirajunnisa A, Fazal Mohamed M I and Subramania A, Influence of aqueous extract of sida acuta leaves on corrosion inhibition of Aluminium in alkaline solution, Der Chemica Sinica, 2014; 5: 148-156.
7. Leelavathi S and Rajalakshmi R, Dodonaea viscosa (L.) Leaves extract as acid Corrosion inhibitor for mild steel-A Green approach, Int J Mat Environmental Sci., 2013; 4: 625-638.
8. Sharma Y C and Sharma S, Corrosion inhibition of Aluminium by Psidium Guajava seeds in HCl solution, Portugaliae Electrochimica Acta, 2016; 34: 365-382.
9. Namrata Chaubey, Savitha, Vinod Kumar Singh and Quraishi M A, Corrosion inhibition performance of different bark extracts on aluminium in alkaline solution, J the association of Arab Universities for basic and applied sciences, 2017; 22: 38-44.

10. Hui Cang, Zhenghao Fei, Jinling Shao, Wenyan Shi, Qi Xu, IntJ Electrochem. Sci., vol. 8, (2013) pp 720-734.
11. Aprael S. Yaro, Anees A. Khadom, Rafel K. Wael, Apricot juice as green inhibitor of mild steel in phosphoric acid, Alexandria Engineering Journal, vol. 52, (2013) pp 129-135.
12. Jasna Halambek, Anja Zutinic, Katarina Berkovic, Ocimum basilicum L. oil as corrosion inhibitor for Aluminium in Hydrochloric acid solution, Int J Electrochem. Sci., 2013; 8:11201 – 11214.
13. Alinnor I J and Ejikeme P M, Corrosion Inhibition of Aluminium in Acidic Medium by Different Extracts of Ocimum gratissimum, American Chemical Science Journal, 2012; 2: 122-135.
14. Mathina A and Rajalakshmi R, Corrosion inhibition of mild steel in acid medium using Canna indica as green corrosion inhibitor, Rasayan J Chem., 2016; 9: 56-66.
15. Lakshmi Prabha K, Shameela Rajam, Corrosion inhibition of Aluminium in Alkaline medium using Cyanodon dactylon leaves extract, World Journal of Pharmacy and Pharmaceutical Sciences, 2014; 3: 822-835.
