

Composites of Graphene Oxide and Zeolite as a Potential Inhibitor for Alkaline Corrosion of Aluminium

B. M. Daas^{1*}, P. K. Ghosh² and S. Ghosh²

¹Department of Chemistry, Government Degree College, Dharmanagar – 799253, Tripura, India; basu.maandaas@visva-bharati.ac.in

²Integrated Science Education & Research Centre, Visva-Bharati, Santiniketan – 731235, West Bengal, India; chemistpradip88@gmail.com, susanta.ghosh@visva-bharati.ac.in

Abstract

Background/Objective: Metals and alloys react with corrosive media to form a stable compound, which results loss of metal and the metal surface gets corroded. Aluminium has a lot of application and so resisting aluminium corrosion is a vital step. **Methodology:** The inhibition ability of graphene oxide composite with ZSM-5 and MCM-41 towards aluminium corrosion in 0.01 M NaOH solution was studied using weight-loss measurement, potentiodynamic polarization curves, and SEM-EDS methods. **Findings:** The data from weight loss measurements, tafel plots, SEM micrographs and amperometric study in alkaline medium compared to blank solution indicated an enhancement of inhibition efficiency of graphene in the form of composite with ZSM-5 and MCM-41. SEM-EDS analyses confirmed less corrosion damage of aluminium owing to the surface adsorption of the composites. **Application:** This interesting study can be very vital in the field of corrosion and battery science mainly in Al-air cell.

Keywords: Aluminium, Corrosion, Corrosion Inhibition, Graphene Oxide-Zeolite Composite, Zeolites

1. Introduction

Aluminium (Al) is a second choice after iron for multiple applications¹. Al is thermodynamically very reactive but in most natural environments it is stabilized by formation of a thin protective oxide layer. However, it succumbs to localized pitting corrosion, due to inter metallic inclusion which leads to exfoliation corrosion which hampers its utilization in various applications^{2,3}.

Al-air batteries have high theoretical energy density (gravimetric and volumetric) because of its high electrical conductivity with standard potential of 1.676 V vs. Standard Hydrogen Electrode (SHE)^{4,5}. But during the electrochemical processes when Al comes in contact with alkaline solution in Al-air battery, it undergoes rapid corrosion^{6,7}. Al corrosion is associated with passivation of the cathode active material, deposition of its solid products on to electrode surface which increase the electrical resistance, and its soluble products contaminate the

electrolyte increasing the self-discharge rate that hampers implementation of Al-air batteries as sustainable energy storage system⁸. So, it is extremely necessary to overcome the corrosion problem for constant performance of Al-air battery using corrosion inhibitors, either to the metal or to the electrolyte.

Various methods are used to reduce Al-corrosion rate; use of corrosion inhibitor is most popular. Corrosion inhibitors get adsorbed on Al-surfaces creating corrosion resistant layers and reduce corrosion rate mainly by either increasing or decreasing anodic or cathodic reactions, decreasing diffusion rate for corrosive reactants and increasing electrical resistance. Price, toxicity, availability and environment-friendliness of inhibitors are vital for large-scale applications^{9,10}.

Graphene, an environment friendly, low cost, chemically inert and nontoxic 2-d monoatomic sp² hybridized carbon nanostructure, is a strong candidate for corrosion resistance and protective coating on metal¹¹⁻¹⁷. It

* Author for correspondence

can easily be converted to water dispersible graphene oxide (GO) by simplified or modified Hummer method¹⁸⁻²³. GO can provide an anti-corrosion protection layer without affecting electrical and optical properties of coated surface which is very useful for various applications³. However, inhibition efficiency for GO decreases on formation of a multi-layer coating onto metal surfaces which retard ion transport and oxygen diffusion.

Silica (SiO_2) has excellent corrosion inhibition properties on metal surfaces due to interaction between metal and -O-Si-O-Si-O- network²⁴⁻²⁸. But its application creates micro-cracks on surface that permeates corrosive reactants; however, application of nanoparticles as corrosion inhibitor onto metal surfaces can increase corrosion protection by decreasing roughness factor²⁹⁻³². Zeolites are non-toxic aluminosilicates, effective in inhibiting metal surfaces in both acidic and alkaline media.

Corrosion inhibition of zeolite coatings seems independent of coating thickness and an ultrathin coating of a few hundreds of nanometers is sufficient. A condensation reaction between anodized aluminium and Al-O-Si covalent bonds of zeolites occur to form a zeolitic coating^{33,34}. So, GO:zeolite composites in ultrathin layers can be potential corrosion inhibitors.

2. Materials and Methods

99.9% pure Al-rod (from Johnson Matthey, UK); 99.9995% pure graphite powder (from Alfa Aesar, US); ZSM-5, with $\text{SiO}_2:\text{Al}_2\text{O}_3$ ratio of 30 ± 5 , Si:Al ratio of 38 and MCM-41, with $\text{SiO}_2:\text{Al}_2\text{O}_3$ ratio of 20 (from Greenstone, Switzerland); HCl (98.0%), H_2SO_4 (98.0%), H_2O_2 , NaOH and NaNO_3 of analytical grade (from Merck, India); KMnO_4 (from BDH Corporation, India); and triple-distilled water were used at room temperature (RT).

2.1 Synthesis of Graphene Oxide

Graphene oxide (GO) is prepared by Hummers method. Into 40 mL concentrated H_2SO_4 , 1 g of graphite powder and 0.5 g of NaNO_3 were added at RT and stirred for 15 minutes in ice-bath. 5 g of KMnO_4 is slowly added to prevent temperature $> 20^\circ\text{C}$. It was stirred for 3 h in ice-bath and then stirred overnight for 18 h under RT. Temperature of mixture was raised to 35°C in another 30

min, with constant stirring; mixture gradually thickened into a brownish grey colored paste. 80 mL distilled water was added into the paste in 15 min, maintaining temperature $> 80^\circ\text{C}$. Resulting solution was then cooled down to RT under tap water and preserved for another 10 min. The suspension was further diluted with distilled water to 245 mL approximately, followed by addition of 40 mL of 3% H_2O_2 ; the suspension turned bright yellow. It was filtered, resulting biscuit-colored filter cake was washed thrice with 3% diluted HCl and warm water. GO produced was dried for few days in vacuum. GO solution was obtained by exfoliating graphite oxide in distilled water with ultrasonic vibration for 45 min.

2.2 Characterization

GO was characterized employing various spectroscopic techniques, such as (i) UV-visible spectroscopy by Lambda 35 Perkin Elmer UV/VIS spectrometer; (ii) Fourier transform infrared spectroscopy (FTIR) by Shimadzu FTIR 8400S; (iii) Powder x-ray diffraction (XRD) by Ultima IV Rigaku ($\text{CuK}\alpha$, $\lambda = 1.5406\text{\AA}$); (iv) Selected area electron diffraction (SAED) by SAED by JEOL JEM-2100 S; (v) Raman spectroscopy by Olympus BX41 and TRIAX iHR 550; (vi) Thermo gravimetric analysis (TGA) by Perkin Elmer STA 6000; (vii) Fluorescence spectroscopy by Perkin Elmer LS 55; and (viii) Transmission electron microscopy (TEM) by Tecnai G2 20 S-Twin. ZSM-5 and MCM-41 were characterized employing (i) Powder x-ray diffraction (XRD) by Ultima IV Rigaku ($\text{CuK}\alpha$, $\lambda = 1.5406\text{\AA}$); (ii) Transmission electron microscopy (TEM) by Tecnai G2 20 S-Twin; and (iii) Scanning electron microscope (SEM) and Energy dispersive spectroscopy (EDS) analysis by Jeol JSM-6390.

3. Results and Discussion

3.1 Characterization Results

3.1.1 UV-Vis Analysis of GO

UV-VIS spectrum recorded in wavelength region of 200 - 800 nm by dispersing GO in distilled water shows two distinct absorption maxima (λ_{max}) at 230 nm and 305 nm; former is mainly due to $\pi \rightarrow \pi^*$ transition of C=C bond and latter is attributed to $n \rightarrow \pi^*$ transition of carbonyl groups²¹ are shown in Figure 1.

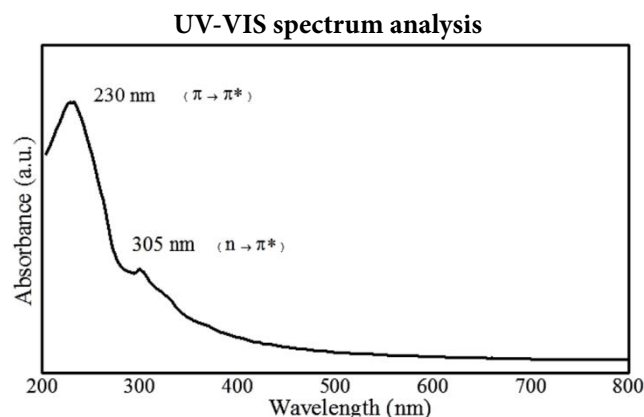


Figure 1. UV-VIS absorption spectrum of GO.

3.1.2 FTIR Analyses of GO & Graphite

FTIR spectra were recorded to confirm different functional groups present with vacuum dried samples of GO and graphite in wave-number region of 500 - 4000 cm^{-1} after preparing KBr pellets of samples are shown in Figure 2.

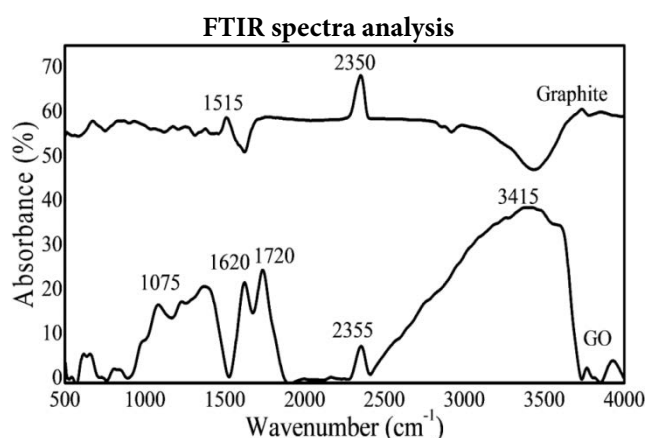


Figure 2. FTIR spectra of graphite and GO.

Peak at 3415 cm^{-1} is credited to O-H stretching, at 1720 cm^{-1} is credited to C=O stretching vibration, at 2355 cm^{-1} is credited to symmetric and asymmetric C-H stretching mode and peaks at 1620 cm^{-1} is credited to C = C stretching vibration in unoxidized sp^2 C=C bonds. Peak at 1075 cm^{-1} is credited to C-O vibrations of GO^{20,21}.

3.1.3 XRD Analyses of GO, Graphite & Zeolites

Powder XRD diffraction were performed with solid samples in region of $2\theta = 5 - 70^\circ$ to verify the crystalline nature of graphite oxide, GO, ZSM-5 and MCM-41 is shown in Figure 3.

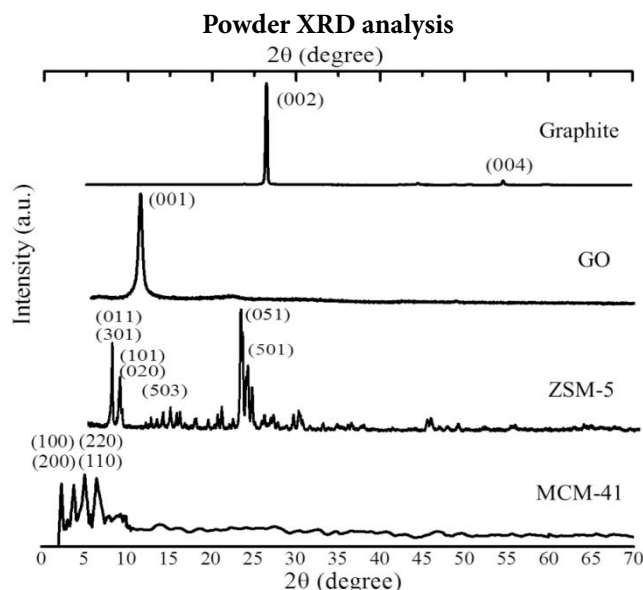


Figure 3. Powder XRD of graphite, GO, ZSM-5 & MCM-41.

A distinct diffraction peak at 10.93° for GO for (001) plane and two distinct diffraction peaks at 26.47° for (002) plane and at 54.5° for (004) plane of graphite are observed. Interlayer distance values for graphite (d_{002}) and GO (d_{001}) are found to be 0.34 nm and 0.8 nm, respectively. Increase in interlayer spacing value of GO is attributed to the presence of oxygen functional groups to carbon basal plane via chemical oxidation reaction and some other structural defects^{15,20}. Distinct diffraction peaks, (301) and (011) at 7.9° , (101) and (020) at 8.8° , (503) at 14.8° , (051) at 23° and (501) at 23.86° confirm ZSM-5, and distinct diffraction peaks, (100), (110), (200) and (210) within $2 - 7^\circ$ confirm MCM-41³⁵.

3.1.4 SAED Analyses of GO & Zeolites

SAED analysis performed to verify crystalline environment shows that a perfect six part ring patterns in GO which is attributed to crystalline environment of GO that validate result of powder XRD spectroscopy³⁶⁻³⁸ is shown in Figure 4.

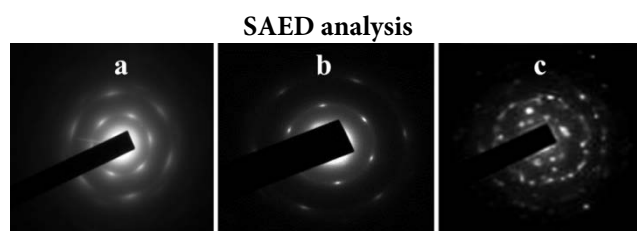


Figure 4. SAED images of (a) GO, (b) ZSM-5 and (c) MCM-41.

Figure 4b and Figure 4c both show crystalline nature of ZSM-5 and MCM-41, former being more crystalline than the latter.

3.1.5 Raman Analyses of GO & Graphite

Raman spectra of graphite oxide and GO were recorded at $1000\text{--}3500\text{ cm}^{-1}$ by $\lambda = 488\text{ nm}$, 50 xL objectives lens to realize structural properties are shown in Figure 5. 'G' band is credited to inplane vibration of sp^2 carbon atoms of GO and graphite samples, whereas 'D' band is credited to a breathing mode of a K-point photons of A_{1g} symmetry for GO^{19,21,39}. GO shows a prominent D band at $\sim 1350\text{ cm}^{-1}$ with an intensity comparable to 'G' band at $\sim 1587\text{ cm}^{-1}$ whereas, graphite shows only one 'G' band at $\sim 1581\text{ cm}^{-1}$.

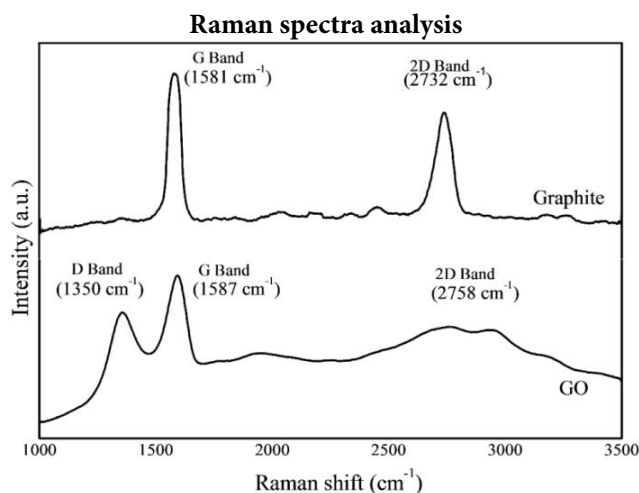


Figure 5. Raman spectra of graphite and GO.

Besides, 2D band at 2758 cm^{-1} arises from a two photon double resonance Raman process confirming successful formation of GO.

3.1.6 TGA Analyses of GO & Graphite

TGA analyses of graphite and GO were analyzed by heating from 40 to $800\text{ }^{\circ}\text{C}$, at a rate of $20\text{ }^{\circ}\text{C min}^{-1}$ is shown in Figure 6.

Graphite shows a very negligible weight loss up to $800\text{ }^{\circ}\text{C}$, around 8.45% of its total weight. But GO shows constant weight loss from very beginning due to removal of adsorbed moisture; however, a major weight loss, up to 99.3% of its total weight, is observed around $200\text{ }^{\circ}\text{C}$ with

an exothermic peak. Major weight loss of GO is attributed to pyrolysis of oxygen bearing functional groups linked with $\text{GO}^{21,40}$. TGA analyses clearly confirm that thermal stability of GO is very less compared to graphite.

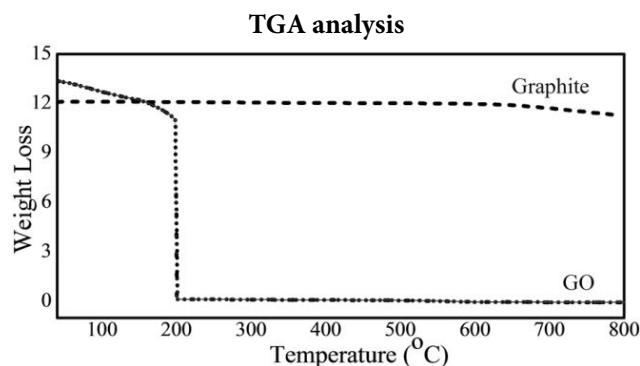


Figure 6. TGA curves of Graphite and GO.

3.1.7 Fluorescence Analysis of GO

Emission measured with 280 nm and 440 nm excitation at the pH of GO suspension ($\text{pH} = 5.3$) shows a broad peak near 625 nm attributed to exposure of more H_2O molecules with exfoliation of GO thus layer enhancing polarity of solution⁴¹⁻⁴⁴ is shown in Figure 7.

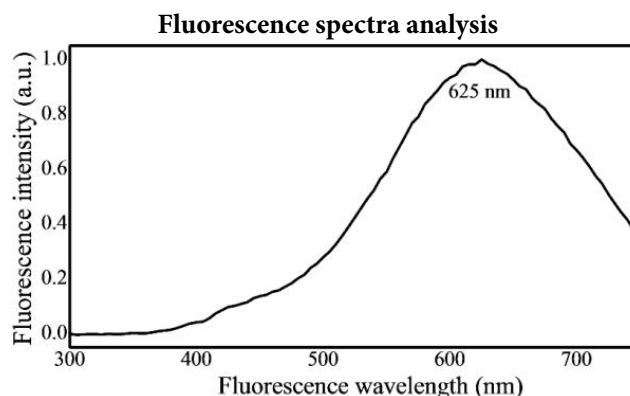


Figure 7. Fluorescence spectra of GO.

3.1.8 TEM Analyses of GO & Zeolites

A small droplet of dispersed sample was added to copper grid and allowed to dehydrate for 24 h and then TEM images were taken at resolution $2.4\text{ \AA}$ is shown in Figure 8.

Determined by image J software, particle sizes of ZSM-5 are around 200 nm . The sizes of MCM-41 are on higher side of 200 nm ^{45,46}.

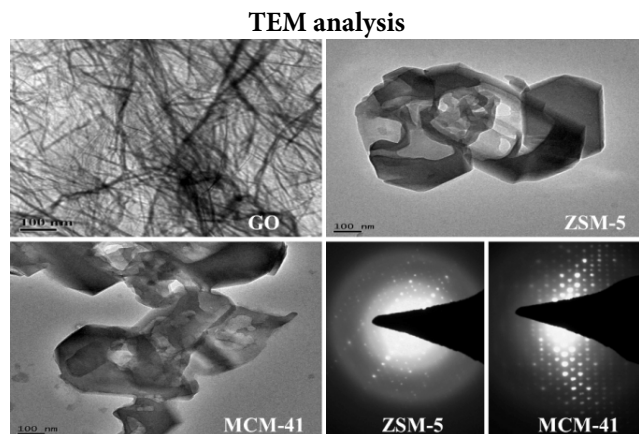


Figure 8. TEM micrographs of GO, ZSM-5 and MCM-41.

3.1.9. SEM-EDS Analyses of Zeolites

In SEM micrograph of ZSM-5 is shown in Figure 9a, particle sizes are 150-200 nm as determined by imageJ software. Again from EDS analysis, it is found that weight percentage (wt%) of Si, Al and O are approximately 53, 22 and 25 % respectively confirming ZSM-5 is shown in Figure 9c.

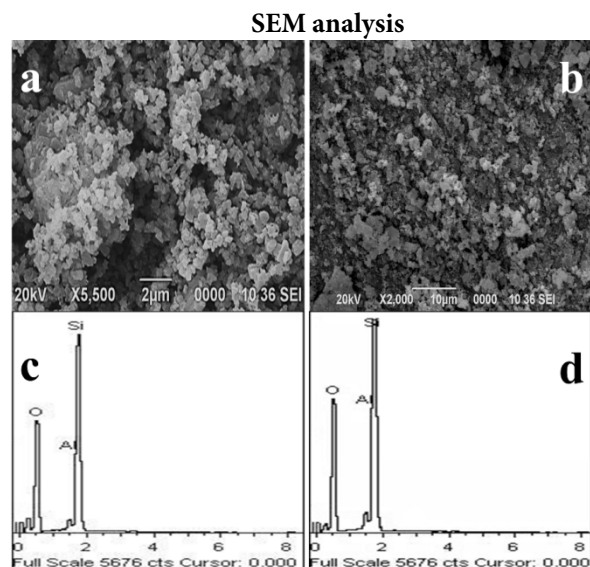


Figure 9. SEM micrographs of (a) ZSM-5 and (b) MCM-41. EDS analysis of (c) ZSM-5 and MCM-41.

In SEM image of MCM-41 is shown in Figure 9b, particle sizes > 200 nm. EDS spectrum of MCM-41 is shown in Figure 9d proves presence of elements of MCM-41 with weight percentage (wt%) of Si, Al and O were approximately 57, 21 and 22% respectively which confirms MCM-41.

3.2 Corrosion Analysis

3.2.1 Weight Loss Study of Corrosion

Weight loss study is chemical analysis of corrosion⁴⁷. Initial weight loss of Al was determined at RT in absence and presence of potential corrosion inhibitors (GO, GO:ZSM-5 or GO:MCM-41 composite) in a corrosive alkaline solution. Blank system contained 10 mL of 0.01 M NaOH solution and 10 mL of triple-distilled H₂O while system with potential corrosion inhibitors contained 10 mL of 0.01 M NaOH solution, 5 mL of 0.5 g L⁻¹ aqueous solution of potential corrosion inhibitor and 5 mL of triple-distilled H₂O. Weighed Al-foils of dimension 1 × 1 × 0.1 cm³ were suspended in 50 mL beakers containing 25 mL of three potential corrosion inhibitor solutions for 1 day. Then the Al-foils were cautiously washed with triple-distilled water and dil. acetone to halt further corrosion. After drying in a stream of air at RT, foils were stored in a desiccator. Then the dried mass of Al-foils were recorded. The experiments were repeated thrice for average.

Corrosion Rate (V_{corr}) of Al is calculated from V_{corr} (mm y⁻¹) = $k\Delta w / DA t$ (1)

where, Δw = Corrosion weight loss of Al (g), D = Metal density in g cm⁻³, A = Surface area of Al-rod (cm²); and t = Time of contact (h)⁴⁸⁻⁵⁰. Here, $K = 8.76 \times 10^4$, $D = 2.70$ g cm⁻³, $A = 2.4$ cm², and $t = 24$ h.

Degree of surface coverage (θ) is calculated from $\theta = (\Delta w^0 - \Delta w) / \Delta w^0$ (2)

where, Δw^0 = Weight loss without potential corrosion inhibitor (g), and Δw = Weight loss with potential corrosion inhibitor (g)⁵¹.

Finally, as there is a direct relationship between η (%) and θ , Percentage Inhibition Efficiency, η (%), is calculated from

$$\eta(\%) = \frac{[(\Delta w^0 - \Delta w) / \Delta w^0] \times 100}{[(V_{\text{corr}}^0 - V_{\text{corr}}) / V_{\text{corr}}^0] \times 100} \quad (3)$$

where, V_{corr}^0 and V_{corr} are corrosion rates of Al in 0.01 M NaOH in absence and presence of potential corrosion inhibitors^{50,52-56} (Figure 10).

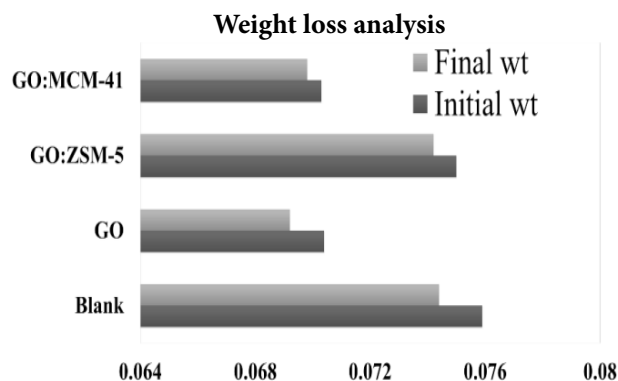


Figure 10. Weight loss for blank, GO, GO: ZSM-5 and GO: MCM-41.

$\eta(\%)$ of Al-foils in absence and presence of potential corrosion inhibitors in 0.01 M NaOH solution by weight loss measurement in Table 1 and Figure 10 show that GO acts as Al-surface protector but GO:ZSM-5 and GO:MCM-41 composites are better stronger inhibitors may be due to effective surface coverage of Al which increases by preferred adsorption of zeolites; GO:MCM-41 composite shows maximum inhibition efficiency.

3.2.2 Potentiodynamic Polarization Study of Corrosion

Corrosion rates calculated from weight losses can be misleading in highly localized pitting corrosion of aluminium; potentiodynamic polarization study is better than classical weight loss estimation as corrosion is an electrochemical process and potentiodynamic polarization study is electrochemical analysis^{47,49}.

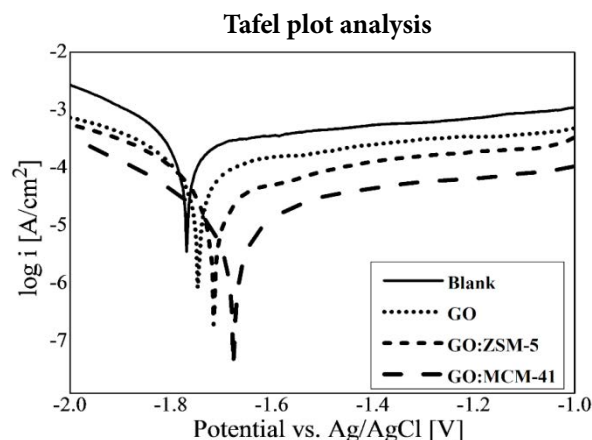


Figure 11. Tafel plots of blank, GO, GO:ZSM-5 and GO:MCM-41.

It was performed to measure corrosion potential (E_{corr}) and corrosion current (i_{corr}) of Al in 0.01 M NaOH solution in absence and presence of potential corrosion inhibitors using a Autolab Cyclic voltammeter (Model PGSTAT128N) at 300 K (Figure 11).

It was executed by exposing Al-rod of 3.5 cm² area as working electrode, platinum metal as counter electrode and a saturated Calomel electrode (SCE) as reference electrode. Al-surface was polished with silicon carbide (SiC) abrasive paper, washed with triple distilled water and acetone and dried in warm air. Prior to each experiment, working electrode was immersed in electrolyte for 30 min to achieve equilibrium. Polarization measurements were performed over a potential range from - 0.25 V to + 0.25 V vs. Ag/AgCl electrode w.r.t. open circuit potential (OCP) at a scan rate 0.5 mV s⁻¹.

Table 1. Weight loss, corrosion rate, degree of surface coverage and percentage inhibition efficiency, for Blank, GO, GO:ZSM-5 and GO:MCM-41

Inhibitor	Initial wt. W_i (g)	Final wt. W_f (g)	Weight loss	Average wt. loss ΔW (g)	V_{corr} (mm y^{-1})	θ	$\eta(\%)$
Blank	0.0759	0.0744	0.0015	0.0015	8.45	-	-
	0.088	0.0864	0.0016				
	0.0892	0.0875	0.0017				
GO	0.0992	0.0991	0.0001	0.0012	6.76	0.2	20
	0.0704	0.0692	0.0012				
	0.0768	0.0754	0.0014				
GO:ZSM-5	0.075	0.0742	0.0008	0.0008	4.51	0.47	46.67
	0.0881	0.0874	0.0007				
	0.0777	0.0768	0.0009				
GO:MCM-41	0.0893	0.0887	0.0006	0.0005	2.82	0.67	66.67
	0.0796	0.0792	0.0004				
	0.0703	0.0698	0.0005				

Linear tafel segments of anodic and cathodic curves were extrapolated to find i_{corr} values. Corrosion Rate (V_{corr}) is determined by extrapolation for polarization curves near corrosion potential (E_{corr}) from

$$V_{\text{corr}} (\text{mm y}^{-1}) = 3272 \cdot i_{\text{corr}} \cdot \text{eq} / AD \quad (4)$$

where, i_{corr} = Corrosion current density, eq = Electrochemical equivalent of Al, A = Surface area of Al-rod (cm^2), and D = Metal density (g cm^{-3})⁵⁶. Here, eq = 0.09316, D = 2.70 g cm^{-3} , and A = 2.4 cm^2 .

θ and $\eta(\%)$ were calculated from (R_p) values obtained from linear polarization data from

$$\theta = (i_{\text{corr}}^0 - i_{\text{corr}}) / i_{\text{corr}}^0 \quad (5)$$

and

$$\eta(\%) = [(i_{\text{corr}}^0 - i_{\text{corr}}) / i_{\text{corr}}^0] \times 100 \quad (6)$$

where, i_{corr}^0 and i_{corr} are corrosion current densities of Al in 0.01 M NaOH in absence and presence of potential corrosion inhibitors⁵⁶.

A close inspection of Figure 11 clearly indicates that i_{corr} decreased noticeably with introduction of potential corrosion inhibitors and descending order of current density is Blank > GO > GO:ZSM-5 > GO:MCM-41. Again, Al without any potential corrosion inhibitor has highest current density (i_{corr}^0) along with most cathodic corrosion potential (E_{corr}) which implies highest corrosion rate³⁴. In presence of potential corrosion inhibitors, E_{corr} shifts towards less -ve values implying suppression of anodic reaction on Al-surface⁵⁶⁻⁵⁹. Descending order of corrosion potential as Blank > GO > GO:ZSM-5 > GO:MCM-41 may be explained by physical adsorption process in which adsorbed inhibitor, GO composite ZSM-5 and MCM-41 molecules, may undergo surface reaction; producing surface coating. Obtained $\eta(\%)$ values were in agreement with values of weight loss measurements (Table 2).

Table 2. Parameters measured during the corrosion tests

Inhibitor	E_{corr} (V)	i_{corr} ($\mu\text{A.cm}^{-2}$)	V_{corr} (mm.y^{-1})	θ	$\eta(\%)$
Blank	-1.72	213.9	0.010	-	-
GO	-1.75	114.8	0.005	0.46	46.32
GO:ZSM-5	-1.73	94.2	0.004	0.56	55.96
GO:MCM-41	-1.70	75.8	0.003	0.65	64.55

3.2.3 SEM-EDS Study of Corrosion

Surface morphology of Al in absence and presence of potential corrosion inhibitors in 0.01 M NaOH solution were analyzed by scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS) (Figure 12, Figure 13).

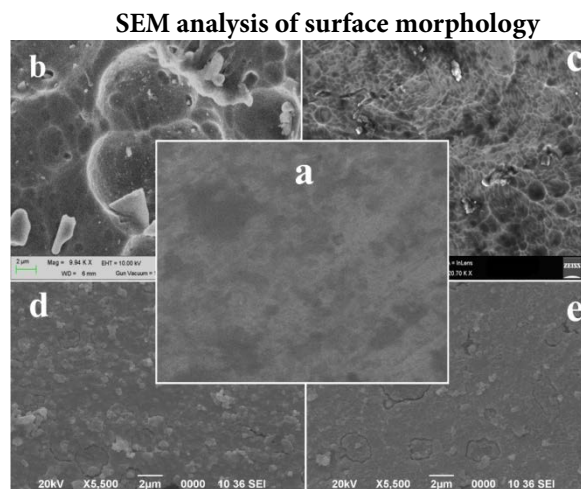


Figure 12. SEM of Al-surface (a) Uncorroded, and corroded by NaOH with (b) blank, (c) GO, (d) GO:ZSM-5, (e) GO:MCM-41.

SEM and EDS analyses indicate changes of surface morphology with corrosion of Al in presence of potential corrosion inhibitors in alkaline environment. SEM micrograph of bare and uncorroded Al shows a more or less uniform pattern (Figure 12a).

SEM micrographs of Al-surface immersed in 0.01 M NaOH solution in absence (Figure 12b) and presence (Figure 12c) of GO indicate more corrosion in absence of GO than that in presence of GO. SEM micrographs of Al-surface immersed in 0.01 M NaOH solution in presence of GO:ZSM-5 (Figure 12d) and GO:MCM-41 (Figure 12e) confirm better corrosion inhibition credited to formation of an improved defensive layer by GO: zeolite composite. Wt% of Al in presence of GO, GO:ZSM-5 and GO:MCM-41 further validates corrosion inhibition by the potential corrosion inhibitors (Figure 13).

As 99.9 % pure Al was used, so we can assume that weight and atomic percentage of Al initially was 100 %.

Then corroded Al-surface in presence of GO, GO:ZSM-5 and GO:MCM-41 (Table 3) confirm that Al is preserved more by potential corrosion inhibitors; in order of GO < GO:ZSM-5 < GO:MCM-41; it is again confirmed that these potential corrosion inhibitors are really effective.

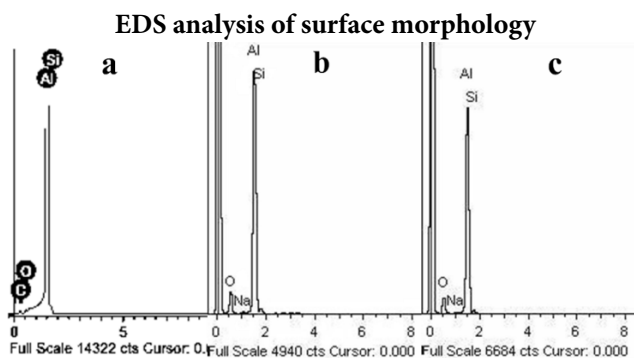


Figure 13. EDS of Al-surface in 0.01 M NaOH solution in presence of (a) GO, (b) GO:ZSM-5, (c) GO:MCM-41.

Table 3. Weight and atomic percentage of elements

Inhibitor	Element	Weight%	Atomic%
GO	Si	1.25	1.08
	Al	88.91	79.85
	O	1.54	2.34
	C	8.29	16.73
GO:ZSM-5	Si	1.79	1.43
	Al	68.74	57.25
	O	29.3	41.16
	Na	0.17	0.16
GO:MCM-41	Si	2.75	2.18
	Al	65.73	54.17
	O	31.17	43.31
	Na	0.35	0.34

3.2.4 Amperometric Study of Corrosion

Amperometric analysis of systems with and without potential corrosion inhibitors was done to verify current generated due to corrosion reaction (Figure 14).

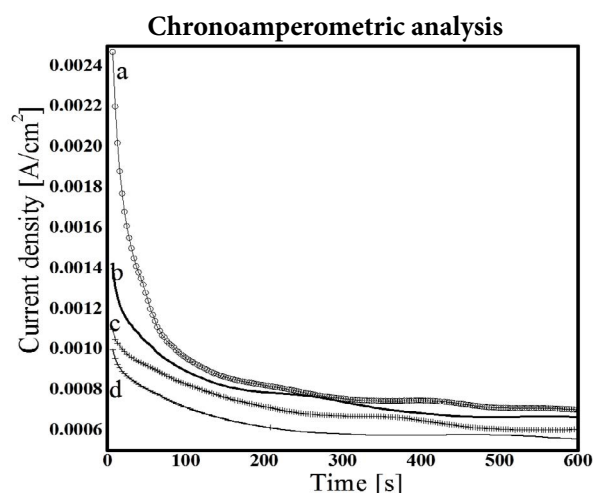


Figure 14. Chronoamperometric analysis in 0.01 M NaOH with (a) blank, (b) GO, (c) GO:ZSM-5, (d) GO:MCM-41.

Current generated in absence of any potential corrosion inhibitors is found maximum. Then current decreases with use of potential corrosion inhibitors in system, in order of $GO < GO:ZSM-5 < GO:MCM-41$. This shows that both GO: zeolite composites can inhibit Al-corrosion in 0.01 M NaOH solution but GO:MCM-41 composite is better inhibitor as validated by minimum current.

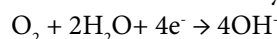
3.3 Proposed Mechanism of Corrosion Inhibition

Al-corrosion in alkaline medium occurs through two steps⁶⁰.

Anodic reaction is metal dissolution:



Cathodic reaction is oxygen reduction:



The mechanism of the corrosion inhibition can be explained based on the chemical and physical characteristics of GO and zeolites. The water molecules that get adsorbed on the Al- surface in aqueous phase are replaced by GO. GO films are thus formed by electrostatic interactions between Al metal and the functional groups of GO. The number of epoxy (-O-) groups in GO decrease after the reaction with NaOH owing to conversion of epoxy groups to hydroxyl (-OH) groups and -ONa groups and thus GO colloid becomes negatively charged⁶¹. Again, Al forms Al^{3+} in alkaline solution and thus adsorbs onto negatively charged GO; GO colloid act as anchor to Al surface⁶². The strength of adsorption depends on the charge on the anchoring group and the presence of zeolite stabilizes the negative charge density on the anchoring group⁶³. Na^{+} ions are also accommodated in the zeolite walls by replacement of protons. Zeolites, ZSM-5 and MCM-41, also provide mechanical stability to the adsorbed layer of GO:zeolite composites without cracks, intercrystalline voids or defects due to its high sorption ability that directly facilitates corrosion inhibition⁶⁴. This physisorption of GO: zeolite composites layer hinders the anodic and cathodic reactions of corrosions.

4. Conclusion

Both composites GO:ZSM-5 and GO:MCM-41 are very effective in preventing alkaline corrosion of Al-surface, although latter is more effective. Inhibition is attributed to formation of improved defensive layer on

Al-surface. Adsorption of composites are enhanced by presence of -O-Si-O-Si-O- network. Stable ultrathin layer of composite then prevents propensity of corrosion. The high adsorption and mechanical stability provided by the zeolites can be utilized in corrosion inhibition applications.

5. References

- Craig BD, Anderson DS. Handbook of Corrosion Data. 2nd ed. Ohio (OH): ASM International; 1994.
- Liu Z, Chong PH, Butt AN, Skeldon P, Thompson G. Corrosion mechanism of laser-melted AA 2014 and AA 2024 alloy. *Appl Surf Science*. 2005; 247(1-4):294-9. Crossref
- Lih ETY, Zaid RM, Ling TL, Chong KF. Facile corrosion protection coating from graphene. *Int J ChemEng Appl*. 2012; 3:453-5. Crossref
- Park SM. Boron, aluminum and scandium, in Standard Potentials in Aqueous Solution, IUPAC. Standard potentials in aqueous solution. New York: Marcel Dekker; 1985.
- Amin MA, Abd ESS, El-Sherbini EEF, Hazzazi OA, Abbas MN. Polyacrylic acid as a corrosion inhibitor for aluminum in weakly alkaline solutions. Part I: Weight loss, polarization, impedance EFM and EDX studies. *Corros Sci*. 2009; 5:658-67. Crossref
- Singh A, Quraishi MA. Pipali (*Piper longum*) and Brahmi (*Bacopamonnieri*) extracts as green corrosion inhibitor for aluminum in NaOH solution. *J Chem Pharm Res*. 2012; 4:322-5.
- Oguzie EE. Corrosion inhibition of aluminium in acidic and alkaline media by *Sansevieria trifasciata* extracts. *Corros Science*. 2007; 49:1527-39. Crossref
- Kawakita J, Kobayashi K. Anodic oxidation behaviour of aluminium in propylene carbonate. *J Power Sources*. 2000; 90:182-7. Crossref
- Muthukrishnan P, Prakash P, Jeyaprabha B, Shankar K. Stigmasterol extracted from *Ficus hispida* leaves as a green inhibitor for the mild steel corrosion in 1 M HCl solution. *Arab J Chem*. Forthcoming. 2015; 1-12.
- Khan G, Newaz KMS, Basirun WJ, Ali HBM, Faraj FL, Khan GM. Application of natural product extracts as green corrosion inhibitors for metals and alloys in acid pickling processes - a review. *Int J Electrochem Sci*. 2015; 10:6120-34.
- Chen S, Brown L, Levendorf M, Cai W, Ju SY, Edgeworth J, Xuesong L, Magnuson C, Velamakanni A, Piner RR, Park J, Ruoff RS. Oxidation resistance of graphene-coated Cu and Cu/Ni alloy. *ACS Nano*. 2011; 5:1321-7. Crossref PMID:21275384
- Kirkland NT, Schiller T, Medhekar N, Birbilis N. Exploring graphene as a corrosion protection barrier. *Corros Sci*. 2012; 56:1-4. Crossref
- Tassel JJV, Randall CA. Mechanisms of electrophoretic deposition. *Key Eng Mater*. 2006; 314:167-74. Crossref
- An SJ, Zhu Y, Lee SH, Stoller MD, Emilson T, Park S, Velamakanni A, An J, Ruoff RS. Thin film fabrication and simultaneous anodic reduction of deposited graphene oxide platelets by electrophoretic deposition. *J PhysChemLett*. 2010; 1:1259-63. Crossref
- Ban FY, Majid SR, Huang NM, Lim HN. Graphene oxide and its electrochemical performance. *Int J Electrochem Sci*. 2012; 7:4345-51.
- Zhu Y, Murali S, Cai W, Li X, Suk JW, Potts JR, Ruoff RS. Graphene and graphene oxide: synthesis, properties, and applications. *Adv Mater*. 2010; 22:3906-24. Crossref PMID:20706983
- Dreyer DR, Park S, Bielawski CW, Ruoff RS. The chemistry of graphene oxide. *ChemSoc Rev*. 2010; 39:228-40. Crossref
- Dimiev AM, Tour JM. Mechanism of graphene oxide formation. *ACS Nano*. 2014; 8:3060-8. Crossref PMID:24568241
- Shahriary L, Athawale AA. Graphene oxide synthesized by using modified Hummers approach. *Int J Renew Energ Environ Eng*. 2014; 2:58-63.
- Song J, Wang X, Chang CT. Preparation and characterization of graphene oxide. *J Nanomater*. 2014; 276143. Crossref
- Marciano DC, Kosynkin DV, Berlin JM, Sinitskii A, Sun Z, Slesarev A, Alemany LB, Lu W, Tour IM. Improved synthesis of graphene oxide. *ACS Nano*. 2010; 4:4806-14. Crossref, PMID:20731455
- Huang X, Yin Z, Wu S, Qi X, He Q, Zhang Q, Yan Q, Boey F, Zhang H. Graphene based materials: synthesis, characterization, properties and applications. *Small*. 2011; 14:1876-902. Crossref, PMID:21630440
- Hummers W, Offeman R. Preparation of graphitic oxide. *JACS*. 1958; 80(6):1339. Crossref
- Borisova D, Mohwald H, Shchukin DG. Mesoporous silica nanoparticles for active corrosion protection. *ACS Nano*. 2011; 5(3):1939-46. Crossref, PMID:21344888
- Ooi J WJV, Zhu DQ, Prasad G, Jayaseelan S, Fu Y, Teredesai N. Silane based chromate replacements for corrosion control, paint adhesion, and rubber bonding. *Surf Eng*. 2000; 16(5):386-96. Crossref
- Brusciotti F, Batan A, Graeve ID, Wenkin M, Biessemans M, Willem R, Reniers F, Pireaux JJ, Piens M, Vereecken J, Terryn H. Characterization of thin water-based silane pre-treatments on aluminium with the incorporation of nano-dispersed CeO₂ particles. *Surf Coat Technol*. 2010; 205(2):603-13. Crossref
- Palomino LM, Suegama PH, Aoki IV, Montemor MF, Melo HG. Electrochemical study of modified non-functional bis-silane layers on Al alloy 2024-T3. *Corros Science*. 2008; 50(5):1258-66. Crossref
- Rosero-Navarro NC, Pellice SA, Duran A, Aparicio M. Effects of Ce containing sol-gel coatings reinforced with SiO₂ nanoparticles on the protection of AA2024. *Corros Science*. 2008; 50(5):1283-91. Crossref
- Quinet M, Neveu B, Moutarlier V, Audebert P, Ricq L. Corrosion protection of sol-gel coatings doped with an organic corrosion inhibitor: Chloranil. *Prog Org Coat*. 2007; 58(1):46-53. Crossref

30. Raps D, Hack T, Wehr J, Zheludkevich ML, Bastos AC, Ferreira MGS, Nuyken O. Electrochemical study of inhibitor containing organic-inorganic hybrid coatings on AA2024. *Corros Science*. 2009; 51(5):1012–21. Crossref
31. Dalmor V, Santos JHZD, Armelin E, Aleman C, Azambuja DS. Phosphonic acid/silica-based films: a potential treatment for corrosion protection. *Corros Science*. 2012; 60:173–80. Crossref
32. Mitra A, Wang Z, Cao T, Wang H, Huang L, Yan Y. Synthesis and corrosion resistance of high-silica zeolite MTW, BEA, and MFI coatings on steel and aluminum. *J Electrochem Soc*. 2002; 149(10):B472–8. Crossref
33. Cheng X, Wang Z, Yan Y. Corrosion-resistant zeolite coatings by in situ crystallization. *Electrochem Solid-State Lett*. 2001; 4(5):B23–6. Crossref
34. Wojciechowski J, Szubert K, Peipmann R, Fritzc M, Schmidt U, Bund A, Lot G. Anti-corrosive properties of silane coatings deposited on anodized aluminium. *Electrochim Acta*. 2016; 220:1–10. Crossref
35. Beck JS, Vartuli JC, Roth WJ, Leonowicz ME, Kresge CT, Schmitt KD, Chu CTW, Olson DH, Sheppard EW, McCullen SB, Higgins JB, Schlenker JL. A new family of mesoporous molecular sieves prepared with liquid crystal templates. *J Am Chem Soc*. 1992; 114(27):10834–43. Crossref
36. Stankovich S, Dikin DA, Dommett GH, Kohlhaas KM, Zimney EJ, Stach EA, Piner RD, Nguyen ST, Ruoff RS. Graphene-based composite materials. *Nature*. 2006; 442(7100):282–6. Crossref, PMID:16855586
37. Zhang J, Yang H, Shen G, Cheng P, Zhang J, Guo S. Reduction of graphene oxide via L-ascorbic acid. *Chem Commun*. 2010; 46(7):1112–4. Crossref, PMID:20126730
38. Kim KH, Yang MH, Cho KM, Jun YS, Lee SB, Jung HT. High quality reduced graphene oxide through repairing with multi-layered graphene ball nanostructures. *Sci Rep*. 2013; 3:3251. Crossref
39. Sahoo S, Hatui G, Bhattacharya P, Dhibar S, Das CK. One pot synthesis of graphene by exfoliation of graphite in ODCB. *Graphene*. 2013; 2(01):42. Crossref
40. Singh BP, Jena BK, Bhattacharjee S, Besra L. Development of oxidation and corrosion resistance hydrophobic graphene oxide-polymer composite coating on copper. *Surf Coat Tech*. 2013; 232:475–81. Crossref
41. Sun X, Lui Z, Welshe K, Robinson JT, Goodwin A, Zaric S, Dai H. Nano-graphene oxide for cellular imaging and drug delivery. *Nano Res*. 2008; 1:203–12. Crossref, PMID:20216934, PMCID:PMC2834318
42. Luo Z, Vora PM, Mele EJ, Johnson ATC, Kikkawa JM. Photoluminescence and band gap modulation in graphene oxide. *Appl Phys Lett*. 2009; 94(11):1119091–3. Crossref
43. Eda G, Lin YY, Mattevi C, Yamaguchi H, Chen HA, Chen IS, Chen CW, Chhowalla M. Photoluminescence from chemically derived graphene oxide. *Adv Mater*. 2010; 22:505–9. Crossref, PMID:20217743
44. Galande C, Mohite AD, Naumov AV, Gao W, Ci L, Ajayan A, Gao H, Srivastava A, Weisman RB, Ajayan PM. Quasi-molecular fluorescence from graphene oxide. *Sci Rep*. 2011; 1(85):1–5. Crossref
45. Razavian M, Fatemi S. Synthesis and evaluation of seed-directed hierarchical ZSM-5 catalytic supports: inductive influence of various seeds and aluminosilicate gels on the physicochemical properties and catalytic dehydrogenative behavior. *Mater Chem Phys*. 2015; 165:55–65. Crossref
46. Jamalzadeh Z, Haghighi M, Asgari N. Synthesis, physicochemical characterizations and catalytic performance of Pd/carbon-zeolite and Pd/carbon-CeO₂ nanocatalysts used for total oxidation of xylene at low temperatures. *Front Environ Science Engineering*. 2013; 7(3):365–81. Crossref
47. El-Maksoud SAA. The effect of organic compounds on the electrochemical behaviour of steel in acidic media - a review. *International J Electrochem Science*. 2008; 3:528–55.
48. Oparaodu KO, Okpokwasili GC. Comparison of percentage weight loss and corrosion rate trends in different metal coupons from two soil environments. *Int J Biodeterior Biodegrad*. 2014; 2(5):243–9.
49. Standard practice for preparing, cleaning, and evaluating corrosion test specimens. G1-03. Pennsylvania: ASTM; 1999.
50. Gayathri VS, Yamuna KI, Prakash DG, Kameshwari R, Supraja R. Green inhibitors: anti corrosive propensity of *Garcinia mangostana* for aluminum 1100. *Solid State Phenom*. 2012; 85:109–12. Crossref
51. Abiola OK, James A. The effects of Aloe vera extract on corrosion and kinetics of corrosion process of zinc in HCl solution. *Corros Science*. 2010; 52(2):661–4. Crossref
52. Saleh RM, Ismail AA, Hosary AA. Corrosion Inhibition by Naturally Occurring Substances: VII. The effect of aqueous extracts of some leaves and fruit-peels on the corrosion of steel, Al, Zn and Cu in acids. *Brit Corros J*. 1982; 17(3):131–5. Crossref
53. Al-Mhyawi SR. Corrosion inhibition of aluminum in 0.5 M HCl by garlic aqueous extract. *Orient J Chem*. 2014; 30(2):541–52. Crossref
54. Zarrok H, Oudda H, Zarrouk A, Salghi R, Hammouti B, Bouachrine M. Weight loss measurement and theoretical study of new pyridazine compound as corrosion inhibitor for C38 steel in hydrochloric acid solution. *Der PharmaChemica*. 2011; 3(6):576–90.
55. Irshadat MK, Nawafleh EM, Bataineh TT, Muhaidat R, Al-Qudah MA, Alomary AA. Investigations of the inhibition of aluminum corrosion in 1 M NaOH solution by *Lupinus varius* l. extract. *Port Electrochim Acta*. 2013; 31(1):1–10. Crossref
56. Ta-ski T, Labisz K, Dobrza-ski LA. Effect of Al additions and heat treatment on corrosion properties of Mg-Al based alloys. *J Achiev Mater Manufacturing Engineering*. 2011; 44(1):64–72.
57. Halambek J, Bubalo MC, Redovnikovic IR, Berkovic K. Corrosion behaviour of aluminium and AA5754 alloy in 1% acetic acid solution in presence of Laurel oil. *Int J Electrochem Science*. 2014; 9:5496–506.
58. Popoola A, Olorunniwo OE, Ige OO. Corrosion resistance through the application of anti-corrosion coatings. *Developments in Corrosion Protection*. Rijeka. InTechOpen; 2014.

59. Dariva CG, Galio AF. Corrosion inhibitors–principles, mechanisms and applications. Developments in Corrosion Protection. Rijeka. InTechOpen; 2014.
60. Adhikari S, Hebert KR, Factors controlling the time evolution of the corrosion potential of aluminum in alkaline solutions. *Corros Science*. 2008; 50:1414–21. [Crossref](#)
61. Lee D, Seo J. Three-dimensionally networked graphene hydroxide with giant pores and its application in supercapacitors. *Sci Rep*. 2014; 4(7419):1–6.
62. Papavinasam S. Corrosion Inhibitors. In: Revie RW. *Uhlig's Corrosion Handbook*. 2nd ed. New Jersey: Wiley; 2000.
63. Kumar H, Yadav V. Corrosion Characteristics of Mild Steel under Different Atmospheric Conditions by Vapour Phase Corrosion Inhibitors. In: Sastri VS, editor. *Corrosion Inhibitors: Principles and Application*. New York: Wiley; 1998.
64. Lauridant N, Daou TJ, Arnold G, Soulard M, Nouali H, Patarin J, Faye D. Key steps influencing the formation of ZSM-5 films on aluminum substrates. *Micropor Mesopor Mater*. 2012; 152:1–8. [Crossref](#)