Adsorption properties of *Azadirachta indicia* extract on corrosion of Aluminium in 1.85 M Hydrochloric acid

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Abstract

The crude extract of *Azadirachta indica* was used in the corrosion inhibition study of aluminium metal coupons in 1.85 M hydrochloric acid environment by gasometric technique. The coupons were immersed in test solutions of uninhibited 1.85 M HCl and those containing extract concentrations of 10%, 20%, 30%, 40% and 50% (v/v) at room temperature. The rate of the reaction was captured by monitoring the volume of hydrogen gas evolved as a result of the interaction. The inhibition efficiency of the extracts and the adsorption isotherm of the process were calculated using Frumkin, Freundlich, Langmuir and Temkin adsorption theories and the surface morphology studied using Scanning Electron Microscopy (SEM). It was observed that the plant extract retarded the acid induced corrosion of aluminium and the volume of hydrogen gas evolved reduced with increasing extract concentration. The adsorption studies revealed that Langmuir isotherm is the best model for the adsorption of *Azadirachta indica* (R^2 = 0.999) on aluminium surface. This implied that the *Azadirachta indica* extracts with aluminium metal undergoes chemisorption.

Key words: Inhibition, Corrosion, Adsorption, Aluminium, *Azadirachta indica*, morphological study.

Introduction

Metal interaction with environment is a process that cannot be disregarded when the issue of corrosion and its effect comes to play. The effect is seen when metal in the combined state tends to revert back to its most stable natural state on exposure to certain environmental conditions. The effect of corrosion process has drastically affected a number of industries resulting in loss and damages with huge deficit (Barbara and Robert, 2006; Rosliza, 2012).

The effect of corrosion on the aqueous environment of sea water, salt water and rain, can be felt when pipes corroded with toxic metals are allowed to sips into the environment thereby causing health complications to the living system as contained in the aqueous environment. Other causes can be hazardous, which may results in loss of capital, loss of equipment and alienation of workforce, fire and explosion etc. (Holsen *et al.,* 1991).

The ability to protect metallic materials especially those used in engineering becomes important and a number of ways have been deployed in controlling corrosion such as electroplating and use of inhibitors. These are substances added in small concentrations to corrosive media to decrease or prevent the reaction of the metal in the media (Chauhan and Gunasekaran, 2007). The inhibitors can be organic or inorganic, and most credible

option is the use of natural inhibitors as an eco-friendly option. The synthetic inhibitors has heteroatom such as O, N, and S and multiple bonds in their molecules through which they become adsorbed on the metal preventing the metals from corroding, they are highly basic with high electron density which gives the characteristics of an inhibitor (James *et al.* 2009; 2011; Rani and Bharathi, 2012). However, investigation has shown that some of the synthetic and inorganic inhibitors are toxic causing kidney failure, liver failure, and mutation of the enzymes etc. (Singh *et al.*, 2012).

Since synthetic inhibitors have been proven to have acute hazardous effect to human, therefore natural products have been scrupulously analyzed and found to be effective in prevention of corrosion. Plant extracts have been found to be eco-friendly, inexpensive and obtainable in large quantities (Ambish *et al.*, 2010; Omotoso *et al.* 2012; Olusegun *et al.*, 2013). The availability of organic compounds in the natural product such as tannin, saponins, and alkaloids give it its inhibitive traits (Abdel-Gaber *et al.*, 2008; Ajanaku *et al.,* 2012). A number of researchers are now attracted to the trend of using natural products as inhibitors. Kliskic *et al.*, (2000) found that Rosemary leaves had an inhibiting effect on Al-Mg alloy corrosion in chloride solution. Amuradha *et al.*, (2008) investigated the inhibition of carbon steel in low chloride media by an aqueous solution of *Hibiscus rosa-sinensis Linn*. The extraction of these natural products is also cheap and easy to accomplish.

Azadirachta indica (Neem) is an evergreen tree growing in almost every state of India where it has been used for centuries for medicinal purpose and pest management (Ermel, 1995). Neem kernels contain 30–50% of oil and many active ingredients having antifeedant, growth-inhibiting, anti-oviposition and insecticidal activities (Schmutterer, 1995). Neem oil fatty acids comprise oleic, stearic, palmitic and linoleic acids, mainly used by the soap, pesticide and pharmaceutical industries. Therapeutically, its crude extracts from bark and leaves have been used in folk medicine to control diseases such as leprosy, intestinal helminthiasis and respiratory system (Prieto *et al.,* 1999). Besides these uses, there are several other reports on the biological and pharmacological actions such as antiviral, antibacterial, antifungal, anti-inflammatory, antipyretic, antiseptic and antiparalitic uses (Prieto *et al.,* 1999; Eshrat and Ali, 2002; Britto and Sheeba, 2011). The rationale for this work is to investigate the effect of the extract of *Azadirachta indica* on aluminium metal in 1.85 M HCl environment.

Materials and Methods

Preparation of Aluminium coupons

Rectangular specimen of the wrought Aluminium alloy of AA 2xxx were mechanically pressed cut into coupons of 24 mm x 14 mm and 1 mm thickness using manual edge metal cutter. The coupons were examined to eradicate rough edges, which could influence the corrosion monitoring process. Surface treatment of the coupons was done by degreasing in ethanol and further drying in acetone and then stored in desiccator to avoid moisture absorption. The composition of the Aluminium samples was analyzed using optical emission spectrophotometer and the result were as follows:

Table 1: Composition of the Aluminium sample used for the study

Elements	Wt. %
Si	0.57
Fe	1.18
Mg	0.01
Ti	0.11
Sr	0.31
Cu	0.01
Pb	0.012
Al	93.10

Extraction of *Azadirachta indica* leaves

Leaves of *Azadirachta indica* were air dried at room temperature and crushed into powder. 10g of the powder was refluxed with 200 cm^3 of 1.85M HCl solution for 2 (two) hours and left overnight before it was filtered.

Extract concentration of 10%, 20%, 30%, 40%, 50% (v/v) was obtained through serial dilution using 1.85% HCl. The experimental set up (Figure 1) is similar in literature (Ajayi *et al*., 2011) and all reagents were of analar grade.

Corrosion inhibition using Gasometric method

Gasometric (gas-volumetric) technique is a rapid and reliable means of ascertaining any perturbation by the inhibition with regard to gas evolution at the metal/corrodent inter-phase. Each of the specimens was dropped into the mylius cell containing 50 cm^3 of the blank solution (1.85 M HCl) at room temperature and the volume of hydrogen (H$_2$) gas evolved per min interval was recorded. A volume/volume (v/v) dilutions of 10%, 20%, 30%, 40%, 50% was utilized, to study the inhibitive effect and the volume of H$_2$ gas evolved per min interval was also recorded. At the end of each experiment of hydrogen evolution, the aluminium specimen was withdrawn from the mylius tube and weighed, in semblance with method used by Eddy *et al*., (2010). A graph of volume against time interval was carried out. The inhibition efficiency (I.E.) was then determined using equation 1 (Okafor *et al*., 2005).
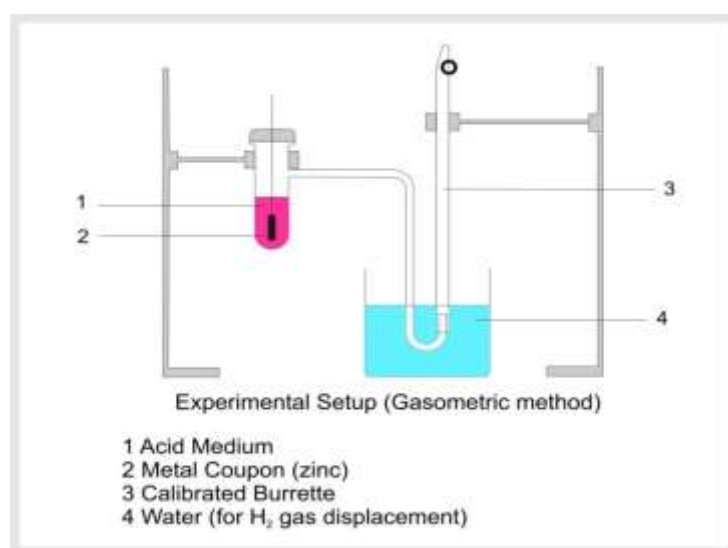

Experimental Setup (Gasometric method)
1 Acid Medium
2 Metal Coupon (zinc)
3 Calibrated Burrette
4 Water (for H$_2$ gas displacement)

Figure 1: Experimental set up for gasometric method

$$I.E(\%) = \frac{V_H - V_{HI}}{V_H} X\ 100...........equ.1$$

VH = Volume of hydrogen evolved without inhibitor
VHI = Volume of hydrogen gas with inhibitor

Since the reaction of Aluminium with HCl gives off hydrogen gas as one of its products, it is easier to infer that the rate of reaction corresponds to the rate of corrosion damage of the aluminium in HCl and can also be monitored in the presence of *Azaradichta indica* extracts as inhibitor. However based on the assumption made in the literature, (Ajayi *et al*., 2011) the following relationships were also obtained. The basis for this is represented in equation 2

$$\Delta V \alpha\ \Delta W.................equ.\ 2$$

$$\frac{d\Delta V}{dt} \alpha\ \frac{d\Delta W}{dt}$$

but

$$\frac{R \; \alpha \; dW_m}{dt} \; \alpha \; \frac{d \; \Delta \; V_{H2}}{dt} ....equ.3$$

Where

α = proportionality sign

ΔV = Volume of hydrogen gas evolved

ΔW = Metal weight loss due to corrosion

R = Corrosion rate

t = Time (sec)

Thus to determine Equation 3, it is important to develop a relationship between volume evolved and time of evolution. This was arrived by at a polynomial regression analysis of the volume of hydrogen gas against time leading to Equation 4 (Noor, 2007).

V = c + bt + at² ……………….*equ. 4*

Thus

$$R = \frac{dv}{dt} = \text{ b} + 2at...............equ. 5$$

Adapting Equation 4 and Equation 5 to the volume-time measurement for individual concentration and using the example for measurement relating to 50 cm³ concentration of *Azadirachta indica* extract in 1.85 M HCl the corrosion rate model is shown as:

V = 0.325t² – 2.725t + 1.375

$$\frac{dv}{dt} = 0.650t - 2.725............equ. 6$$

The corrosion rate K, is derived from the second differential of V_{in} as in $d^2V_{in} / dt^2 = \pm C$

$$\Phi = \frac{IE}{100} ....equ.7$$

Where Φ is surface coverage and I.E is Inhibition efficiency

Results and Discussion

Inhibition properties of *Azadirachta indica* extract

The free corrosion of the aluminium metal in 1.85 M HCl was characterized by rapid effervescence resulting for hydrogen evolution using blank (0 % extract) and also in the presence of the various extract concentrations (10 % - 50 %) for *Azadirachta indica* extract as shown in Figure 2.
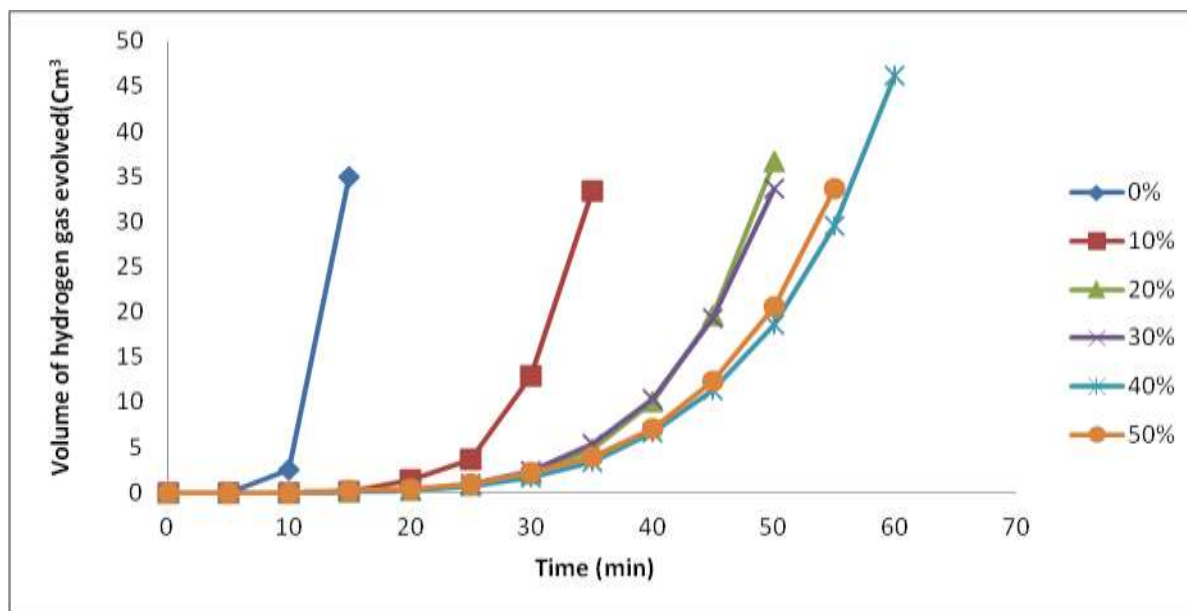
Figure 2: Variation of volume of hydrogen (cm^3) evolved with time (min) of Aluminium coupons for different concentration of *Azadirachta indica* extract in 1.85M HCl at room temperature.

The minimum regression value of 0.9154 was obtained for 10% (v/v) and 0.9158 for 40% (v/v) which indicated that the extract actually inhibits corrosion of aluminium in the acidic environment. Further reduction in the volume of hydrogen gas was observed as the extract concentration increased from 10 % to 50 % v/v; suggestive that the inhibitive action was concentration dependent.

## Inhibitive efficiency of *Azadirachta indica* extract

The plot of the inhibition efficiency against time of *Azadirachta indica* extract in 1.85 M HCl is shown in Figure 3. This revealed that inhibition efficiency increased with extract concentration. All extract concentration has peak I.E (%) values between 8 to 12 minutes hus indicating the period for optimization range. This follows the same pattern reported by Abiola (2007) and Ajanaku *et al.* (2012) in the study of the inhibitive effect of plant extracts on the corrosion of aluminium in acidic media. *Azadirachta indica* leaves have been reported to contain alkaloids, cyanogenic glycosides, flavanoids, phytates saponins and tannins (Nwaogu *et al*., 2007). Hence anti-corrosion activity of *Azadirachta indica* extract can be attributed to phytic acid which binds unto the cathodic sites on the metal surface. Tannin containing extracts are reported to contain varying inhibition efficiency and inhibition mechanism (Ehteram *et al*., 2008). However tannins had demonstrated that inhibitive tendency is a function of molecular properties (absolute electronegativity, absolute hardness and the electron donating ability) of its constituent molecules. This is accountable for the difference in inhibition efficiency observed for *Azadirachta indica* extract as indicated in Figure 3. This observation conforms to Matamalala *et al*., (2000) report of which observed that natural tannins exhibit better corrosion inhibition and better adherence to metallic substrates.
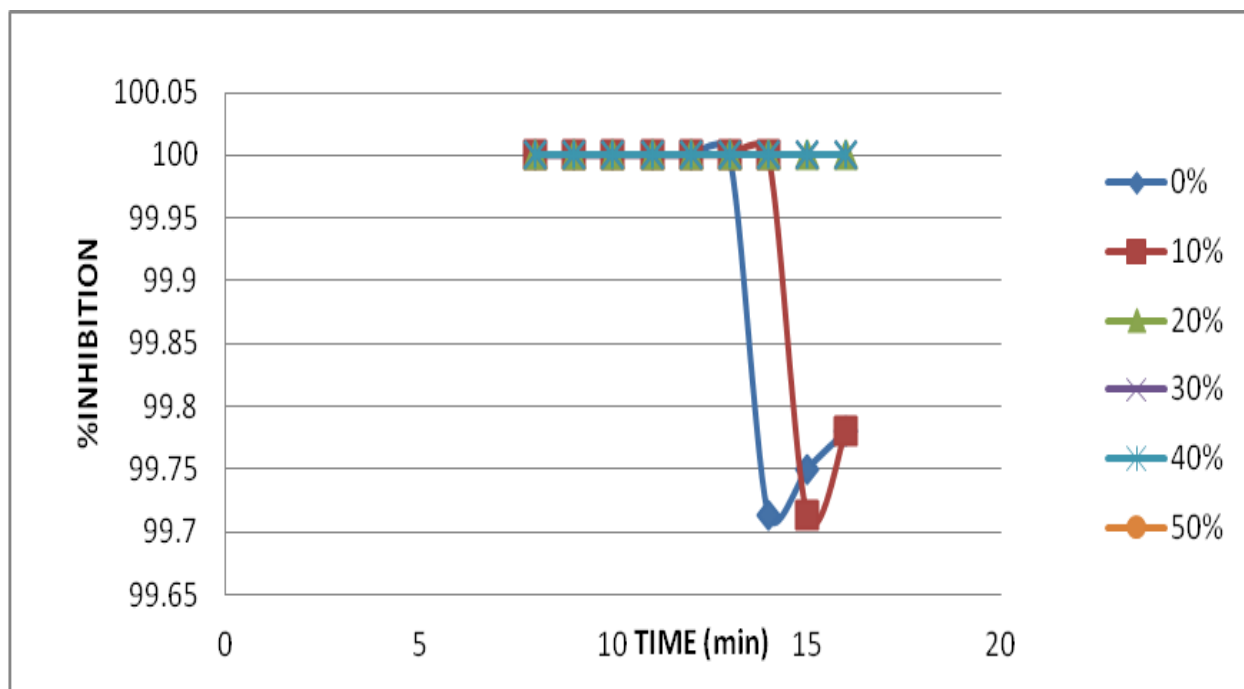
Figure 3: Percentage inhibition efficiency of varying concentration of *Azadirachta indica* extracts with time on Aluminium coupon in 1.85 M HCl solution at room temperature.

Corrosion rate of *Azadirachta indica* extract on Aluminium

Figure 4 shows a plot of corrosion rate against time for *Azadirachta indica* extract. It was observed that the rate of corrosion generally decreases in the presence of the extract. The 50% v/v sequence possesses the lowest corrosion rate, indicative that the inhibitive action of these extracts is concentration dependent. There may be argument as to the chemistry of Aluminium metal forming an oxide which may adsorbed alongside with the *Azadirachta indica* extract by making this less prone to the HCl interaction but it's been known that the presence of heteroatom fused benzene rings may bring about complexity in attributing the certainty of the inhibition. This argument was confirmatory of Li *et al.,* 2014 in the inhibition study of steel in HCl and H_2SO_4 solutions using bamboo leaf extract.
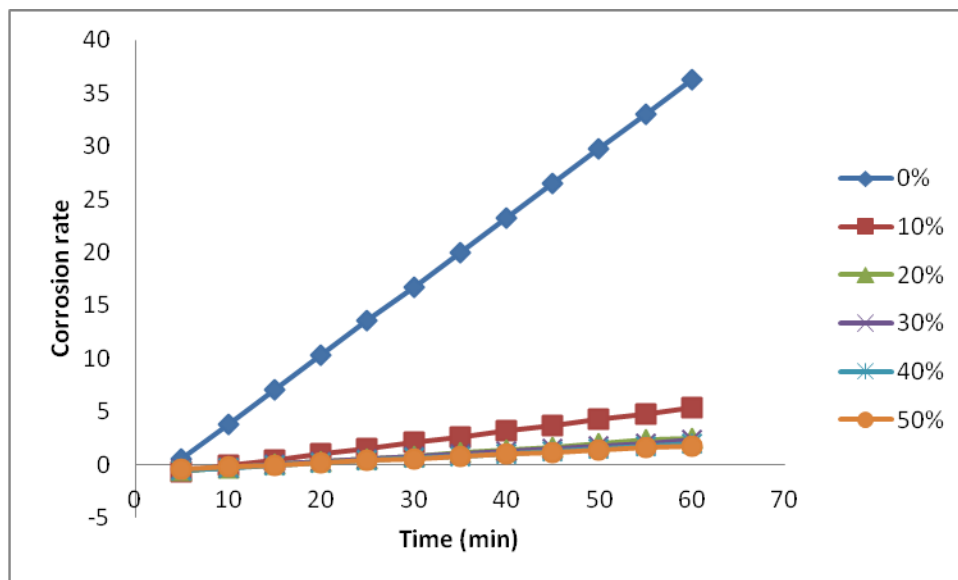
Fig. 4: Corrosion rate of varying concentrations of *Azadirachta indica* extract with time (min) on Aluminium coupon in 1.85 M HCl solutions at room temperature.

Adsorption Isotherms

One possible mechanism for corrosion inhibition using organic compounds is the adsorption of the inhibitor on the metal surface which blocks the active sites and thus prevents further corrosion of the metal from taking place. The adsorption route provides the information about the interaction among the adsorbed molecules themselves as well as with their metal surface whether it is physical adsorption or chemical adsorption.

The degree of surface coverage values for *Azadirachta indica* extract on the Aluminium metal was obtained from the hydrogen evolution measurement using equation 7 by assuming a direct relationship between surface coverage and inhibition efficiency. The results were fitted into adsorption isotherms of Frumkin, Freundlich, Langmuir and Temkin adsorption theories and the correlation coefficient (R^2) determined to check the best fitted isotherm (Table 2).

Table 2: Correlation coefficient of various adsorption isotherms obtained from *Azadirachta indica* extract at 15 minutes

| Adsorption	R^2
Temkin	0.3161
Frumkin	0.882
Freundlich	0.9471
Langmuir	0.9999

The unity value of correlation coefficient obtained in the Langmuir isotherm is an indication that the adsorption of the extract onto aluminium surface best fits into the theory of Langmuir isotherm (Figure 5). This characterizes chemisorptions of the adsorbed species which is expected to have a correlation coefficient of unity in which the monolayer of the extract get attached to metal surface without lateral interaction between the adsorbed species. The observed result of the study shows that *Azadirachta indica* extract inhibit the acid induced corrosion of aluminium by virtue of adsorption on its component onto the metal surface.
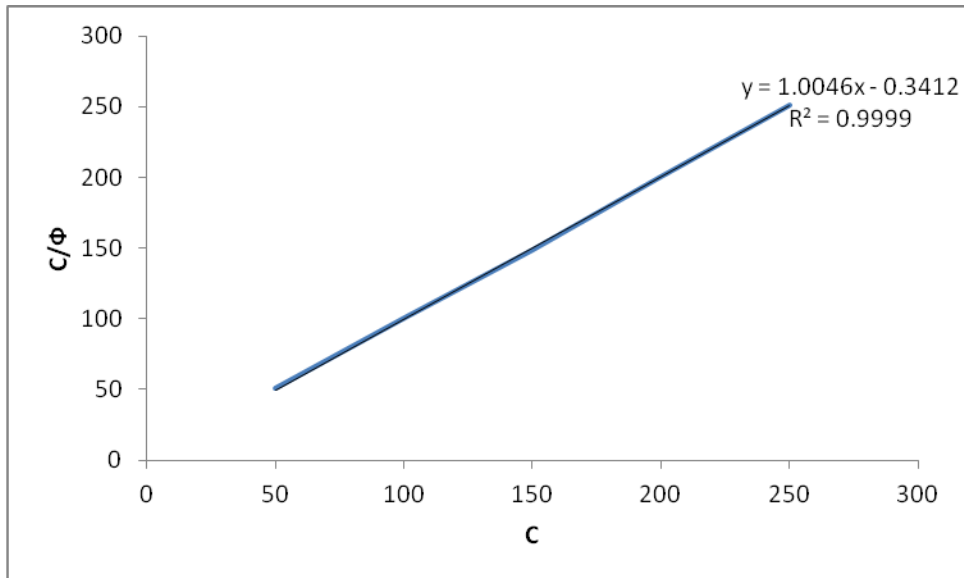
Figure 5: Langmuir adsorption plot for aluminium corrosion in *Azadirachta indica* extract in 1.85 M at 15 min.

Surface Morphological Studies

The surface morphology of the aluminum metal was studied using Carl Zeiss Sigma Field Emission Scanning Electron Microscope and the images at 10μm of the aluminium surfaces at unhibited (0%) and inhibited (10%; 30% and 50% v/v) are shown in Figure 6. The examination of fine structure of cells and the topographical information makes the usefulness of SEM pictures relevant in the study of corrosion prevention on metal surfaces. This helps in examining surface contaminations, provides qualitative chemical analyses and identifies crystalline structures. It was observed that the structural distinctive of the aluminium metal increases with the *Azadirachta indica* extract concentrations with a rapidly oxidized surface in the unhibited (A) to a glinting effect in the 50 % inhibited (D) and partially luminous in the 30% (C). The morphology of B designated 10 % concentration is not enough to effect inhibition. This cannot be fully ascertained because there is inclination of strong bond interaction at the surface of Aluminium, which may prevent relative sliding motion along the grain boundary when studied in acidic environment with inhibition thereby promoting embrittlement of the Aluminium alloy.
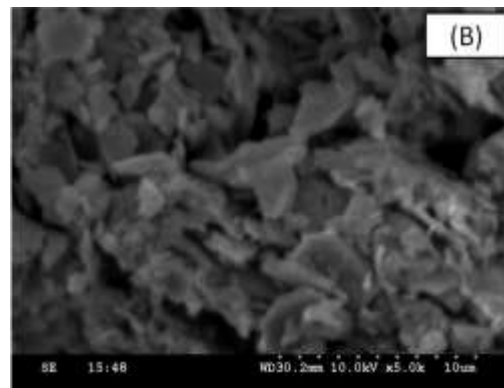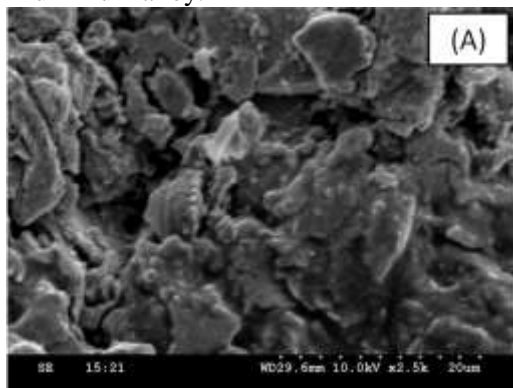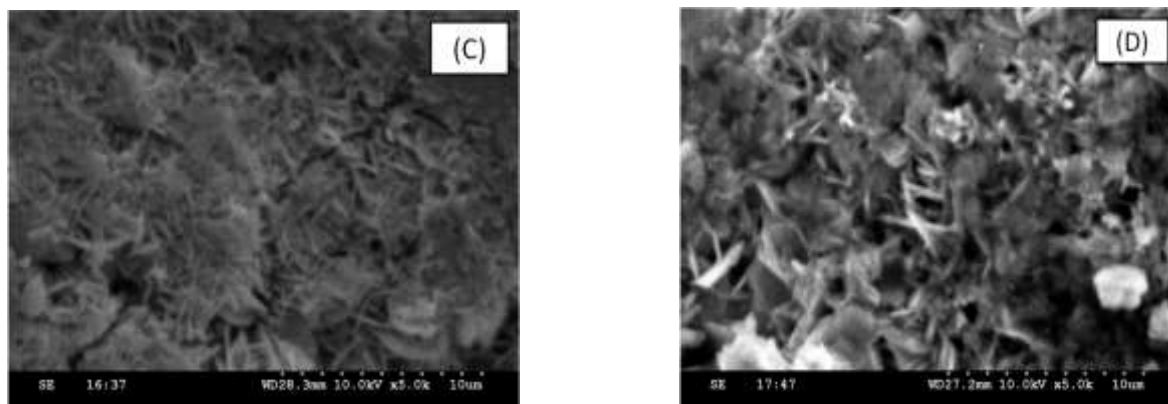
Figure 6: SEM images of aluminium coupons in 0% (A); 10% (B); 30% (C) and 50% (D) *Azadirachta indica* leaf extract in 1.85 M HCl solution

Conclusion

The use of crude extract of *Azadirachta indica* as an inhibitor for Aluminium metal has been investigated in 1.85 M HCl and has been found effective. The inhibition efficiency of the extract increases in concentration of the inhibitor in which optimum inhibition concentration observed was 50% v/v of the *Azadirachta indica* extract. This is mainly due to the photochemical constituents of the extract on the metal surface thereby blocking its active sites by phenomenon of chemical adsorption. The morphological images as well as the adsorption isotherm study implies chemisorption pathway in the inhibition process.

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