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International Journal of ChemTech Research
CODEN( USA): IJCRGG ISSN : 0974-4290
Vol.5, No.4, pp 1714-1723, April-June 2013

# Inhibition Performance On The Surface Of Aluminium In Alkaline Medium

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**Abstract:** The inhibition efficiency of polymethylmethaacrylate (PMMA) in controlling corrosion of aluminium in well water at pH11, in the absence and presence of $Zn^{2+}$ has been evaluated by the weight loss method. The formulation consisting of 250ppm of PMMA and 25ppm of $Zn^{2+}$ offers 85% inhibition efficiency to aluminium metal. A synergistic effect exist between PMMA and $Zn^{2+}$, polarization study reveals that PMMA-$Zn^{2+}$ System function as an mixed inhibitor and the formulation controls both both anodic and cathodic reaction.AC impedance spectra reveal that a protective film is formed on the metal surface.FTIR spectra reveal that the protective film consists of PMMA- $Zn^{2+}$Complex and $Zn(OH)_2$. The protective film is found to be atomic force microscopy also.
**Keywords :** aluminium,corrosion inhibition,synergistic effect,protective film,mixed inhibitor.

## Introduction :

Corrosion is commonly known as rust, an undesirable phenomena which destroys the luster and beauty of objects and shortens their life [1]. Corrosion is largely an electrochemical phenomenon.In our day-to-day life,we use many things that are made out of aluminium metal. Inorder to protect aluminium metal from atmospheric environment gases by using Several inhibitors to control corrosion of aluminium. On the effect of polyamide compounds on the corrosion behaviour of aluminium by potentiostatic and potentiodynamic polarization techniques[2],the corrosion and inhibition behavior of aluminium in acid medium in presence of polyvinyl pyrrolidone and polyacrylamide blends in the temperature of 30-60$^0$c using weight loss,hydrogen evolution and thermometric techniques reported by Umoren et al[3],polyvinyl alcohol to inhibit corrosion of aluminium using gravimetric and gasometric methods[4],to investigate the corrosion behavior of aluminium by gumarabic using weight loss and thermometric methods[5],the mechanism of corrosion of aluminium and the effect of polyethylene glycol polymer as corrosion inhibitor in acid medium has been studied using weigh loss and potentiodynamic polarization method [6], Noreen Anthony et al investigated the inhibition efficiency of carboxymethyl cellulose by potentiodynamic polarization study [7],to investigate the corrosion behavior of polyacrylamide with the help of electrochemical studies[8], Polyethylene glycol-Anthranillic of acid composite used to study corrosion behaviour of mild steel[9],Yuvan et al reported that the corrosion behaviour of Poly (1-vinylimidazole)[10],polyaniline used to reported that inhibiting nature of iron in acidic medium by electrochemical studies[11], the adsorption of Polyvinylpyrrolidone and Polyacrylamide on aluminium surface investigated by hydrogen evolution and thermometric method[12], anticorrosion property of Polypyrrole studied by electrochemical method[13].

Corrosion inhibition of aluminum in alkaline medium by the use of water soluble polymers because of its adsorption capacity on surface of metal. Poly(methyl methacrylate) (PMMA) is a clear, colorless polymer used extensively for optical applications.It possess properties like weatherability and scratch resistance.

Much work has not been done using PMMA as corrosion inhibitor.

## Experimental

### Materials and methods

### Preparation of the specimens

The commercial aluminium specimens(95% of purity) of the dimentions 1.0 x 4.0 x 0.2cm were polished to a mirror finish and degreased with trichloroethylene and used for the weightloss method and surface examination studies, were made.

### Weight – loss method

Aluminium specimens were immersed in various concentrations of the inhibitor solution in the presence and absence of $Zn^{2+}$ for a period of 24 hours.The weight of the specimens before and after were determined using shimadzu balance, model AY62. The corrosion products were cleansed with Clarke's solution [21] .The inhibition efficiency (IE) was then calculated using the equation

$$IE = 100\,[1 - (W2 / W1)]\ \%$$

Where W1 = Corrosion rate in the absence of the inhibitor and

W2 = Corrosion rate in the presence of the inhibitor.

### AC impedance measurements

The AC impedance Spectra were recorded in the same instrument which was used for polarization study. The cell set up was the same as that used for polarization measurements. The real part (Z') and imaginary part (Z'') 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.

$$R_t = (R_s + R_t) - R_s$$

Where $R_s$ = Solution resistance

$$C_{dl} = 1 / 2\pi R_t f_{max}$$

Where

$f_{max}$ = maximum frequency

### Synergism parameter ($S_I$)

The synergism parameter ($S_I$) is calculated using the below relation.

$S_I = 1 - \theta_{1+2} / 1 - \theta'_{1+2}$, Where ,

$\theta_{1+2} = (\theta_1 + \theta_2) - ((\theta_1 . \theta_2)$

$\theta_1$ = Surface coverage of inhibitor (PMMA )

$\theta_2$ = Surface coverage of co-inhibitor ($Zn^{2+}$ )

$\theta'_{1+2}$ = Combined surface coverage of inhibitors (PMMA) and ($Zn^{2+}$ )

Surface coverage = IE / 100

### Surface examination study

The aluminium specimens were immersed in various test solutions for a period of 24 hours and then taken out and dried. The nature of the film formed on the surface of the metal specimens was analysed for surface analysis technique of FTIR spectra and SEM.

### FTIR Spectra

The film formed on the metal surface was carefully removed and mixed thoroughly with KBr. The FTIR spectra were recorded in a Jasco $460^{+}$ spectrophotometer.

### Scanning Electron Microscope

Scanning Electron Microscope uses a focused beam of high energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derive from electron-sample interactions about the sample including external morphology, chemical composition, crystalline stucture and orientation of materials making up the sample .Areas ranging approximately from 1cm to 5 microns in width can be imaged in a scanning mode using conventional SEM technique.

## Result and Discussion

### Analysis of the results of weight loss method

The corrosion inhibition efficiencies (IE) and corrosion rates of PMMA in controlling the corrosion of aluminium metal immersed in well water at pH11, for a period of one day both in absence and presence of Zinc ions by weight loss method have been tabulated in Table 1.

As the concentration of $Zn^{2+}$ is increased, IE also increases. A synergistic effect exists between PMMA and $Zn^{2+}$ .for example,250ppm of PMMA has 75% IE and 25ppm of 25ppm of $Zn^{2+}$ has 20%IE. But the formulation consisting of 250ppm of PMMA and 25ppm of $Zn^{2+}$ has 85%IE,(i.e) mixture of inhibitors shows better IE than individual inhibitors [14-16].

**Table 1 Inhibition efficiency (IE) of PMMA- $Zn^{2+}$ system in the corrosion of aluminium immersed in well water (Immersion period- one day)**

| PMMA ppm | $Zn^{2+}$ ppm | | | | | |
|---|---|---|---|---|---|---|
| | 0 | | 25 | | 50 | |
| | I.E % | CR mdd | I.E % | CR mdd | I.E % | CR mdd |
| 0 | ---- | ------ | 20 | 5.4 | 10 | 3.6 |
| 50 | 65 | 6.4 | 70 | 5.4 | 60 | 7.3 |
| 100 | 68 | 5.8 | 80 | 3.6 | 63 | 6.7 |
| 150 | 70 | 5.4 | 85 | 2.7 | 65 | 6.4 |
| 200 | 72 | 5.1 | 85 | 2.7 | 68 | 5.8 |
| 250 | 75 | 4.5 | 85 | 2.7 | 70 | 5.4 |

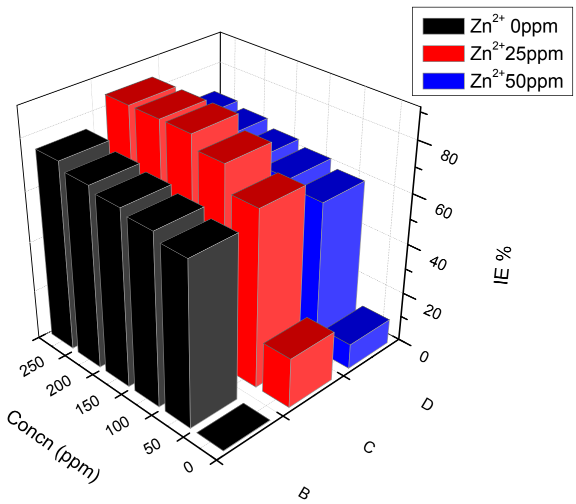


**Fig 1 Graph of Inhibition efficiency (IE) of PMMA- $Zn^{2+}$ system in the corrosion of aluminium immersed in well water (Immersion period- one day)**

**Synergism parameter ($S_I$)**

The synergism parameter ($S_I$) is calculated using the relation[17].It is given in Table 2.

$S_I = 1- \theta_{1+2} / 1 - \theta'_{1+2}$

$S_I$ approaches 1 when no interaction between the inhibitors. $S_I > 1$,synergistic effect exist between the two inhibitors [18-20].In the case of . $S_I < 1$, negative interaction takes place between the two inhibitors, (i.e CR increases).The calculated synergism parameter values for PMMA and $Zn^{2+}$ system are given in table 2. In the case of PMMA - $Zn^{2+}$ system ,the $S_I$ value is found to be greater than one for 25ppm of $Zn^{2+}$ with various concentrations of PMMA indicating the synergistic effect exist between $Zn^{2+}$of concentrations of 25ppm with various concentrations of PMMA. $S_I$ value is found to be less than unity for 50ppm $Zn^{2+}$ with various concentrations of PMMA which indicates a lack of synergism between 50ppm of $Zn^{2+}$ with various concentrations of PMMA. The result are given in Table 2.

**Table 2 Synergism parameters for PMMA- $Zn^{2+}$ system when aluminium immersed in well water**

| PMMA (ppm) | $\theta_1$ | $Zn^{2+}$ 25 (ppm) $\theta_2$ | PMMA-$Zn^{2+}$ $\theta'_{1+2}$ | $S_I$ | $Zn^{2+}$ 50 (ppm)$\theta_2$ | PMMA- $Zn^{2+}$ $\theta'_{1+2}$ | $S_I$ |
|---|---|---|---|---|---|---|---|
| 50 | 0.65 | 0.20 | 0.72 | 0.93 | 0.24 | 0.73 | 0.66 |
| 100 | 0.68 | 0.20 | 0.74 | 1.28 | 0.24 | 0.76 | 0.65 |
| 150 | 0.70 | 0.20 | 0.76 | 1.6 | 0.24 | 0.77 | 0.65 |
| 200 | 0.72 | 0.20 | 0.77 | 1.5 | 0.24 | 0.78 | 0.66 |
| 250 | 0.75 | 0.20 | 0.8 | 1.33 | 0.24 | 0.81 | 0.63 |

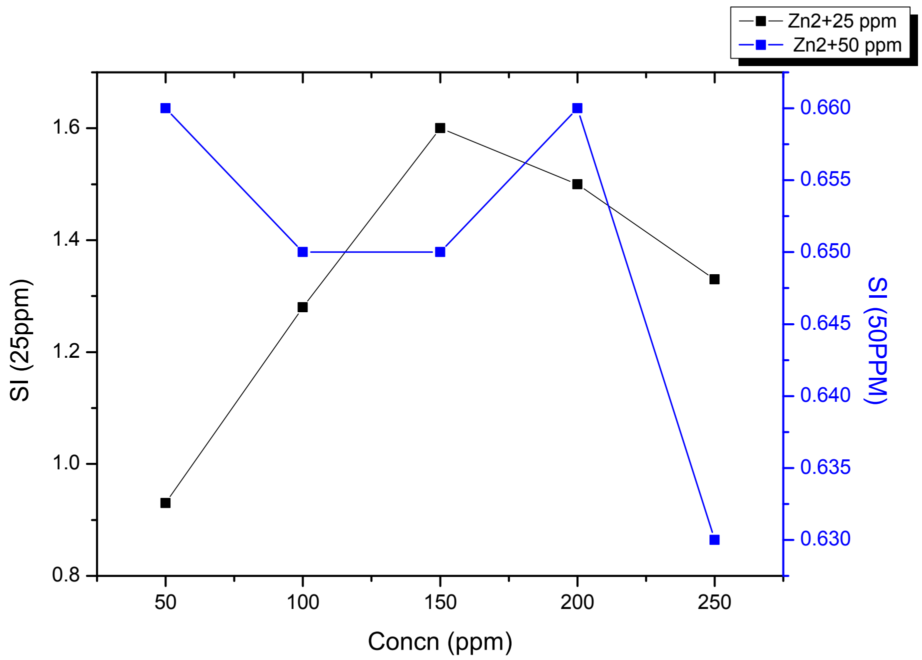


**Fig 2 Inhibition efficiencies and synergism parameters for various concentrations of PMMA-$Zn^{2+}$ (250ppm)system,when aluminium is immersed in alkaline solution at $P^H$ 11 ((Immersion period- one day)**

**Analysis of results of potentiodynamic polarisation study of PMMA- $Al^{3+}$ system**

Potentiodynamic polarisation curves of aluminium in various test solutions are shown in Fig 3 The corrosion parameters are given in Table3.

When aluminium is immersed in well water, the corrosion potential is -1220 mV vs SCE. The formulation consisting of 250ppm of PMMA and 25ppm of $Zn^{2+}$ shifts the corrosion potential is -1216 mV vs SCE. The corrosion potential shift is very small.This suggest that the PMMA- $Zn^{2+}$ formulation function as a mixed inhibitor controlling the anodic reaction and cathodic reaction, to the same extend. This is further confirmed from the data that shifts in the anodic slope (from 338 mV vs SCE to 333 mV vs SCE ) and in the cathodic slope (from 134 mV / dec to 133 mV / dec ) are nearly equal indicating that this system acts as a mixed inhibitor.The above observation is in line with the result obtained by Ruba Florence et al.,[21].

The corrosion current value and LPR value for well water are $1.30 \times 10^{-6}$ A/cm$^2$ and $3.21 \times 10^{4}$ Ω cm$^2$. For the formulation of PMMA (250ppm) + $Zn^{2+}$ (25ppm), the corrosion current value has decreased to $4.29 \times 10^{-7}$ A/cm$^2$ ,and the LPR value has increased to $9.63 \times 10^{4}$ Ω cm$^2$.The fact that the LPR value increases with decrease in corrosion current indicates adsorption of the inhibitor on the metal surface to block the active sites and inhibit corrosion and therefore reduces the CR.

**Table 3 Corrosion parameters of aluminium immersed in solution containing 250ppm of PMMA and 25ppm of $Zn^{2+}$ at pH11in the presence and absence of inhibitor obtained by polarisation method:**

| System | $E_{corr}$ mV vs SCE | $b_a$ mV / dec | $b_c$ mV / dec | $I_{corr}$ A/cm$^2$ | LPR Ω cm$^2$ |
|---|---|---|---|---|---|
| Well water at pH11 | -1220 | 338 | 134 | $1.30 \times 10^{-6}$ | $3.21 \times 10^{4}$ |
| solution containing 250ppm of PMMA and 25ppm $Zn^{2+}$ at pH11 | -1216 | 333 | 133 | $4.29 \times 10^{-7}$ | $9.63 \times 10^{4}$ |

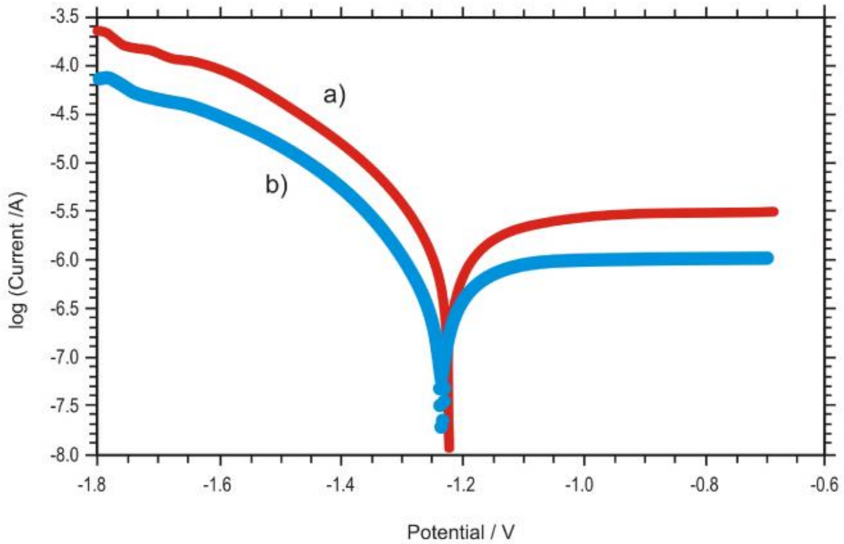


**Fig 3 polarisation curves of aluminium immersed in various test solution containing a) well water b)250ppm of PMMA and 25ppm of $Zn^{2+}$**

**Analysis of the results of AC impedance spectra**

Ac impedance spectra have been used to detect the formation of film on the metal surface. If a protective film is formed, the charge transfer resistance (Rt ) increases and double layer capacitance ($C_{dl}$) value decreases. AC impedance of spectra of aluminium immersed in various solutios are given in Fig 4[22]

It is found that when aluminium in well water at pH11,the $R_t$ value is 396.4 Ohmcm$^2$ and $C_{dl}$ value is $1.2865 \times 10^{-8}$ µF/cm$^2$. When 250ppm of PMMA and 25ppm $Zn^{2+}$ are added the $R_t$ value tremendously increased to 2203 ohmcm$^2$ and the Cdl value is decreased to $2.314 \times 10^{-9}$ µF/cm$^2$.This indicates the protective film is formed on the metal surface in the presence PMMA [23-24].the bode plots are shown in Fig 4. It is observed that in the absence of the inhibitors the real impedance value [(log(Z / ohm)] is 2.69.In the presence of inhibitors this value increases to 3.43.

**Table 4 The impedance parameters of aluminium immersed in well water at pH11 in presence and absence of inhibitor obtained by AC impedance method**

| System | $R_t$ ohmcm$^2$ | Cdl F/cm$^2$ | Impedance (logZ / ohm) |
|---|---|---|---|
| Well water at pH11 | 396.4 | $1.2865 \times 10^{-8}$ | 2.69 |
| solution containing 250ppm of PMMA+ 25ppm of $Zn^{2+}$ | 2203 | $2.314 \times 10^{-9}$ | 3.43 |

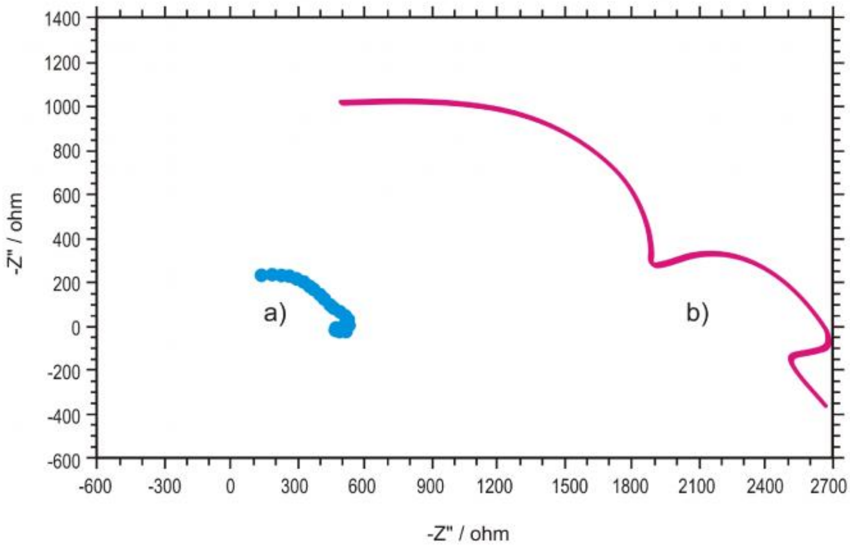


**Fig 4 AC Impedence spectra of Aluminium immersed in various test solutions a) well water b) well water containing 250ppm of PMMA and 25ppm of $Zn^{2+}$**

**Analysis of the FT-IR spectra**

FTIR spectra have been used to analyze the protective film formed on metal surface. FTIR spectrum(KBr) of pure PMMA is given in Fig.5a.The peaks at 2812.17cm$^{-1}$ are due to C-C stretching frequency. The C = O stretching frequency appears at 1592 cm$^{-1}$.

The bands at 1383 cm$^{-1}$ and 765.88 cm$^{-1}$ are due to bending C-H of methyl groups.

The FT-IR spectrum of the film scratched from the surface of the metal using a pointed glass rod after immersion in the well water for one day containing 250ppm of PMMA and 25ppm of $Zn^{2+}$ is shown in Fig 5b. The peak at 515 cm$^{-1}$ which may be due to Zn-O bending mode of vibration. The band at 3463.31 cm$^{-1}$ is due to OH stretching frequency of $Zn(OH)_2$[25].

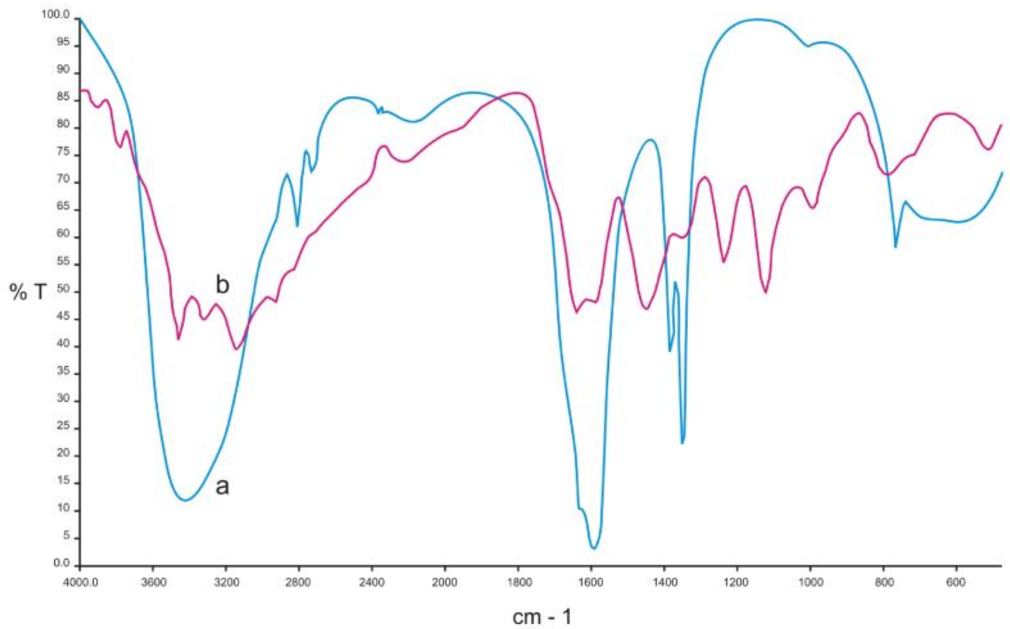


**Fig 5 :FTIR Spectra**
**a) Pure PMMA**
**b) Film formed on metal surface after immersion in well water containing 250ppm of PMMA and 25ppm of $Zn^{2+}$**

**Analysis of surface metal by SEM**

SEM technique provides a pictorial representation of the surface.To understand the nature of the surface film in the presence and absence of inhibitors and the extent of corrosion products of aluminium, the SEM micrographs of the surface are examined[26-28].

The SEM images of different magnifications (1000 X2000) of aluminium specimen and aluminium immersed in well water for one day in the presence and absence of inhibitors system are shown in Fig 6 as images (a,b & c) respectively.

The SEM micrographs of the surface of the polished aluminium metal(control) in Fig 6 images (a),illustrate smooth surface of the metal. These show the absence of any corrosion products formed on the metal surface.

The images (b) denote the SEM micrographs of aluminium surface immersed in well water.They show the type of rough surface of the uniform corrosion of the aluminium surface in well water, indicating in an inhibitor free solution, the surface is highly corroded.Images (c) confirm that in the presence of 250ppm of PMMA and 25ppm of $Zn^{2+}$ at pH11in well water, the rate of corrosion is suppressed , as it seen from the decrease in corroded areas. This is a result of the formation of insoluble complex on metal surface (PMMA - $Al^{3+}$) and the surface is covered by a thin layer of inhibitors which effectively controls the dissolution of aluminium metal from corrosion process. The above results are line with the interpretation made by [29-30].

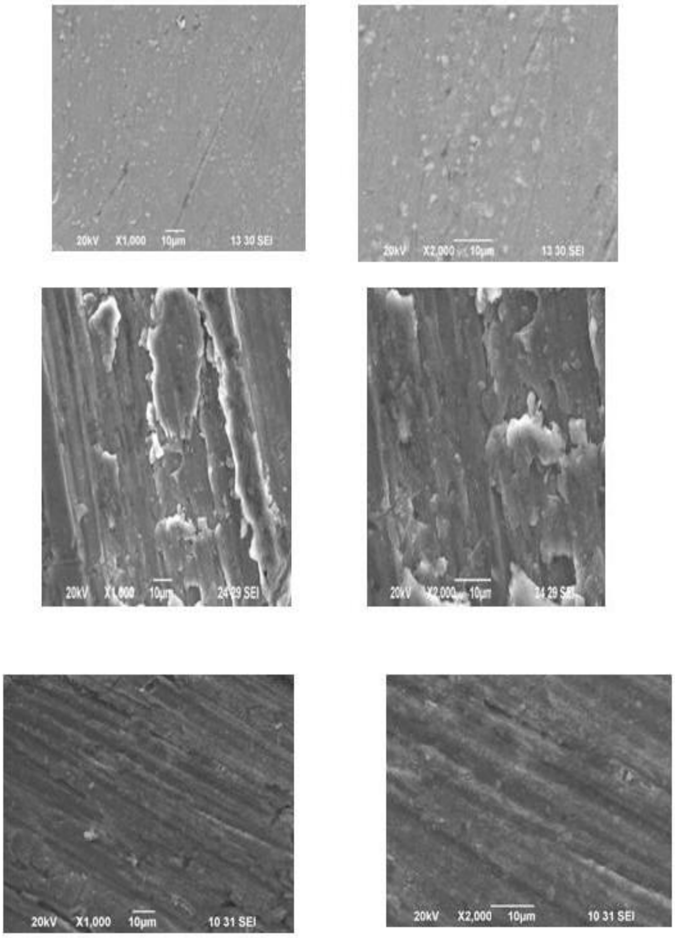

**Fig 6: SEM micrograpsh of**
**(a) Aluminium metal;magnifications 2000 X1000 (control)**
**(b) Aluminium immersed in well water 2000 X1000**
**c) Aluminium well water containing 250ppm of PMMA and 25ppm of $Zn^{2+}$**

## Acknowledgements

The authors are thankful to their management for their help and encouragement.

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