

Effect of Aminobenzene Concentrations on the Corrosion inhibition of Mild Steel in Sulphuric acid

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The inhibiting action of aminobenzene concentration against the corrosion of mild steel in dilute sulphuric acid contaminated with 5% sodium chloride was studied using weight-loss method, calculated corrosion rates from the obtained weight loss data, potentiodynamic polarization measurements and metallographic macrographs. Results show aminobenzene has strong inhibitory effects with inhibitor efficiency increasing with increase in inhibitor concentration at ambient temperature. Maximum efficiency of 99.83% was obtained at 20% concentration of aminobenzene due to adhesion of the inhibitive precipitates through physisorption on the mild steel. This is further justified by the graphs of weight-loss and corrosion rate against exposure which illustrates the corrosion inhibition performance of the inhibitor. Results obtained from potentiodynamic experiments had good correlation with those of the gravimetric methods. The obtained macrographs could also be correlated with the gravimetric method data.

Keywords: Corrosion, aminobenzene, sulphuric acid, sodium chloride, mild steel

1. INTRODUCTION

Corrosion has been known to man since the earliest metallurgical times and has been a constant drain on his productive activities, as such, purposeful attention have been focused on the problem both by scientists and engineers [1]. It is the disintegration of an engineered material [metal alloy] into its constituent atoms due to chemical reactions within their surrounding environment [2].

The effects of corrosion in our daily lives are both direct, in that corrosion affects the useful service lives of our possessions, and indirect, in that producers and suppliers of goods and services incur corrosion costs, which they pass on to consumers. At home, corrosion is readily recognized on

automobile body panels, charcoal grills, outdoor furniture, and metal tools. Preventative maintenance such as painting protects such items from corrosion. A principal reason to replace automobile radiator coolant every 12 to 18 months is to replenish the corrosion inhibitor that controls corrosion of the cooling system. Corrosion protection is built into all major household appliances such as water heaters, furnaces, ranges, washers, and dryers. Perhaps most dangerous of all is corrosion that occurs in major industrial plants, such as electrical power plants, chemical processing plants, manufacturing industries, oil and gas industries etc[3]. The total annual estimated direct cost of corrosion in the U.S. is a staggering \$276 billion, approximately 3.1% of the nation's Gross Domestic Product [4].

Material deterioration occurs all around us when we look at many metallic items of common use e.g. chemical industries face numerous corrosion problems, some so serious as to cause the shutdown of plants and collapse of structures causing hazards to human life as such billions of dollars are lost each year because of corrosion. Corrosion is therefore a matter of great concern due to the enormous cost involved in the replacement of metallic parts in all kinds of applications [5]. Mild steel has many industrial applications because of its easy availability, low cost, uncomplicated fabrication of it into water pipe lines [6, 7], cooling water systems [8], boilers etc. Due to the excellent mechanical properties and low cost, mild steel is extensively used as a constructional material in many industries. However, they are susceptible to different forms of corrosion induced by chloride and so on.

Corrosion can often be predictable or totally unpredictable and catastrophic, such as hydrogen embrittlement or stress corrosion of critical structural members and pressure vessels in the aerospace and chemical process industry [9]. Consequence upon the above the economic losses resulting from corrosion is large and further work on terms of research and investigation is desirable. A great number of studies have being devoted to the subject of corrosion inhibitors but most of what is known is as a result of trial and error, both in the laboratory and in the fields.

The application of corrosion inhibitors is an effective means of combating corrosion in aqueous and process industry environments where acids are widely used for applications such as pickling, cleaning, descaling etc. Because of their aggressiveness, inhibitors are used to reduce the rate of dissolution of metals. An inhibitor is a substance which retards or slows down a chemical reaction, thus a corrosion inhibitor is a substance which when added to an environment decreases the rate of attack by the environment on a metal [10]. The costs of corrosion and the savings gained through the use of appropriate corrosion inhibitors are considerable.

Corrosion inhibition is of great practical importance, being extensively employed in curtailing wastage of engineering materials. The use of inhibitors is quite varied often playing an important role in oil extraction and processing industries, heavy industrial manufacturing, water treatment facility etc. to minimize localized corrosions and unexpected sudden failures. Corrosion is most aggressive in industrial solutions containing chloride, bromide, hypochlorite ions, iodides and fluorides, though the later two are much less harmful. Most of the efficient inhibitors used in industry are organic compounds, which mainly contain nitrogen, oxygen, sulfur atoms, and heterocyclic compounds containing functional groups and conjugated double bonds, and multiple bonds in the molecule through which they are adsorbed on metal surface by the formation of an adherent film [11–18]. The compounds containing both nitrogen and sulfur can provide excellent inhibition, compared with

compounds containing only nitrogen or sulfur [12, 16]. Generally, a strong interaction causes higher inhibition efficiency, the inhibition increases in the sequence $O < N < S$ [19, 20].

Indeed, no where else is a metal's reaction to its environment more intense than in the harsh chemicals, elevated temperatures and high pressures encountered in chemical processing. Here, pipes, pumps, valves, vessels and other metallic structures must survive long term exposure to conditions ranging from mildly to severely corrosive, to downright insidious. Inhibitors can be classified broadly according to the rate at which the process is controlled [19]. Anodic inhibitors suppress anodic reactions and the rate of metal ions being transferred into the aqueous environment is reduced. Cathodic inhibitors impede the cathodic reactions. Mixed inhibitors hinder both reactions. On the basis of their mechanism of operation, four major categories of inhibitors have been identified [20]. These are neutralizers, filming inhibitors [or barrier-layer formers], scavengers and miscellaneous types.

In this work filming inhibitors have been used. Filming inhibitors function by strong adsorption or chemisorptions and decrease attack by creating a barrier between the metal and the environment [20]. A filming inhibitor must possess a hydrocarbon portion attached to a strongly polar group. The molecules are oriented on the metal surface with the polar group adsorbed on to the metal surface and the hydrocarbon component extending away from the surface. The hydrocarbon end will attract the molecules of the process stream to provide an additional barrier to a potentially corrosive aqueous solution [20]. The performance of an inhibitor can be assessed by its effectiveness in reducing the corrosion rate. Since corrosive chemicals cannot be eliminated from process applications, their attack must be controlled by high efficiency inhibitors [21]. This is key to the development of new chemical products and processes achieving the desired performance and life expectancy of components and equipment Choice of materials and readily available chemical compounds to considerably minimize the effect of corrosion is vital in ensuring viability of industrial plants, components and finished products.

2. EXPERIMENTAL PROCEDURE

2.1 Material

The mild steel used for this work was obtained in the open market and analyzed at the Nigerian Foundries Limited, Ilupeju Industrial Estate, Lagos, Nigeria. The mild steel has the nominal per cent composition: 0.201C, 0.169Si, 0.440Mn, 0.005P, 0.012S, 0.080Cu, 0.008Ni, 0.025Al, 0.0114Ph, the rest being Fe.

2.2 Inhibitor

Aminobenzene (AMB) is the inhibitor used. The structural formula of AMB is shown in Fig. 1. The molecular formula is C_6H_7N , while the molar mass is 93.13 g mol^{-1} .

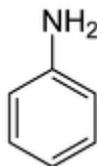


Figure 1. Chemical structure of Aminobenzene (AMB)

2.3 Test Media

1M tetraoxosulphate (VI) acid with 5% recrystallised sodium chloride of Analar grade were used as the corrosive medium

2.4 Preparation of Test Specimens

The cylindrical stainless steel (1.50cm dia.) was mechanically cut into a number of test specimens of different dimensions in length ranging from 0.76 and 0.87cm coupons.. The two surface ends of each of the specimen were ground with Silicon carbide abrasive papers of 80, 120, 220,800 and1000 grits. They were then polished with 6.0 μ m to 1.0 μ m diamond paste, washed with distilled water, rinsed with acetone, dried and stored in a dessicator for further weight-loss test and linear polarization. Aminobenzene was prepared in various concentrations of 0%, 2.5%, 5%, 7.5%, 10%, 12.5%, 15%,17.5% and 20% was used as the inhibiting medium.

2.5 Weight-loss Experiments

Weighted test species were fully and separately immersed in 200ml of the test media at varying concentrations of the inhibitor for 168hrs at ambient temperatures. Each of the test specimens was taken out every three days (24 hours), washed with distilled water, rinsed with acetone, dried and re-weighed. Plots of weight-loss versus exposure time (Figs. 2(a & b), corrosion rate (mmpy) versus exposure time (Fig. 3), corrosion rate versus inhibitor concentration (Fig. 4) and those of percentage inhibition efficiency (%IE) versus exposure time (hours) and percentage inhibitor concentration (Fig. 4 & 5) were made from table 1.

The corrosion rate (R) calculation is from this formula:

$$R = \left[\frac{87.6W}{DAT} \right] \quad \text{eqn. 1}$$

Where W is the weight loss in milligrams, D is the density in g/cm², A is the area in cm², and T is the time of exposure in hours. The % inhibitor efficiency, (I.E), was calculated from the relationship.

$$\left[\frac{W_1 - W_2}{W_1} \right] \times 100 \quad \text{eqn. 2}$$

Where, W_1 and W_2 are the corrosion rates in the absence and presence respectively of a predetermined concentration of inhibitor. The %IE was calculated for all the inhibitors on the 7th day of the experiment (Table 1), while the surface coverage is calculated from the relationship:

$$\theta = \left[1 - \frac{W_2}{W_1} \right] \text{ eqn. 3}$$

Where θ is the substance amount of adsorbate adsorbed per gram (or kg) of the adsorbent, the unit of m is mol.g^{-1} . W_1 and W_2 are the weight loss of austenitic stainless steel coupon in free and inhibited acid solutions, respectively.

2.6. Linear polarization Resistance

Linear polarization measurements were carried out using, a cylindrical mild steel coupon embedded in resin plastic mounts with exposed surface of 1.33 cm^2 . The electrode was polished with different grades of silicon carbide paper, polished to $6\mu\text{m}$, rinsed with distilled water and dried with acetone. The studies were performed at ambient temperature with Autolab PGSTAT 30 ECO CHIMIE potentiostat and electrode cell containing 200 ml of electrolyte, with and without inhibitor. A graphite rod was used as the auxiliary electrode and silver chloride electrode (SCE) was used as the reference electrode. The steady state open circuit potential (OCP) was noted. The potentiodynamic studies were then made from -1.5V versus OCP to $+1.5 \text{ mV}$ versus OCP at a scan rate of 0.002V/s and the corrosion currents were registered. The corrosion current density (j_{corr}) and corrosion potential (E_{corr}) were determined from the Tafel plots of potential versus $\log I$. The corrosion rate (r), the degree of surface coverage (θ) and the percentage inhibition efficiency (% IE) were calculated as follows

$$r \text{ (mmpy)} = \frac{0.00327 \times i_{\text{corr}} \times \text{eq.wt}}{D} \text{ eqn.4}$$

Where i_{corr} is the current density in $\mu\text{A/cm}^2$, D is the density in g/cm^3 , eq. is the specimen equivalent weight in grams;

The percentage inhibition efficiency (% IE) was calculated from corrosion current density values using the equation.

$$\% \text{I.E} = 1 - \left[\frac{C_2}{C_1} \right] 100 \text{ eqn.5}$$

where C_1 and C_2 are the corrosion current densities in absence and presence of inhibitors, respectively.

2.7. Micrographs

The micrographs of the test specimens before and after immersion were taken with metallurgical microscope.

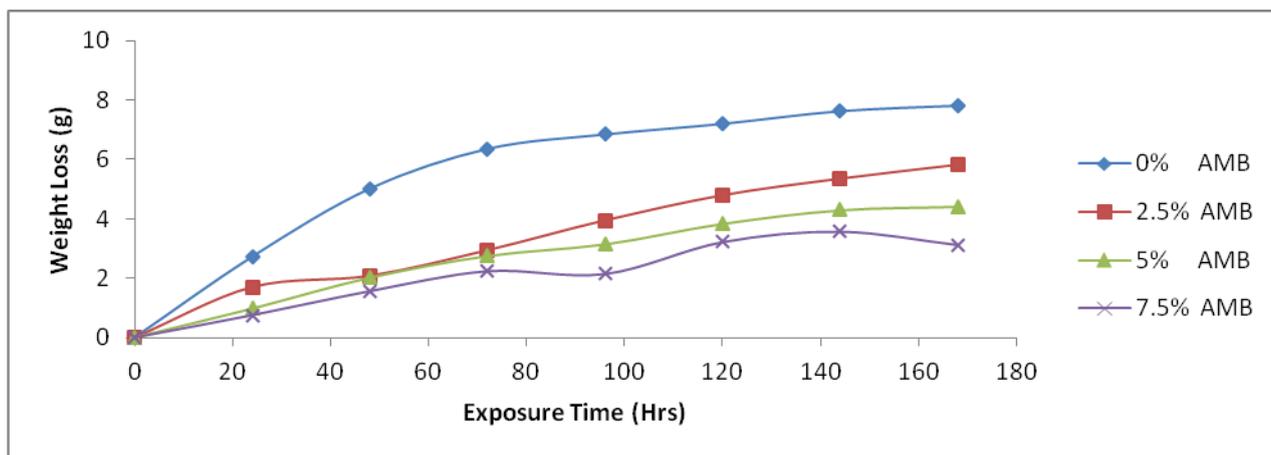
3. RESULTS AND DISCUSSION

3.1. Weight-loss measurements

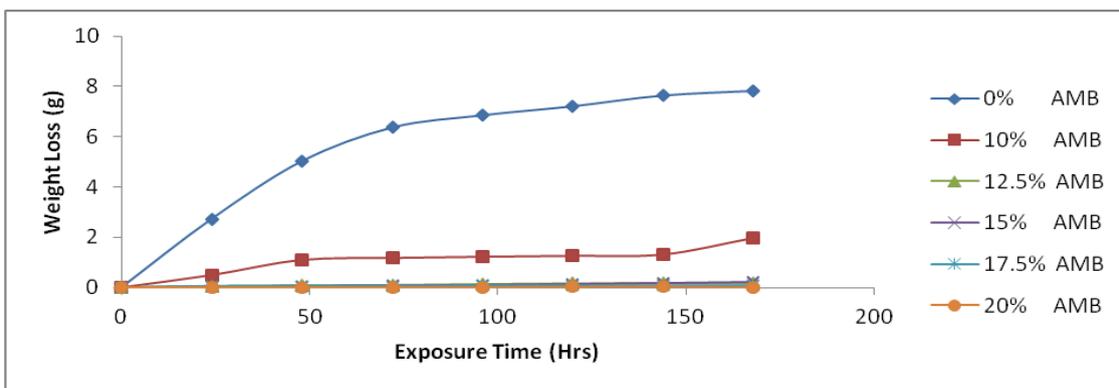
Weight-loss of mild steel at various time intervals, in the absence and presence of different concentrations of (AMB) in 1M sulphuric acid at 25°C was studied. The values of weight-loss (wt), corrosion rate (CR) (mmpy) and the percentage inhibition efficiency (IE %) are presented in Table 1. It is clear that the decreasing corrosion rate is associated with increase in the inhibitor concentration which indicates that more inhibitor molecules are adsorbed on the metal surface, thereby providing wider surface coverage. Figs. (2 & 3) shows the variation of weight-loss and corrosion rate versus exposure time while Fig. 4 shows the variation of corrosion rate versus inhibitor concentration. The curves obtained indicate progressive decrease in weight loss and corrosion rate with increase in inhibitor concentration.

Table1. Data obtained from weight loss measurements for Mild steel in 1M H2SO4 in presence of AMB concentrations at 168hrs

Sample	Inhibitor Concentration (%)	Weight Loss (g)	Corrosion Rate (mmpy)	Inhibition Efficiency (%)
A	0	7.8160	104.3813	0
B	2.5	5.8219	65.2189	25.51
C	5	4.4200	48.3862	43.45
D	7.5	3.1319	33.0116	59.93
E	10	1.9743	19.2189	74.74
F	12.5	0.1740	1.4918	97.77
G	15	0.2064	1.7907	97.36
H	17.5	0.0732	0.5783	99.06
I	20	0.0132	0.0854	99.83



(a)



(b)

Figure 2. Variation of weight loss with exposure time for mild steel specimen immersed in 1 M dilute sulphuric acid with and without added inhibitor. (a) 0% - 7.5% (b) 10% - 20%

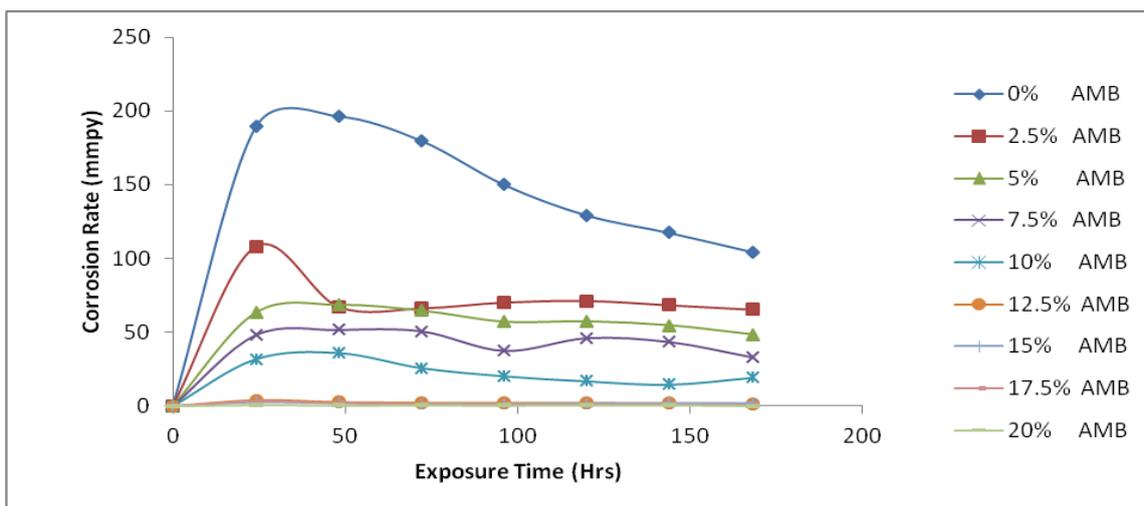


Figure 3. Plot of corrosion rate vs exposure time for the mild steel test specimens immersed in 0% - 20% aminobenzene concentration

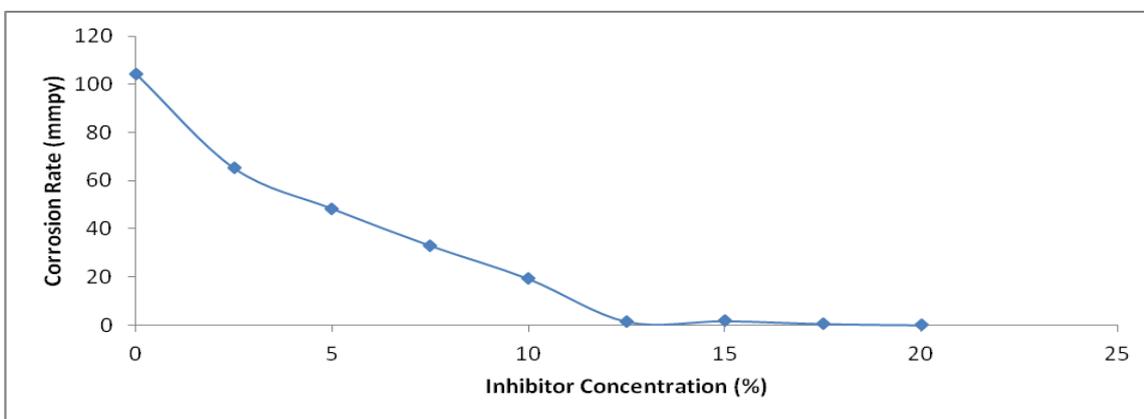


Figure 4. Plot of corrosion rate vs inhibitor concentration for mild steel test specimens after 168hrs of exposure

It could be observed that for all concentrations of the inhibitor used and for the test without inhibitor addition the corrosion rate of the mild steel decreased with time throughout the experimental period. The corrosion deposit from the dissolution of the tested specimens would have contaminated the acidic test medium and weakened it. This caused reduced the chemical activities stifled the corrosion reactions as the experimental period increased. At 20% concentration of aminobenzene no corrosion rate was recorded, the test specimen without inhibitor addition has the highest corrosion rate. This reflected the effectiveness of the inhibitor used.

Mechanistically, the inhibitor used in the test media could cause an increased polarization of the anode [anodic inhibition] and an increased polarization of the cathode [cathodic inhibition]. The thick deposits of the inhibitor depending on concentration could increase the electrical resistance of the circuit, thereby inhibiting corrosion and reducing the corrosion rate with time. The efficiency of the inhibitor used is presented in Table 1. The results obtained [by calculation] are in agreement with those described for the weight-loss method. Fig.5 shows the relationship between inhibition efficiency and inhibitor concentration. Increase in inhibitor concentration lead to relative increase in inhibitor efficiency with maximum efficiency at 99.83% due to an increase in thickness of the blanketing layer caused by the formation of white crystalline precipitate which is absorbed on the metal surface through the nitrogen atom. The aminobenzene form salts with the acid which ionize to give the positive ion, which is absorbed by the negative surface of the metal.

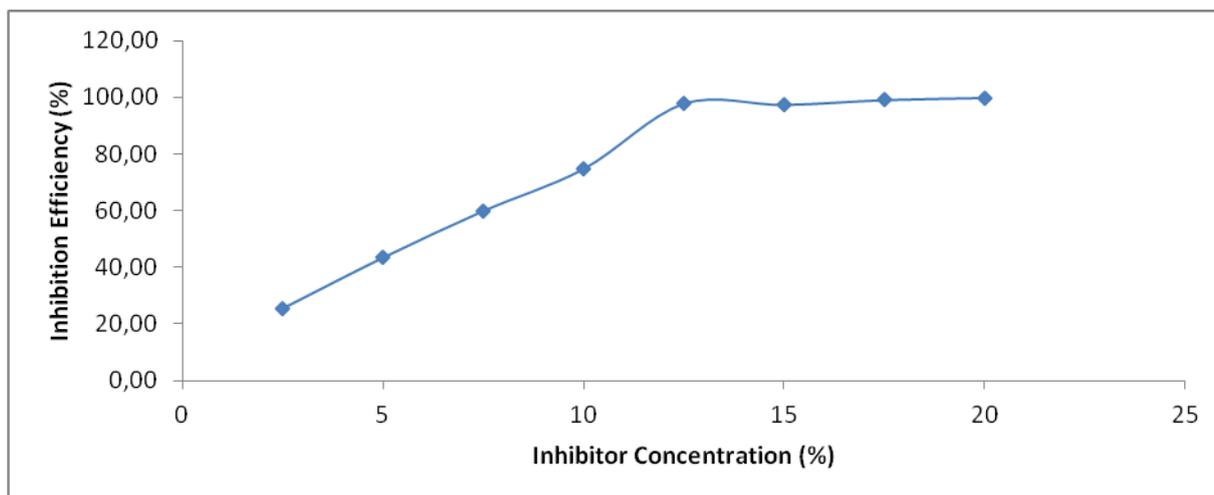


Figure 5. Variation of inhibition efficiency of aminobenzene concentration

3.2. Polarization studies

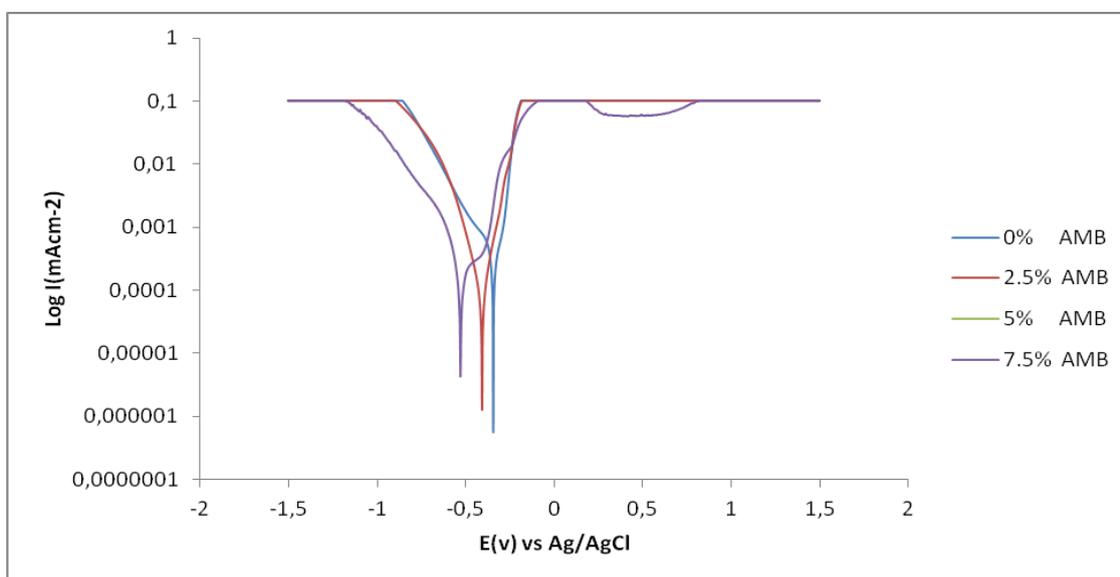
The potential was scanned from -1.50 to 1.50 V vs. SCE at a rate of 0.0166 mV s⁻¹, which allows the quasi-stationary state measurements. The effect of the addition of AMB on the anodic and cathodic polarization curves of mild steel in 1M H₂SO₄ solution at 25 °C was studied. Fig. 6 (a & b) shows the polarization curves of mild steel in absence and presence of AMB at different concentrations. Anodic and cathodic currents were inhibited effectively with increasing concentrations

of inhibitor. The inhibitor appeared to act as mixed type inhibitor since anodic (metal dissolution) and hydrogen evolution reactions were significantly influenced by the presence of compounds in the corrosive medium. Generally, all scans exhibit slightly similar behavior over the potential domain examined, indicating similar electrochemical reactions took place on the metal. The electrochemical parameters such as, corrosion potential (E_{corr}), corrosion current (i_{corr}), corrosion current density (I_{corr}), cathodic Tafel constant (bc), anodic Tafel slope (ba), surface coverage θ and percentage inhibition efficiency (%IE) were calculated and given in Table 2. These results show that the %IE increased while the corrosion current density generally decreased with the addition of AMB until 10% concentration where there was a sharp increase before decreasing gradually until 20% concentration. The corrosion current density (I_{corr}) and corrosion potential (E_{corr}) were determined by the intersection of the extrapolating anodic and cathodic Tafel lines, % IE was calculated from Eq. 6

$$\% I.E = \dots \text{eqn. 6}$$

Table 2. Data obtained from polarization resistance measurements for mild steel in 1M H₂SO₄ in presence of different concentrations of the AMB

Inhibitor Concentration (%)	ba (V/dec)	bc (V/dec)	E _{corr} , Obs (V)	j _{corr} (A/cm ²)	i _{corr} (A)	Corrosion rate (mmpy)	Polarization resistance (Ω)	Inhibition Efficiency (%)
0	0.268	0.090	-0.343	1.04E-03	1.38E-03	12.0260	21.287	0
2.5	0.288	0.057	-0.406	8.08E-04	1.07E-03	9.3886	19.371	21.93
5	0.262	0.095	-0.378	5.17E-04	6.88E-04	6.0066	44.026	50.05
7.5	0.255	0.180	-0.528	4.17E-04	5.55E-04	4.8494	82.563	59.68
10	0.207	0.231	-0.522	1.46E-04	1.95E-04	1.7003	243.59	85.86
12.5	0.187	0.081	-0.515	9.65E-05	1.28E-04	1.1206	191.51	90.68
15	0.062	0.212	-0.544	4.77E-05	6.34E-05	0.5542	329.59	95.39
17.5	0.131	0.059	-0.537	1.41E-05	1.87E-05	0.1636	947.29	98.64
20	0.037	0.084	-0.642	7.02E-06	9.34E-06	0.0816	1188.2	99.32



(a)

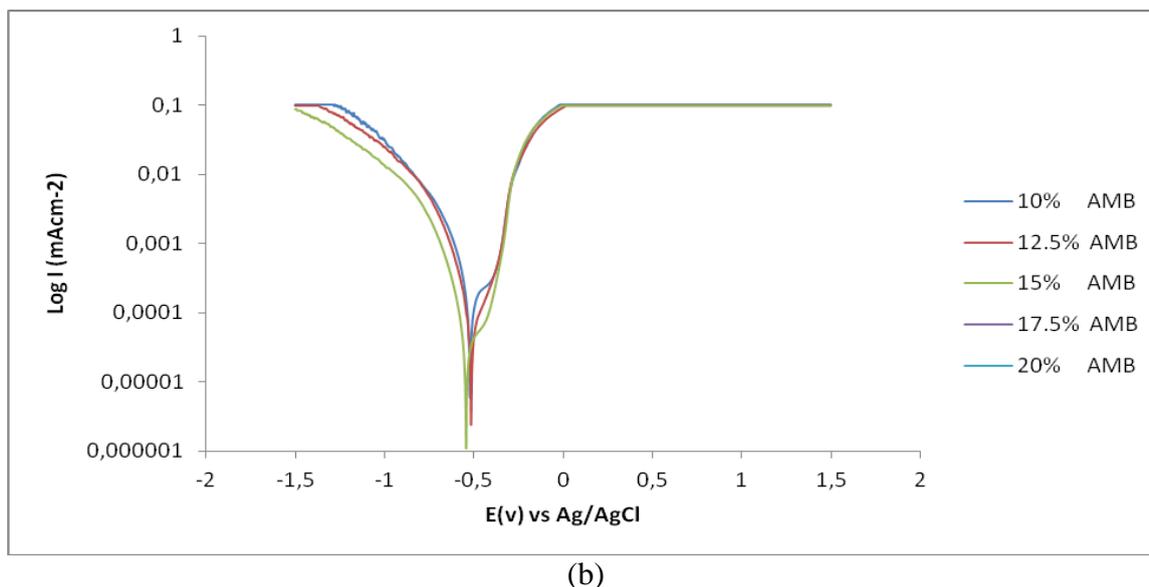


Figure 6. Comparison plot of cathodic and anodic polarization scans for mild steel in 1M H₂SO₄ + 5% NaCl solution in the absence and presence of different concentrations of AMB at 25°C. (a) 0% - 7.5% AMB (b) 10% - 20% AMB

3.3. Mechanism of inhibition

As far as the inhibition process is concerned, the adsorption of the inhibitor at the metal solution interface is the first step in the action mechanism of inhibitors in aggressive acid media. Inhibition of mild steel in H₂SO₄ solution by the AMB can be explained on the basis of adsorption. Adsorption depends on the nature and the state of the metal surface on the type of corrosive medium and on the chemical structure of the inhibitor. Studies report that the adsorption of the organic inhibitors mainly depends on some physicochemical properties of the molecule related to its functional groups, to the possible steric effects and electronic density of donor atoms; adsorption is supposed also to depend on the possible interaction of p-orbitals of the inhibitor with d-orbitals of the surface atoms, which induce greater adsorption of the inhibitor molecules onto the surface of carbon steel, leading to the formation of a corrosion protecting film [22].

Four types of adsorption may take place involving organic molecules at the metal solution interface [i] electrostatic attraction between charged molecules and the charged metal, [ii] interaction of n electrons with the metal, [iii] interaction of uncharged electron pairs in the molecule with the metal and, [iv], a combination of the above [23]. It is apparent that the adsorption of AMB on the steel surface could occur directly on the basis of donor acceptor between the lone pairs of the heteroatoms, the extensively delocalized π electrons of the AMB molecule and the vacant d-orbitals of iron surface atoms [24]. The functional group responsible for AMB adsorption on metal surface is the lone pair of the nitrogen atom: iron ions on metal surface act as a Lewis acid because they accept electrons from a donor group. Amines adsorption is influenced by the electronic properties of the functional groups, R, bound to the nitrogen atom [25].

In acidic solution, these compounds can exist as protonated species; these protonated species may adsorb on the cathodic sites of the steel and decrease the evolution of hydrogen. These compounds are able to adsorb on anodic sites through N atoms, which is an electron donating groups. The adsorption of these compounds on anodic sites decreases anodic dissolution of steel by the electron-rich heteroatoms in AMB which adsorbs on the anodic site through their lone pairs of electrons of nitrogen thus reduces the anodic dissolution of metal. Inhibition of the stainless steel corrosion by AMB was also found to depend on its stability in acidic solutions. Transfer of lone pairs of electrons on the nitrogen to the surface to form coordinate type linkage is favored by the presence of vacant orbital in iron atom of low energy. Polar character of substituent in the changing part of the inhibitor molecule seems to have a prominent effect on the electron charge density of the molecule. The presence of one active adsorption centers [one N-atoms] do not necessarily impact on the electron charge density on the molecule but increase in the inhibition efficiency as this occurs with increasing concentration of the compound.

Generally, the adsorption of organic compounds can be described by two main modes of interaction: physisorption and chemisorption. The former requires the presence of electrically charged metal surface and charged species in the bulk of solution, while the latter involves charge-sharing or charge-transfer from the inhibitor molecules to the metal surface to form a co-ordinate type of a bond [26-28].

3.4. Adsorption isotherm

The mechanism of corrosion protection may be explained on the basis of adsorption behavior [29]. Adsorption isotherms are very important in determining the mechanism of organo-electrochemical reactions. The adsorptive behavior of a corrosion inhibitor is an important part of this study, as it provides important clues to the nature of the metal-inhibitor interaction [30]. Interaction information between the inhibitor molecule and metal surface can be provided by adsorption isotherm [31]. For an inhibitor to have a high surface coverage on the surface, a chemical bond between the inhibitor and the metal atom stronger than the one for water molecules should be formed. The adsorption of corrosion inhibitors at the metal/solution interface is due to the formation of either electrostatic or covalent bonding between the adsorbates and the metal surface atoms. Langmuir adsorption isotherm was found to best describe the adsorption mechanism for AMB compounds as it fits the experimental results at 25 °C.

The conventional form of the Langmuir isotherm is,

$$\frac{\theta}{1-\theta} = KC \quad \text{eqn.7}$$

And, rearranging gives

$$\frac{c}{\theta} = \frac{1}{\theta} + c \quad \text{eqn.8}$$

where θ is the degree of coverage on the metal surface, C is the inhibitor concentration in the electrolyte, and K_{ads} is the equilibrium constant of the adsorption process. The plots of C/θ versus the inhibitor concentration were linear [Fig. 8] indicating Langmuir adsorption.

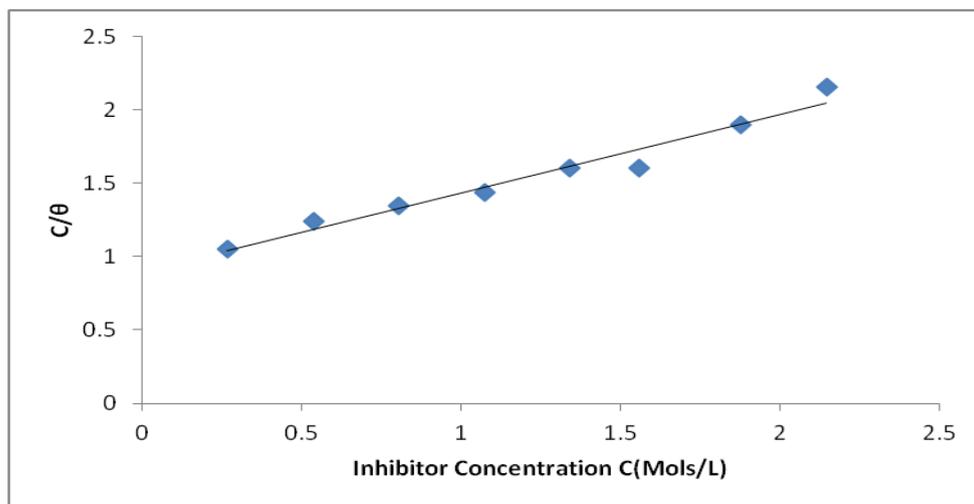


Figure 8. Relationship between $\frac{C}{\theta}$ and inhibitor concentration (C)

The deviation of the slopes from unity is attributed to the molecular interaction among the adsorbed inhibitor species, a factor which was not taken into consideration during the derivation of the Langmuir equation. Langmuir isotherm assumes that:

- (i) The metal surface contains a fixed number of adsorption sites and each site holds one adsorbate.
- (ii) ΔG_{ads} is the same for all sites and it is independent of θ .
- (iii) The adsorbates do not interact with one another, i.e. there is no effect of lateral interaction of the adsorbates on ΔG_{ads} [32].

Table 3. Data obtained for the values of Gibbs free energy, surface coverage and equilibrium constant of adsorption at varying concentrations of AMB

Gibbs Free Energy (ΔG)	Equilibrium Constant of Adsorption (K)	Inhibitor Concentration (Mol/L)	Surface Coverage (θ)
10.561	1.278	0.268	0.255
10.841	1.431	0.537	0.435
11.489	1.858	0.805	0.599
12.465	2.755	1.074	0.747
13.317	3.886	1.342	0.839
17.792	23.640	1.560	0.974
19.942	56.294	1.879	0.991
23.874	275.196	2.148	0.998

The free energies of adsorption, ΔG_{ads} , were calculated from the equilibrium constant of adsorption using the following equation:

$$\Delta G_{ads} = -2.303RT \log [55.5K] \quad \text{eqn. 9}$$

Where 55.5 is the molar concentration of water in the solution, R is the universal gas constant and T is the absolute temperature. Generally, values of ΔG_{ads} around -20 kJ/mol or lower are consistent with the electrostatic interaction between the charged molecules and the charged metal [physisorption]; those around -40 kJ/mol or higher involve charge sharing or transfer from organic molecules to the metal surface to form a coordinate type of bond [33]. The value of ΔG_{ads} reflects the weak adsorption capability. The negative values of ΔG_{ads} showed that the adsorption of inhibitor molecules on the metal surface is spontaneous [34]. The values of ΔG_{ads} calculated ranges between -10.561 and -23.874 kJ mol⁻¹ for AMB. Accordingly, the values of ΔG_{ads} obtained in the present study indicate that the adsorption mechanism of AMB on mild steel is simply physisorption, thus inhibitor protection is through film formation providing an unbreakable barrier against aggressive ions of the electrolyte. Indeed, due to the strong adsorption of water molecules on the surface of steel, one may assume that adsorption occurs first due to the physical forces [35]. The removal of water molecules from the surface is accompanied by physical interaction between the metal surface and the adsorbate with increasing concentration of AMB which is most likely to turn to chemisorptions [35]. From the observation, it was assumed that the adsorbed layer was more than one-molecule thickness at all sites, resulting in unequal energies and enthalpies of adsorption. The intermolecular bonding to the adsorption sites can be either chemical or physical, but is sufficiently strong to prevent displacement of adsorbed molecules along the surface.

The nitrogen and oxygen atoms of the inhibitor molecules are readily adsorbed onto the metal surface, forming insoluble stable films on the metal surface, thus decreasing metal dissolution [35].

3.5. Macrographs

The macrographs made of the test specimens are presented in Fig. 7 (A-J). The A specimen was the sample that was not immersed. The macrographs, [B-J] showed the different features obtained with the addition of different concentrations of aminobenzene inhibitor. There was very severe corrosion of the specimens from B to F representing 0% - 20% inhibitor concentration respectively. However, the greatest magnitude of corrosion degradation was in B, where there was no inhibitor addition. Specimens G to J, representing 12.5% - 20% inhibitor concentrations respectively, showed appreciable corrosion inhibition when compared with the former above. These observations are very much in agreement with results obtained for the weight loss method.



A



B



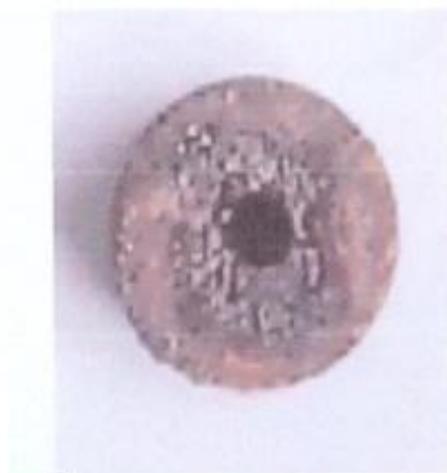
C



D



E



F

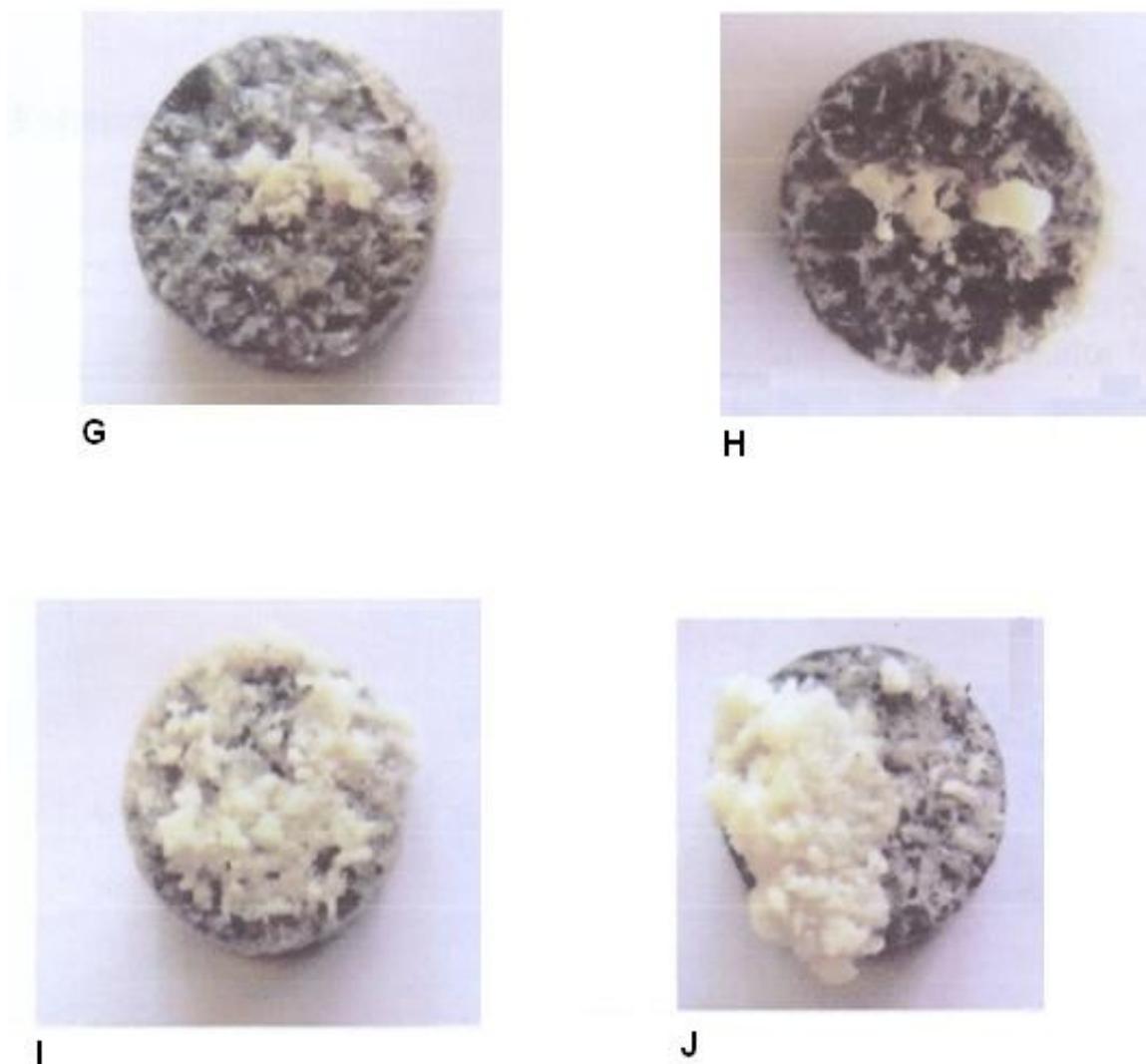


Figure 7. Macrographs of samples before and after exposure periods Mag. X4: A – before immersion; B-J features are for 0%, 2.5%, 5%, 7.5%, 10%, 12.5%, 15%, 17.5% and 20% inhibitor additions respectively.

In general, amino-benzene has been confirmed to be an effective inhibitor in the sulphuric acid medium at the appropriate concentrations such as used in this work. It can be said, plausibly, that it is a filming inhibitor. Just as reviewed above in the introduction, a filming inhibitor must possess a hydrocarbon portion attached to a strongly polar group such as obtained in the amino -benzene. The molecules are known to be oriented on the metal surface with the polar group adsorbed on to the metal surface and the hydrocarbon component extending away from the surface. The hydrocarbon end will attract the molecules of the test environment to provide an additional barrier to a potentially corrosive aqueous solution [17]. Amino-benzene is an organic aromatic chemical compound that could be associated with this reactions mechanism. It was the stable film provided by the inhibitor under the test conditions that decreased the active corrosion reactions at specimen/test environment interface. Thus what could have been continuous severe anodic dissolution of the test electrode as experienced at the lower concentrations of the inhibitor was averted. The film might have, expectedly, hindered and/or

prevented the penetration of the $\text{SO}_4^{=}$ ion reacting species through the film barrier to initiate and perpetrate corrosion reactions on the metal surface. The passive film indeed stifled further active corrosion reactions at the higher concentrations, [10 – 20%] of the inhibitor.

4. CONCLUSIONS

The inhibitor used in this work was effective in inhibiting corrosion of mild steel in sulphuric acid depending on the concentration. This was indicated by the weight-loss method and the corrosion rate values [calculated] from the results obtained. The more obvious effectiveness in this regard was evidenced from the macrographs made. In addition, an inhibitor efficiency of 99.3% was achieved with the use of 20% inhibitor concentration. The corrosion inhibition effectiveness started from the 10% concentration with 82.40% inhibitor efficiency.

The corrosion inhibition performance of amino-benzene is due largely to its ability to provide a strong adherent and stable film on the metal's surface that hindered the penetration of sulphate ion reacting species to initiate and sustain corrosion reactions; particularly at the higher concentrations of the inhibitor.

References

1. P.H. Michiel, C.C. Brongers, H.K. Gerhardus, G. Neil, *Technologie and NACE*(2010).
<http://www.corrosioncost.com/prodmanu/idex.htm>.
2. M.G. Fontana.,N.D, Greene. *Corrosion Engineering*, McGraw –Hill, 2nd. Edition (1982) 2-10
3. ASM International, *Corrosion: Understanding the Basics*. 2000,
[www.asminternational.org/content/Asm/Store Files/06691G Chapter_1.pdf](http://www.asminternational.org/content/Asm/Store%20Files/06691G%20Chapter%201.pdf), Pg. 9
4. G.H. Koch,P.H. Michiel, C.C. Brongers, N.G. Thompson, Y.P.Virmani, J.H. Payer, *Corrosion Costs and Preventive in the United States*. [http:// events. Race.org/ publications / images. cocorr/cssupp.pdf](http://events.Race.org/publications/images/cocorr/cssupp.pdf)
5. S.K,Hajra. *Material Science and Process*, Sree Saraswaty Press Ltd. India (1997)
6. R.E. Melchers, R. Jeffery, *Corrosion Reviews*, 1 (2005) 84.
7. R.E. Melchers, R. Jeffery, *Corrosion Reviews*, 6(2005)297.
8. G. Saha, N. Kurmaih, N. Hakerman, *J. Physis. Chem.*, 59 (1955)707.
9. Key to Metals AG, 1999-2011. *Corrosion of Metals and their Alloys*.
<http://www.keytometals.com/page.aspx?ID=CheckArticle&site=ktn&NM=13>
10. Wikipaedia, <http://en.wikipedia.org/wiki/pitting>. (2007)
11. S.A. Abd El-Maksoud, A.S. Fouda, *Mater. Chem. Phys.* 93 (2005) 84.
12. J. Aljourani, M.A. Golozar, K. Raeissi, *Mater. Chem. Phys.*, 121(2010) 320.
13. R. Hasanov, S. Bilge, S. Bilgic, G. Gece, Z. Kıl, *Corros. Sci.* 52 (2010)984.
14. S.A. Abd El-Maksoud, *Appl. Surf. Sci.* 206(2003)129
15. F. Xu, J. Duan, S. Zhang, B. Hou, *Mater. Lett.*, 62 (2008) 4072.
16. Y. Abboud, A. Abourriche, T. Saffaj, M. Berrada, M.Charrouf, A. Bennamara, N. Al Himidi, H. Hannache, *Mater. Chem. Phys.* 105 (2007)1.
17. H.S. Awad, S.A. Gawad, *Anti-Corros. Method.* 52(2005)328.
18. A. Chetouani, A. Aouniti, B. Hammouti, N. Benchat, T. Benhadda, S. Kertit, *Corros. Sci.* 45 (2003)1675.

19. Wikipaedia, <http://en.wikipedi.org/wiki/pitting> (2010)
20. Corrosion: Impact, Principles and Practical Solutions (2010).
<http://www.corrosiondoctors.org/Forms-pitting/Pitting.htm>
21. G.M. Kummar, N.S. Chunduwadat, J.S. Jodha, P. Patel, A.K. Goswam, *E-Journal of Chemistry*, (2009)257-260 <http://www.e-journals.in/PDF/V6N1/257-260.pdf>
22. M. Ormellese, L. Lazzari, S. Goidanich, G. Fumagalli, A. Brenna, *Corrosion Sci.*,51(2009)2959-2968.
23. M. Bouklah, B. Hammouti, M. Lagrenée, F. Bentiss, *Corros Sci.* 48(2006) 2831.
24. M.S. Abdel-Aal, M.S. Morad, *Br. Corros. J.* 36 (2001)253
25. S.E. Trautenberg, R.T. Foley, *J. Electrochem. Soc.* 118 (1971)1066
26. C.M. Hansson, L. Mammolite, B.B. Hope, *Cement Concrete Research.* 28(1998)1775-81.
27. N.K. Allam, *Appl. Surf. Sci.* 253 (2007) 4570
28. K.C. Emregul, E. Duzgun, O. Atakol, *Corros. Sci.* 48(2006)3243.
29. R.F.V. Villamil, P. Corio, J.C. Rubin, S.M.I. Agostinho, *J. Electroanal. Chem.* 472 (1999)112–119
30. M.S. Abdel-Aal, M.S. Morad, *Br. Corros. J.*36 (2001)253
31. I.B. Obot, N.O. Obi-Egbedi, S.A. Umoren, *Der Pharma Chemica.*1(2009)151-166
32. M.G. Hosseini, S.F.L. Mertens, M.R. Arshadi, *Corros. Sci.*45 (2003)1473.
33. L.M. Vračar, D.M. Dražić, *Corros. Sci.*44 (2002), 1669
34. A. Da browski, *Adv. Colloid Interf. Sci.* 93 (2001)135–224.
35. V.R. Saliyan, A.V. Adhikari, *Corros. Sci.* 50(2008)55–61.